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Influence of Electron Molecule Resonant Vibrational Collisions over the Symmetric Mode and Direct Excitation-Dissociation Cross Sections of CO_2 on the Electron Energy Distribution Function and Dissociation Mechanisms in Cold Pure CO_2 Plasmas.

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ABSTRACT: A new set of e-V processes linking the first ten vibrational levels of the symmetric mode of CO_2 is derived by using a decoupled vibrational model and inserted in the Boltzmann equation for the electron energy distribution function (eedf). The new eedf and dissociation rates are in satisfactory agreement with the corresponding ones obtained by using the e-V cross sections reported in the database of Hake and Phelps (H-P). Large differences are, on the contrary, found when the experimental dissociation cross sections of Cosby and Helm (C-H) is inserted in the Boltzman equation. Comparison of the corresponding rates with those obtained by using the low energy threshold energy, reported in the H-P database, shows differences up to orders of magnitude, which decrease with the increasing of the reduced electric field.

In all cases, we show the importance of superelastic vibrational collisions in affecting eedf and dissociation rates either in the direct electron impact mechanism (DEM) or in the pure vibrational mechanism (PVM).

1. INTRODUCTION

Presently, there is a great interest in the activation of CO_2 in cold plasmas for its importance in different technological applications in energy, environment and aerospace fields[1]. Several experimental devices are being used to activate the CO_2 molecule, including DBD[2], microwave pulsed discharge[3], nanosecond pulsed discharges[4], gliding arc[5] and microhollow cathode discharges[6].

The main idea is to enhance the activation rate, i.e. the dissociation one of CO_2, by using the vibrational energy introduced by electrons in cold plasmas, an idea coming from the old studies of Russian[7,8] and Italian groups[9,10]. The numerous recent experimental attempts try to understand their results with a generic reference to the importance of vibrational excitation in affecting them. The most comprehensive recent theoretical approach has been presented in several papers by Bogaerts et al.[11,12]. The developed global model includes sophisticated plasma chemistry reaction schemes, a non-equilibrium vibrational kinetics on the asymmetric vibrational mode of CO_2, and a Boltzmann solver for obtaining the electron-molecule rates. The Boltzmann solver contains the electron molecule cross sections, mainly derived from Hake and Phelps (H-P)[13] compilation.

The existing three databases[13-15] contain information on the electron molecule cross sections, involving the ground electronic state of CO_2, implying an inadequacy of their use when the plasma starts containing no-negligible concentrations of vibrationally and electronically excited states. Excited states largely affect the electron energy distribution function (eedf) through superelastic (second kind) collisions, both in discharge and post discharge conditions. Moreover, transitions from excited vibrational levels can strongly affect dissociation and ionization rates. These effects have been emphasized by Pietanza et al. in a series of papers[16-18], based on a parametric solution of the Boltzmann equation in the presence of excited states. Attention was also devoted to the influence of electron molecule vibrational excitation of the asymmetric mode[17,18]. The relevant cross sections, in this case, were

calculated by using a semiempirical equation formulated by Fridman[19] and also used by Bogaerts et al.[11,12]. The introduction of this set of cross sections decreases the tail of the electron energy distribution functions and, therefore, reduces the direct electron impact dissociation (DEM) and ionization rates. As a consequence, the dominance of pure vibrational mechanisms (PVM) over the DEM is extended to a large range of reduced electric field (E/N) values[17,18].

In this paper, we report a further study on the role of electron molecule cross sections, by including electron vibrational (e-V) excitation transitions among the symmetric mode levels of CO_2 and by studying their influence on eedf and dissociation rates. In the previous works[16-18], we have used, for these collisions, the cross section data reported in the H-P database[13], which, while allowing the intermode coupling of symmetric and bending modes, considers the relevant interactions starting from the ground state and ending towards five Fermi resonance levels, describing symmetric and bending modes.

One of the goals of the present work is to insert new e-V processes, in particular those linking the first 10 vibrational levels of the symmetric mode, i.e. the transitions

$$e^- + CO_2(v,0,0) \rightarrow e^- + CO_2(w,0,0),\ v<w \qquad (1)$$

calculating the relevant cross sections by considering all CO_2 vibrational modes as independent oscillators (decoupled vibrational model)[20]. The calculated e-V cross sections are shown in section 2, and compared with other theoretical and experimental cross sections present in literature, i.e. Szmytkowski's[21], Poparic's[22] and Rescigno's[23] ones. The set of cross sections is then inserted in the Boltzmann equation comparing the new eedf with the corresponding ones obtained by using the set of H-P cross sections[13]. The relevant differences propagate in the different rate coefficients, directly affecting the electron dissociation rates in the PVM and, indirectly, the rates of DEM, through the change in the eedf.

In the case of PVM, we estimate only upper limits of the corresponding rates[16-18], under the assumption that the vibrational quanta introduced by electron vibration energy exchange processes are dissipated by the dissociation process, instead of vibration-translation (V-T) energy exchange processes, which are important in the CO_2 system[24,25].

Concerning the electron impact dissociation cross section, in our previous papers[17,18], we have used the cross section reported in the H-P database, corresponding to the excitation of an electronic state with a threshold energy of 7 eV.

This cross section is not reported in the compilation by Itikawa[15], which considers a dissociation channel with a threshold at 12 eV. To a given extent, the experimental dissociation cross section by Cosby and Helm (C-H)[26], partially confirms the Itikawa cross section, being, however, up to a factor 5 larger.

The paper is subdivided in 5 sections. After the introduction, section 2 reports the electron molecule vibrational excitation cross sections over the first ten levels of the pure symmetric vibrational mode, calculated by using the decoupled vibrational model[20], and their comparison with existing literature data. Then, in section 3, we compare the eedf and the corresponding dissociation rates, obtained by solving the electron Boltzmann equation, with two different sets of electron impact cross sections. The first set corresponds to the H-P database (model 1), the second, is obtained by substituting the cross sections of model 1, those which involve the Fermi resonance levels, with the cross sections involving the symmetric mode levels, calculated in the present work and shown in section 2. Section 4, instead, examines the different electron impact dissociation cross sections existing in the literature and discuss the effect over the eedf and the relevant rates by adding the C-H[26] dissociation cross section to the H-P database (model 3). Finally, model 4, while keeping the dissociation channel of C-H, does eliminate the dissociation reported in the H-P database. Finally, section 5 presents conclusions and perspectives, describing, in particular, a road map for future improvements of theoretical models on CO_2 vibrational kinetics.

