RATES FOR EXCITATION OF THE CO_2 FERMI RESONANCE MEMBERS IN RF ELECTRIC FIELD

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ABSTRACT

Rate coefficients for electron impact excitation of the members of the Fermi resonance of CO_2 in non-equilibrium conditions were calculated. Monte Carlo simulation of electron transport trough gas in the presence of radio frequency electric field was employed in order to determine proper electron energy distribution functions for the given parameters – 100 MHz field frequency and the reduced field magnitude of 100 Td.

INTRODUCTION

Electron collisions with CO_2 gas molecules occur frequently inside devices (which generate plasma by radio frequency discharge) and influence the further molecular dynamics. Vibrational excitation has great capacity to store energy which is later transferred between excited molecules. This is being used to achieve energy efficient dissociation, which is a key process in CO_2 conversion to ecologically friendly fuels. Rate coefficients are important input data in modeling conditions in discharge devices. Fermi resonance was first recognized by Enrico Fermi in 1931 (Fermi 1931) as quasi degeneration of two vibrational levels, by which he explained one line in Raman spectra of CO_2, instead of two as then existing theoretical models predicted. Fermi resonances play important role in vibrational energy transfer. CO_2 molecule possesses two groups of nearly degenerate vibrational levels. The first one, called Fermi dyad, includes the lowest symmetrical stretch mode, (100), and the bending mode (020). The second one, named Fermi triad, consists of three modes – (200), (120) and (040). In the present work we are going to show time resolved rate coefficients for electron impact excitation of all these Fermi resonance members, which were obtained by means of a Monte Carlo simulation that treats electrons moving in gas filled space, under the action of a spatially uniform radio frequency electric field. We chose the reduced electric field, E_R/N (root mean square value), to have magnitude of 100 Td. At this E_R/N value period averaged mean electron energy reaches 3.55 eV.

MONTE CARLO SIMULATION

The simulation follows up to 10^7 electrons, which are accelerated by the action of the radio-frequency electric field and subsequently decelerating upon collisions with CO_2 gas molecules, distributed in an infinite space. Electrons are treated one by one and their motion is determined in small time steps by numerical solution of the differential equations of motion. As soon as the steady state is reached, electron energy distribution function is repeatedly sampled, along with other relevant transport parameters, inside one cycle of the electric field and then averaged to acquire better statistics.

Data read from the input cross section database are used to calculate collision probabilities. A collision event is simulated by calling a random number generator.

RESULTS AND DISCUSSION

The simulation was prepared for the electric field parameters of 100 Td (1 Td = 10^{-21} Vm^2) and 100 MHz The gas pressure was set to 1 Torr (133.3 Pa). EEDFS obtained within one period of oscillation by the simulation were used to determine the coefficients.

Time resolved rate coefficients for excitation of (100) and (020) modes, belonging to Fermi dyad of CO_2, are shown in figure 1. The results obtained for excitation of the members of Fermi triad, namely of the (200), (120) and (040) modes, are shown in figure 2.

The obtained results indicate that rates for (100) and (020) are slightly shifted in phase, whereas all shown excitation rates for the members of Fermi triad are in phase. Another difference one may observe when comparing these two figures is that the amplitude of the members of Fermi dyad, shown in figure 1, is the same, but in case of Fermi triad (figure 2) amplitudes differ in magnitude for all three members. The intensity arrangement for these modes follows from the magnitudes of the corresponding cross sections. The time modulation of all these rates can be understood after performing detailed analysis of the position of the effective cross section function for the given mode with respect to the EEDF at the specific moment in time.

