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EXCITATION OF THE (001) MODE OF CO_2 IN 2.45 GHz MICROWAVE E FIELD AND DC B FIELD

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Abstract. This paper presents rate coefficients for excitation of the (001) mode of CO_2, determined for microwave electric field crossed at right angle with static magnetic field. The rate coefficient data were obtained for the reduced electric field amplitude of 50 Td and frequency of 2.45 GHz. Both time dependent behavior and time averaged results are analyzed. Rate coefficients were calculated on the basis of electron energy distribution functions, provided by our Monte Carlo simulation.

1. INTRODUCTION

The ever increasing danger of the global warming calls for immediate actions to be taken in order to reduce carbon dioxide emission in the atmosphere. Scientists are faced to a great challenge to find the fastest and the most cost effective response. Carbon dioxide conversion to ecologically friendly fuels stands out among the most promising research directions. As CO_2 splitting is crucial for the conversion process, different technologies are being developed in order to achieve energy efficient plasma assisted CO_2 dissociation. It is already established that highest energy efficiency is achieved in non-thermal plasma produced in a microwave discharge device that usually operates at 2.45 GHz with the reduced electric field, E_R/N (root mean square value of the electric field reduced to number density), having the magnitude of 50 Td (1 Td = 10^{-21} Vm^2) (Britun and Silva 2018). The secret lies in low energy excitation of the first asymmetrical stretch level (001) of CO_2.This process is followed by energy transfer between different vibrational levels (V-V transfer); higher vibrational states are being populated, which eventually leads to dissociation. The described dissociation mechanism requires less energy than it is required in electronic excitation (Bogaerts et al. 2016).

Due to necessity of rate coefficient data for plasma modeling and the importance of (001) excitation for CO_2 dissociation, it is mandatory to determine, as reliable as possible, (001) excitation rate coefficients. In our recent paper

(Vojnović et al. 2019), we published the results obtained for orthogonal DC electric and magnetic fields. The increase of rates with application of the magnetic field in a wide range of E_R/N was observed and explained. Since microwave discharge is mostly used in CO_2 conversion for the reasons already mentioned, we continue our study for the conditions of the presence of 2.45 GHz electric field and static magnetic field. In these conditions, electrons will move in elliptical path. This kind of motion is caused by the Lorenz force and it is done with cyclotron frequency, f_c, whereby:

$$2\pi f_c = \mathrm{e}B/m_e \qquad (1).$$

In this equation e, B and m_e denote the electron charge, the magnetic induction and electron mass, respectively. Electrons will absorb energy from the alternating electric field. With increase of the magnetic field, more and more energy is absorbed up to a certain point, after which the absorbed energy begins to decline. This is the well known electron cyclotron resonance (ECR) effect with resonance condition that cyclotron frequency equals the field frequency, f. For 2.45 GHz this condition is fulfilled at B = 875 G. In this study we will follow the rise of the (001) rates with increasing magnetic field, showing the time resolved data and the increase/decrease of the period averaged rates with the increase of the magnetic field.

2. SIMULATION

In the simulation electrons are traveling through a space uniformly filled with gas molecules under the influence of the forces of the present alternating electric and static magnetic fields. Numerical solving of the differential equation of motion provides the electron position and velocity in each small time step in the simulation. Random number generator is used to simulate the collision event and angular distribution of electrons after scattering. The probabilities of these events rely on the cross section database, which was successfully tested by comparison of the obtained transport parameters with data from different experimental groups (Vojnović et al. 2019). Since study is performed for low E_R/N, superelastic collisions for the transition $(010)^* \rightarrow (000)$ were added to the simulation database (population of the (010) level is non-negligible at room temperature (Kato et al. 2008)). Cross sections for superelastic collisions were calculated by using the Klein-Rosseland relation.

After steady state is reached, electron transport data start being sampled within a period of the field oscillation. The simulation procedure independent on the gas species was tested by comparing transport parameters with benchmark values for model gases (White et al. 1999, Nolan et al. 1997).

3. RESULTS AND DISCUSSION

Rate coefficients were calculated by using the formula:

$$K(<\varepsilon>_t,t)=\sqrt{2/m}\int_{\varepsilon_{th}}^{\infty}\sigma(\varepsilon)\sqrt{\varepsilon}f_e(<\varepsilon>_t,\varepsilon,t)d\varepsilon \qquad (2),$$

where $<\varepsilon>_t$ and $f_e(<\varepsilon>_t,\varepsilon,t)$ are the mean electron energy and the normalized EEDF, respectively, at time t, ε is the electron energy, $\sigma(\varepsilon)$ is the cross section for excitation of the (001) mode and ε_{th} is the threshold energy. Calculations were performed for the commonly used microwave field frequency of 2.45 GHz and for the reduced electric field magnitude of 50 Td, since at this value of E_R/N vibrational level excitations are shown to be the dominant process in plasma (Fridman 2008). The value of the reduced DC magnetic field, B/N, was varied from 0 up to 5000 Hx.