2. ELECTRON VIBRATIONAL EXCITATION CROSS SECTIONS ON THE SYMMETRIC MODE

The cross sections for the electron-impact induced resonant vibrational excitation (RVE), in CO_2 molecule, have been experimentally[13, 22, 27] and theoretically[21,23,28,29] investigated in the past and collected as recommended data[15, 30].

The RVE mechanism

$$e^- + CO_2(n_1,n_2,n_3) \rightarrow CO_2^- \rightarrow e^- + CO_2(w_1,w_2,w_3) \qquad (2)$$

proceeds through the resonant capture of the impinging electron with the formation of an intermediate short-living negative ion (i.e. CO_2^-, with a $^2\Pi_u$ shape resonance at 3.8 eV) eventually undergoing detachment and leading to the formation of vibrationally excited CO_2 molecules. All the excitation/de-excitation transitions involving the symmetric stretching are allowed, this aspect determining the importance of a consistent and complete dataset in the kinetics. It should be stressed that for bending and asymmetric stretching, due to the existence of transient dipole moments, direct non-resonant vibrational excitations have to be also taken into account. Unfortunately, their knowledge is still scarce and, in this context, these reactive channels are neglected.

The theoretical treatment of process in Eq. (2) still poses significant difficulties related to the existence of a resonance due to accidental degeneracy of levels ($n_1 = n_{sym} \approx 2n_{bend} = 2n_2$), coupling the symmetric stretching and the bending modes (*Fermi resonance*), that requires a two-mode treatment of the dynamics.

The RVE dataset here considered has been obtained in the assumption of a decoupled vibrational model[20]. The normal-mode approach allows to freeze some of the internal degrees of freedom in the molecule and to solve the electronic structure problem with *ab-initio* techniques in computational quantum chemistry. Multi Configuration Self

Consistent Field (MCSCF) calculations, adopting a correlation-consistent basis set of quadruple-zeta type (cc-pVQZ) for the construction of configuration states of molecules, including also static-exchange plus polarization (SEP) model, have been performed, by using the UK-*R-matrix* code[31], deriving the potential energy curves for the CO_2 ground ($^1\Sigma_g^+$) and CO_2^- resonant ($^2\Pi_u$) states and the resonance width relevant to the parametric variation of the symmetric stretch coordinate. The scattering problem has been solved in the frame of the *local complex potential theory*[32], deriving cross sections for the mono- and multi-quantum resonant vibrational excitations from/to the first ten levels of the symmetric-stretching mode of the kind (n,0,0).

The consideration of ten levels in the symmetric mode is sufficient in this context due to the large VT deactivation on this mode, which prevents the climbing of vibrational quanta up to the dissociation limit.

The assessment of accuracy goes through the comparison with the available results in the literature. In Fig. 1, the cross sections for the transitions from the ground to the first eight excited symmetric-mode levels are displayed, the energy profiles being characterized by a broad maximum, centred at the equilibrium resonance position, with oscillations, due to the vibrational structure of the molecular ion intermediate.

The (000)→(100) excitation cross section compares satisfactorily with the theoretical results of Szmytkowski[21], obtained in a similar decoupled theoretical framework. One relevant feature is the character of the oscillations, quite pronounced in the present cross sections, while much smoother in Szmytkowski's results[21]. The mixing of states, due to the inter-mode coupling, is identifyed as responsible of the smoothing out of oscillations in Kazanskii's results[28,29], well-reproduced by Szmytkowski[21], by virtue of the adjustment of the resonant state parameters, in order to fit experimental data for symmetric channel. For the (000)→(100) transition, a general discrepancy is found between theory and experiments. In fact, the predicted cross section is lower than the experimental values in literature[13,22,33], crossed beam experiments[22], being in better agreement than the estimation inferred from the swarm data[13]. It is worth

noting that the theoretical model is not able to reproduce the theshold peak (at 0.3-0.4 eV), observed in the experimental cross section[13,33] and attributed to a second low-energy resonant virtual state (Σ_g)[27].

As expected, the process becomes less favourable for multi-quantum transitions and the general agreement between experiment and theory improved.