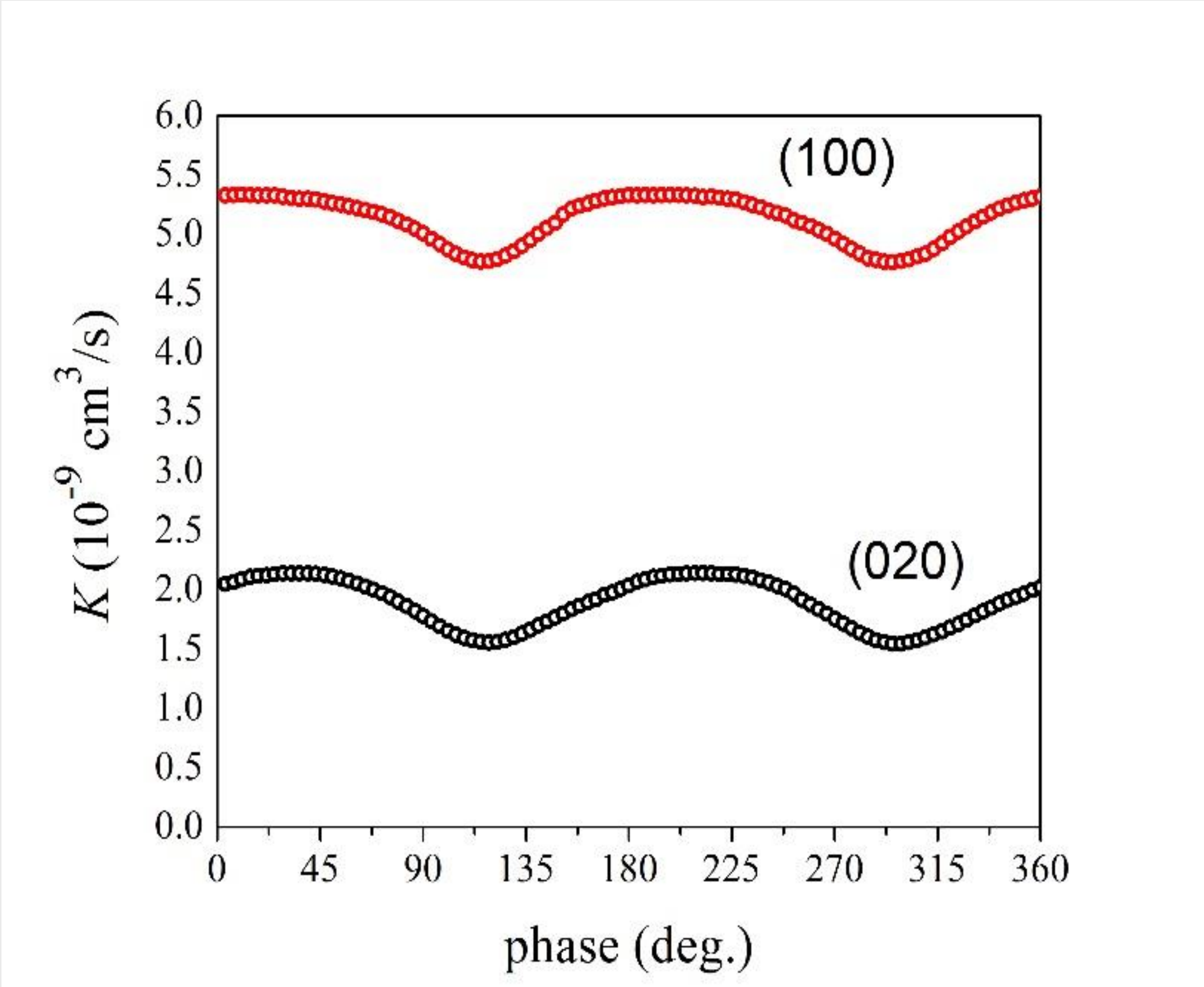

Figure 1. Rate coefficients for excitation of the Fermi dyad members.

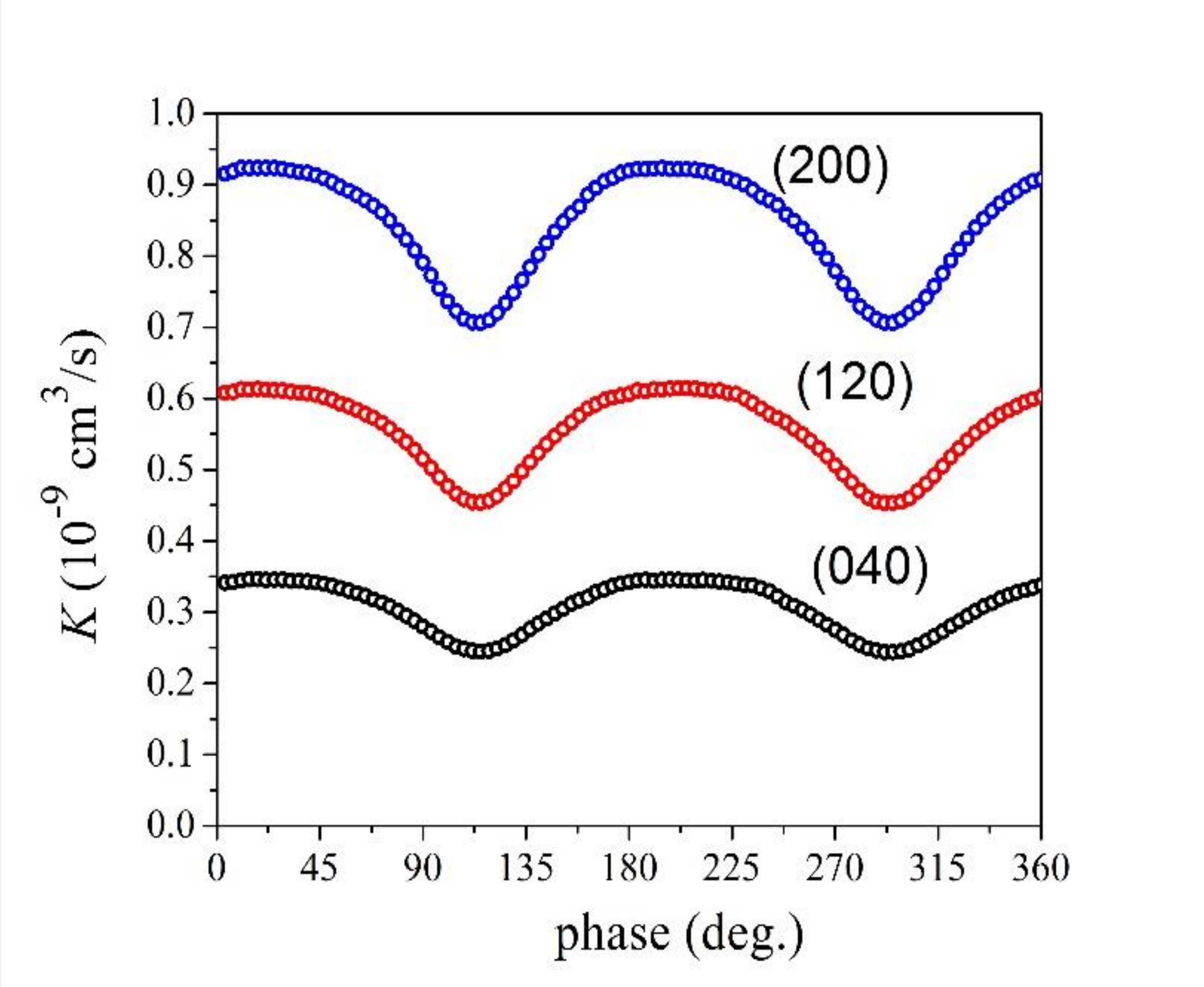

Figure 2. Rate coefficients for excitation of the Fermi triad members.

Acknowledgments

This work is partly supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

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