Figure 1 shows the time-modulated rates for excitation of the first asymmetric stretch mode, (001), for different values of B/N in the range from 0 to 3000 Hx. The amplitude of oscillation is gradually growing with the rise of the magnetic field, until it is damped at 3000 Hx, which is the point very close to the B/N value corresponding to ECR conditions (2720 Hx). It is interesting to note that this behavior is contrary to the situation with the electron mean energy, for which oscillation amplitude is highest at the point of resonance, as expected.

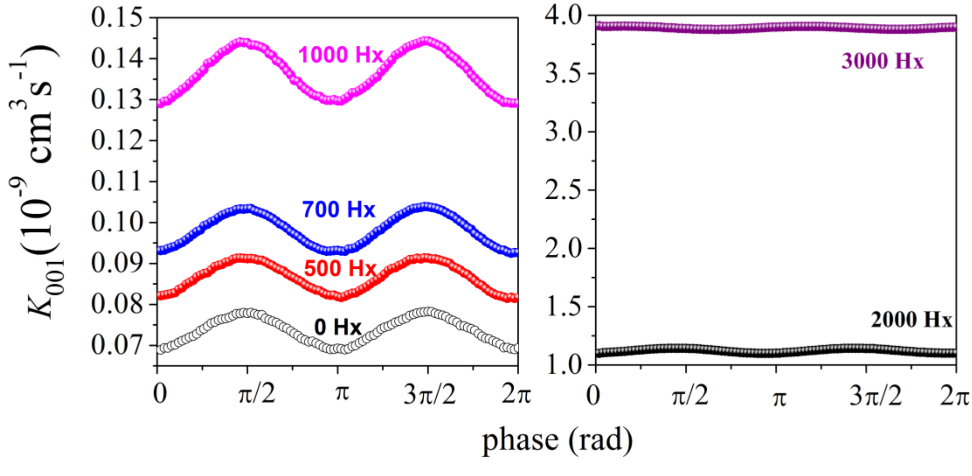

Figure 1: Time modulated (001) mode excitation rates for different B/N.

The fast increase of the rates with increasing magnetic field is also noticeable. To illustrate how fast these rates are rising, we plotted the function of the period averaged rates vs. B/N in the interval from 0 to 5000 Hx (figure 2). In the inset of the figure 2, we also show the dependence of the period averaged mean energy on B/N. It comes as no surprise that the maximal value of the both functions is reached at 2720 Hx, which, for the number concentration N of $3.22\cdot10^{22}m^{-3}$, set in our simulation, corresponds to B = 875 G. Interestingly, the maximal value of the averaged (001) rates that equals $4.52 \cdot 10^{-9} cm^3 s^{-1}$ is very close to the value we obtained for zero *B* field conditions in DC electric field at 50 Td (Vojnović et al. 2019). The obtained data are nearly perfectly fitted by the Gaussian function.

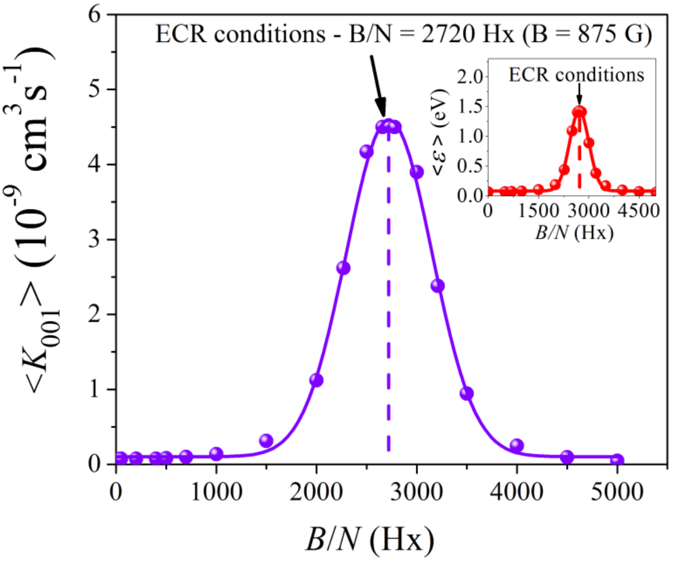

Figure 2: Period averaged rates vs. *B*/*N* – the simulation results (sphere), Gaussian function fit to data (full line), the position of ECR conditions (dash line); the inset: period averaged mean energy vs. B/N

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