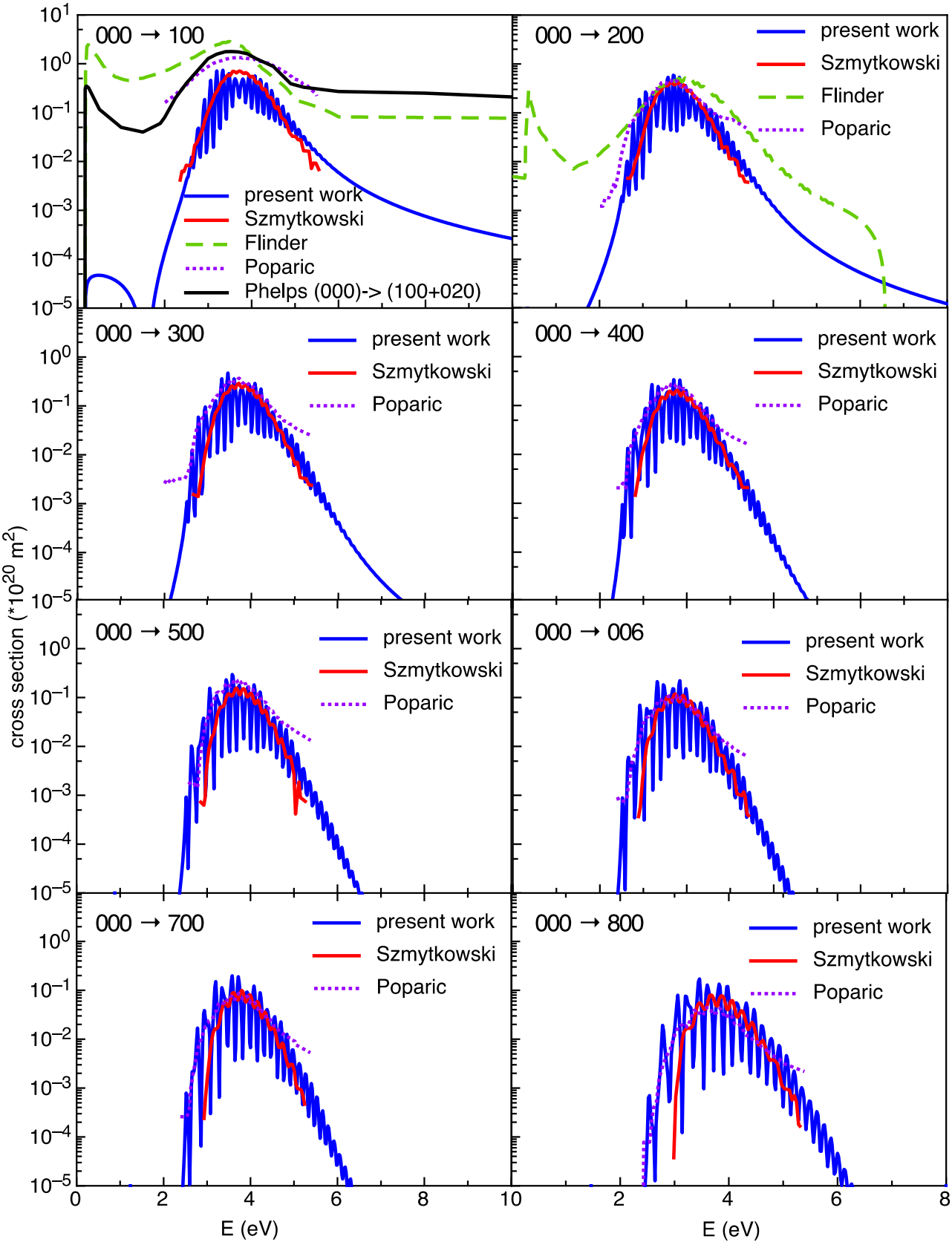

Fig. 1 Cross sections for the resonant vibrational excitations for transitions from the ground state (000) to the first eight excited symmetric-mode vibrational levels (n00), in e-CO_2 collisions, calculated in the present work, compared with the theoretical results by Szmytkowski[21] and the experimental results by Poparic[22], Flinder[33] and Phelphs[13] database.

In Fig. 2, the excitation cross sections, from the (100) level, are compared with results by Szmytkowski[21]. The first evidence is the change in the energy profile, characterized by the lowering of the threshold and by a double peak structure, theoretical results agreeing quite well on both peak position and absolute cross section value. The peaks regularly increase in number with the initial level, while remain located almost at the same energy regardless the final vibrational level as appreciable in Fig. 3, where selected excitation transitions involving (n,0,0) levels with n>1 are displayed. Further increase of n produces a very broad profile where the peak closeness makes them indistinguishable.

The comparison with the results from Rescigno[23] allows estimation of the role of inter-mode-coupling in affecting the RVE cross sections. In Rescigno's work[23], a quantum two-mode treatment of the nuclear dynamics is performed, accounting for the splitting of the doubly degenerate $^2\Pi_u$ resonance in two non-degenerate components, $^2A_1$ and $^2B_1$, when the linear geometry is destroyed by the coupling with the bending mode. In Fig. 4, the cross sections for the so-called Fermi dyade (100+020) (Fig. 4 a) and tryade (200+120+040) (Fig. 4 b) are reported and compared with the corresponding excitations obtained in the decoupled-mode scheme. Though the symmetric-mode excitation reproduces at a certain degree one of the components of the polyad, the bending-mode cross sections are significantly different from the other components, emphasizing the need of a coupled-mode treatment.

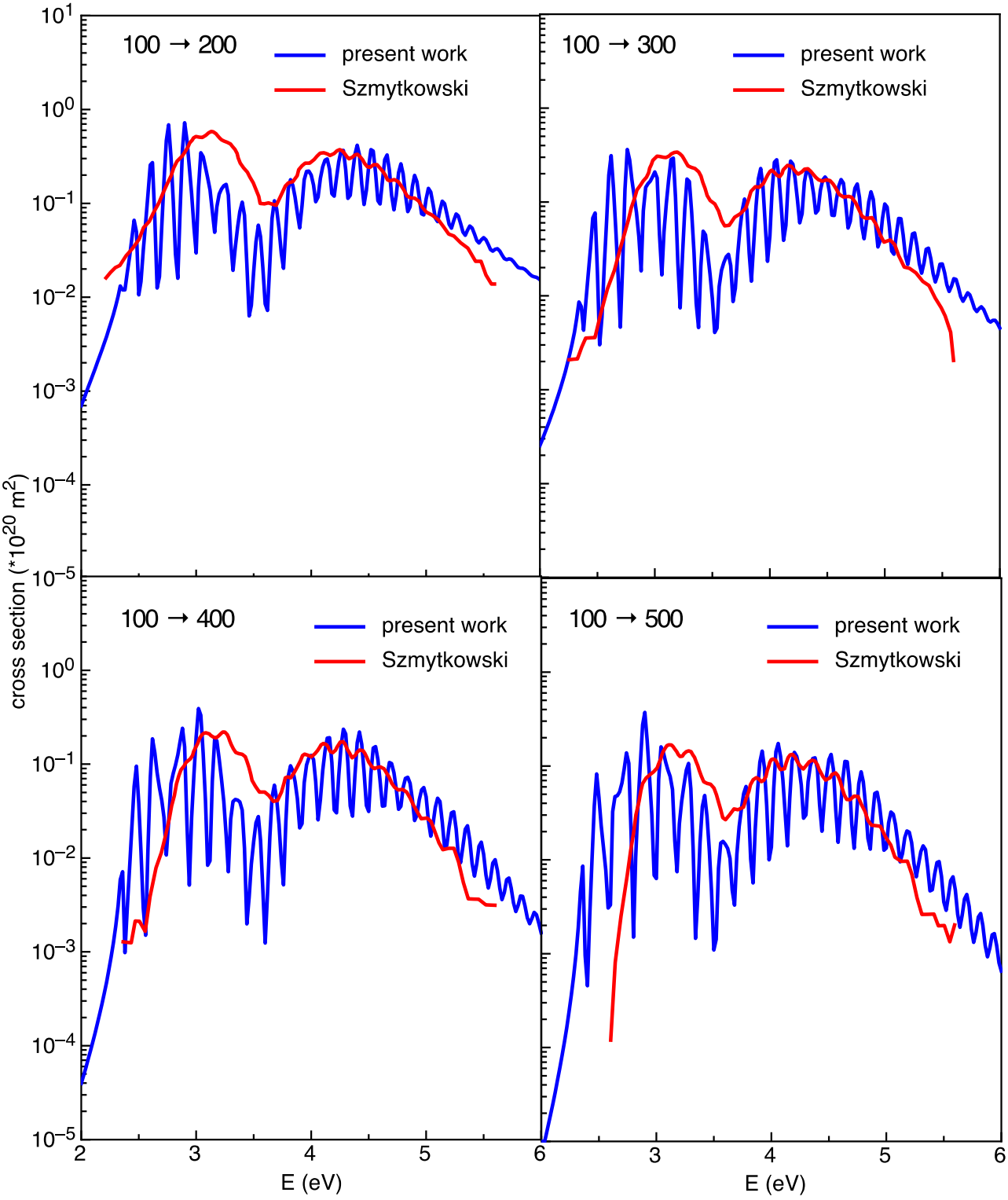

Fig. 2 Cross sections for the resonant vibrational excitations for transitions from the first excited (100) to higher symmetric-mode levels (n00), in e-CO_2 collisions, compared with results by Szmytkowski[21].

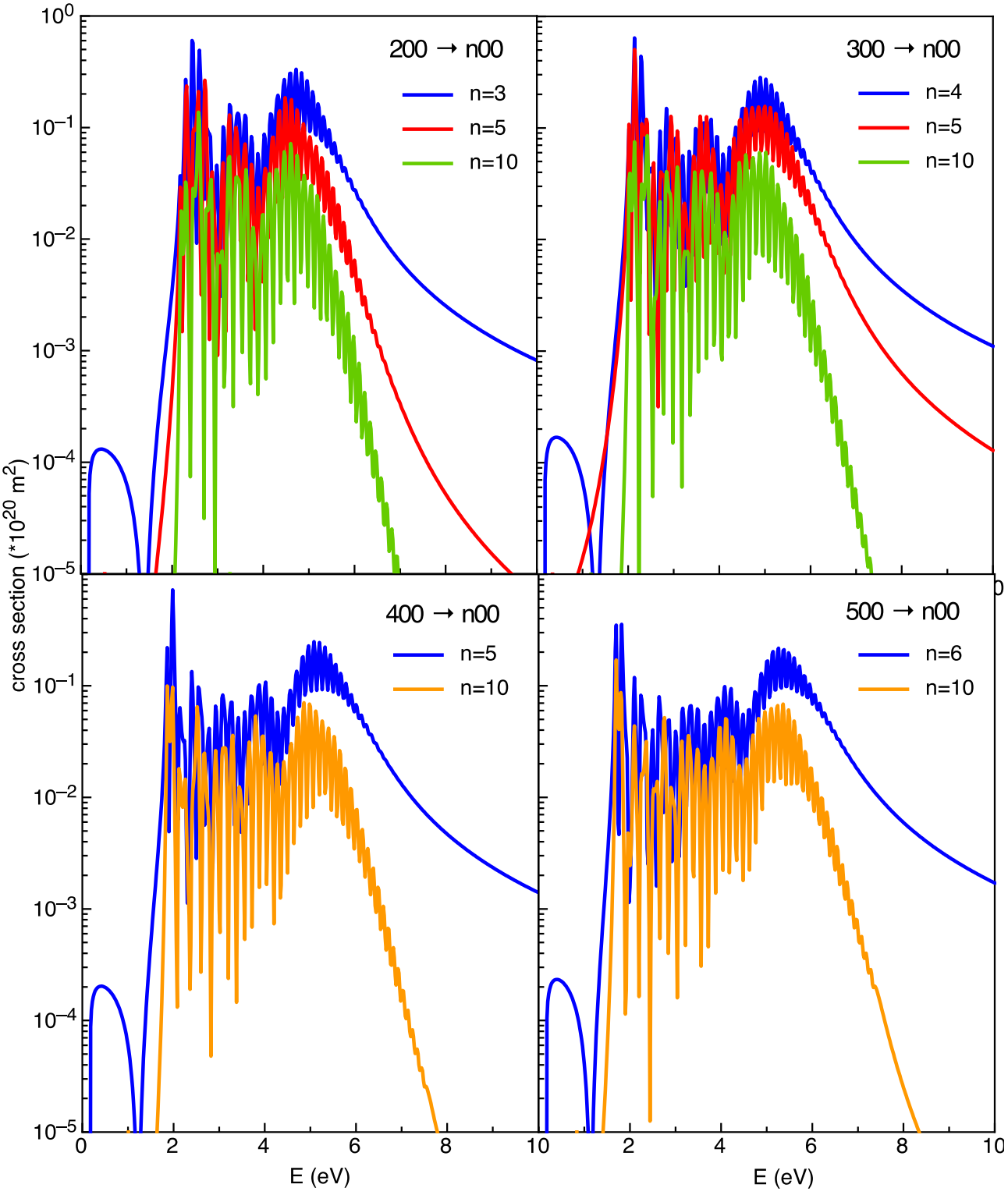

Fig. 3 Cross sections calculated in the present work for the resonant vibrational excitation transitions among excited levels of the symmetric mode, in e-CO_2 collisions.

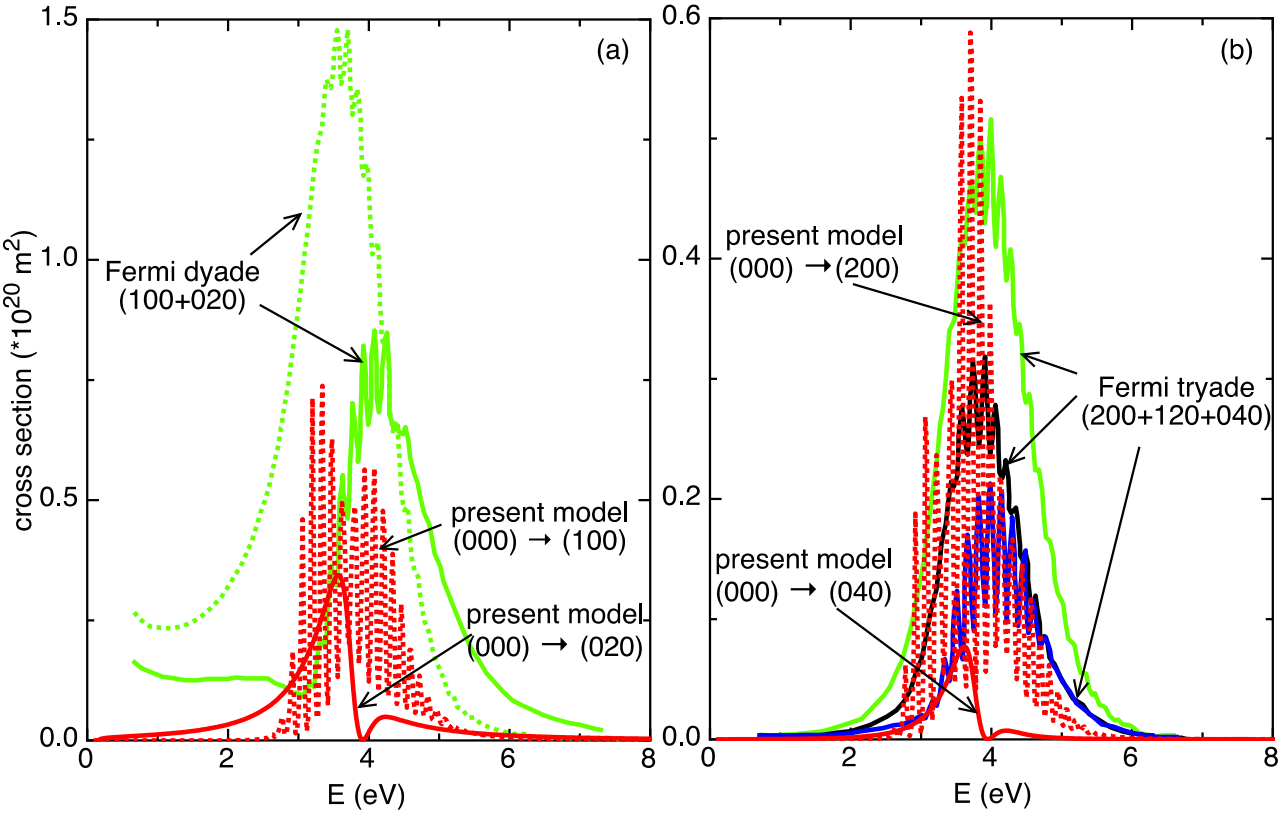

Fig. 4 a, b Cross sections for resonant vibrational excitations, in e-CO_2 collisions, for transitions (a) (000)→(100) and (000)→(020) of the present model (decoupled scheme), compared with the Fermi dyade (100+020) from Rescigno[23] (upper and lower lines denotes, respectively, the high-and low-energy components of dyade); (b) (000)→(200) and (000)→(040) of the present model, compared with the Fermi tryade (200+120+040) from Ref.[23] (lines in order of decreasing magnitude denote high-, middle and low-energy members of triad).

3. METHOD OF CALCULATION AND RESULTS

We solve an appropriate Boltzmann equation written in compact form as[16-18, 34-40]

$$\frac{dn(\varepsilon,t)}{dt} = -\frac{dJ_E}{d\varepsilon} - \frac{dJ_{el}}{d\varepsilon} - \frac{dJ_{e\text{-}e}}{d\varepsilon} + S_{in} + S_{sup} \qquad (3)$$

where $n(\varepsilon,t)d\varepsilon$ represents the number of electrons in the energy range ε and $\varepsilon + d\varepsilon$. The different terms, on the right hand side of Eq. (3), represent the flux of electrons along the energy axis, respectively, due to the electric field $\frac{dJ_E}{d\varepsilon}$, elastic electron-

molecule collisions $\frac{dJ_{el}}{d\varepsilon}$, electron-electron (e-e) collisions $\frac{dJ_{e\text{-}e}}{d\varepsilon}$, inelastic S_{in} and superelastic S_{sup} collisions. Explicit expressions of the different contributions, including the e-e one, can be found in the following papers[36,39,40]. Eq. 3 derives from the work of Rockwood[34] and it is based on a two term Boltzmann expansion, which is considered adequate against the more accurate multiterm approach[39], in this application context, especially considering the poor knowledge of the relevant cross sections.

The H-P database considers the following simplified CO_2 energy ladder including:

1. eight vibrational levels (v_i with $0 \leq i \leq 8$), the fundamental v_0 (000), the first bending mode level v_1 (010), the first asymmetric mode level v_8 (001) and five mixing levels (Fermi resonance levels) v_2-v_7 ($0n0$+$n00$);
2. two electronic levels (e_1, e_2) with threshold energies, respectively, at 7.0 and 10.5 eV, the first one considered as a dissociative channel, the second as an excitation one.

The corresponding electron impact cross sections, in the H-P database, are the vibrational excitation/de-excitation from ground level v_0 towards the first bending mode level v_1, the five Fermi resonance levels v_2-v_7, the first asymmetric mode level v_8 and the electronic excited state e_1 and e_2, and an ionization cross section with a threshold energy of 13.5 eV. All the corresponding threshold energies can be found in previous papers[16-18]. As already stated, we have selected the excitation of the electronic excited state e_1 as a dissociative channel with threshold energy of 7 eV. Note that, the H-P database considers only transitions from ground state, neglecting those among vibrationally excited levels.

The aim of the present work is to investigate how the calculated eedfs change following the selection of electron impact cross sections included into the calculation. For this purpose, as anticipated, we consider four different models.

The first model (model 1), whose results have been already presented in previous works[17,18], includes, in the Boltzmann solver, the electron-CO_2 cross sections of the H-P database. The second model (model 2) is obtained by model 1, by substituting

the e-V processes of H-P database, which link the ground state and the five Fermi resonant levels, with the e-V cross sections of the symmetric mode levels, calculated in this paper and reported in section 2. In particular, the electron impact excitation/de-excitation processes linking the ground state v_0 to the first ten symmetric mode levels of the kind (n00) with $1 \le n \le 10$ and also mono- and multiquantum transitions among excited symmetric levels. These processes substitute, in model 2, the transitions to the five Fermi levels, to avoid double accounting for symmetric vibrational levels.

The third and the fourth model, instead, add, to model 1, the C-H experimental dissociation cross section[26], keeping (model 3) and removing (model 4) the H-P dissociative channel at 7 eV. The results corresponding to the last two models will be presented in section 4.

The solution of the electron Boltzmann equation (eq. 3) has been performed in discharge conditions at different values of the reduced electric field (E/N=15, 30, 50, 80 Td) and by imposing a Boltzmann distribution for the CO_2 vibrational levels.

In particular, two different vibrational temperatures, denoted by T_1 and T_2, have been defined, see[16-18]. The first (T_1) describes the bending mode level (v_1) and the Fermi (v_2-v_7) and the symmetric mode levels (s_i, with $1 \le i \le 10$), when included; the second (T_2), the asymmetric mode levels v_8 and the electronic excited state e_1.

The assumption of a Boltzmann distribution for the CO_2 vibrational levels is an approximation. The use of non-equilibrium vibrational distributions, such as those reported in[11] will increase the PVM rates, especially in the presence of populated plateau in the vibrational distribution function of the asymmetric mode.

The eedf and dissociation rates results, in discharge conditions, do not change if the temperature of the electronic state e_1 is assumed equal to T_1 or T_2. This because, for the chosen T_1/T_2 temperature range, the electronic state level populations are low and the corresponding superelastic electronic collisions have a negligible effect over the eedf and the rates. This is not valid in post discharge conditions, in which the e_1

electronic excited state can be characterized by a very high level population and its corresponding superelastic electronic collisions have a crucial role in the kinetics.

Calculations have been performed at different couples of T_1 and T_2 temperatures (T_1=0 K, T_2=0 K); (T_1=500 K, T_2=1500 K); (T_1=1000 K, T_2=2000 K); (T_1=2000 K, T_2=3000 K); (T_1=3000 K, T_2=5000 K); (T_1=4000 K, T_2=6000 K); (T_1=6000 K, T_2=8000 K), but the rates are displayed only as a function of T_2.

The choice of parameters (E/N, T_1, T_2) has been made by trying to reproduce the average energies found under experimental conditions (electron average energy in the range 1-4 eV, see Kozak et al.[11,12] and Silva et al.[42]). The choice of T_2 is in line with the estimation made in the experiments of Silva et al.[42] (see Fig.11 and comments). On the other hand, we consider $T_1<T_2$, coming from experiments on the CO_2 laser[43] and justified by the small values of V-T rates in the asymmetric mode levels, as compared to the corresponding rates in the other modes.

A comparison of the stationary eedf, coming from models 1-2, has been reported in Fig. 5 a-d and 6 a-d, as a function of the electron energy, for different vibrational temperatures and different reduced electric field values, in the presence or not of e-e Coulomb collisions, respectively. The choice of an ionization degree of 10^{-3} has been selected only to maximize the effect of electron-electron collisions on eedf and can be considered as an upper limit to the actual ionization degrees under many experimental conditions. In all the reported cases, we can see the large effect of the superelastic vibrational collisions in enlarging the eedf's tail, this effect decreasing with both the increase of E/N value and of the vibrational temperature(s). The insertion of e-e collisions is such to decrease the role of superelastic vibrational collisions, as can be appreciated by comparing the results reported in the relevant figures.

On the other hand, the eedf calculated in model 2, qualitatitively and quantitatively, follow those obtained in model 1. Small deviations, between the results from models 1-2, occur at low E/N and T_1, T_2 values in the low energy part of the eedf, becoming no-negligible in the eedf tail. These results can be considered important for the future

development of a state-to-state vibrational kinetics of CO_2 modes, indicating the possibility to consider for the symmetric mode an uncoupled model, at least for the Boltzmann equation.

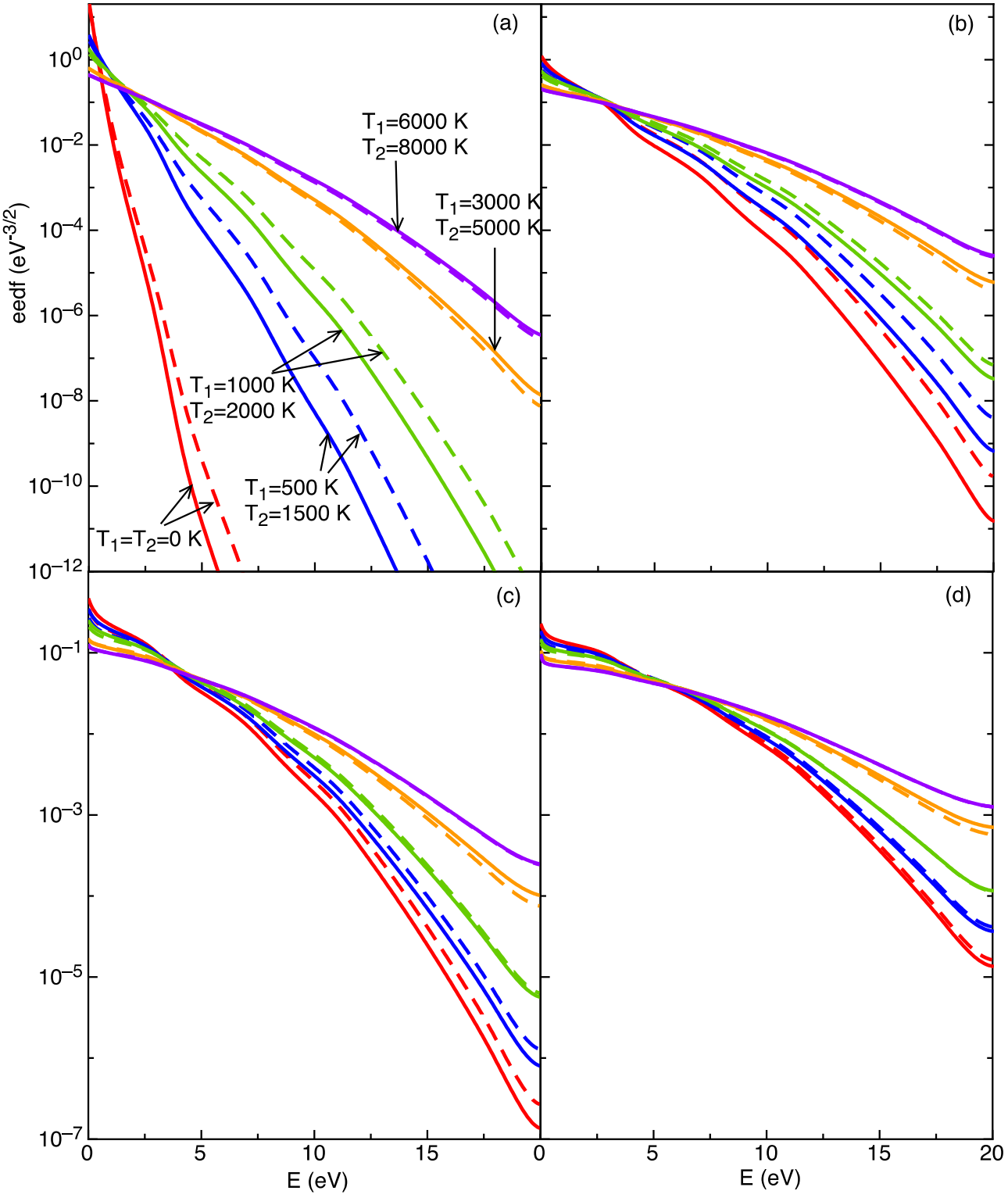

Fig. 5 a-d Stationary eedf as a function of the electron energy in model 1 (full lines) and in model 2 (dashed lines) under discharge conditions with (a) E/N=15 Td; (b) E/N=30 Td; (c) E/N=50 Td; (d)

E/N=80 Td and for different couples of vibrational temperatures (T_1, T_2) (with e-e collisions, ID=10^{-3}).

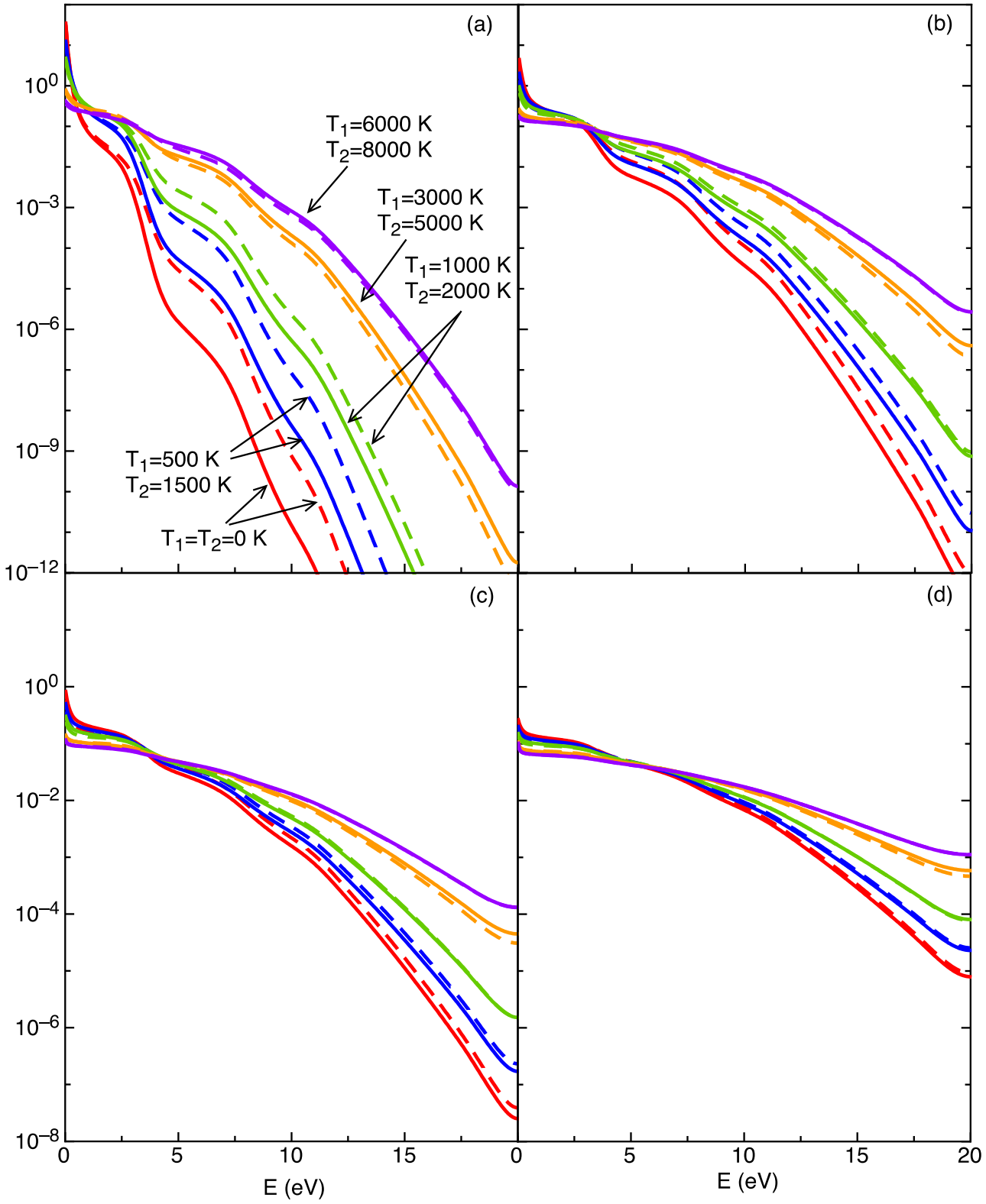

Fig. 6 a-d Stationary eedf as a function of the electron energy in model 1 (full lines) and in model 2 (dashed lines) under discharge conditions with (a) E/N=15 Td; (b) E/N=30 Td; (c) E/N=50 Td; (d) E/N=80 Td and for different couples of vibrational temperatures (T_1, T_2) (neglecting e-e collisions).

It is also interesting to show the differences in selected rates of monoquantum and multiquantum transitions, among the symmetric mode levels (model 2), and reported in Fig. 7 a-b as a function of T_2/T_1 values and for two different E/N values. We can see (Fig. 7 a), that monoquantum transitions over high-lying vibrational states are of the same order of magnitude of the transition starting from the ground state, at E/N=80Td, becoming also important with the increase of vibrational temperature(s) at E/N=15Td. A similar behaviour is presented by multiquantum rates (see Fig. 7 b). The reported trends depend both on the form of the different cross sections and on the eedf dependence on the E/N and T_2, T_1 values.

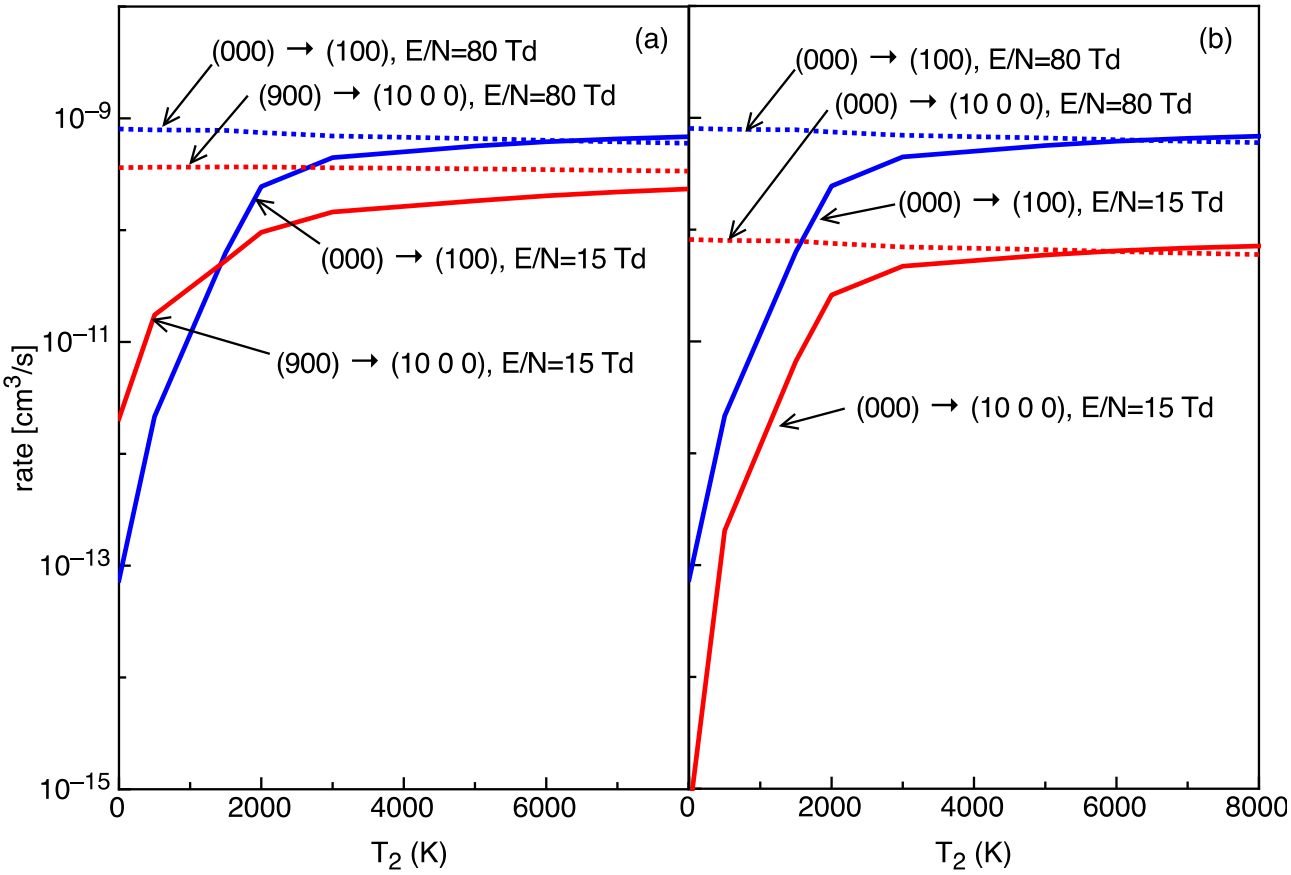

Fig. 7 a-b Rates for e-CO_2 resonant excitation transitions among symmetric-mode vibrational levels (model 2) as a function of the vibrational temperature T_2, for (a) mono-quantum transitions (000)→(100) and (900)→(10 0 0) and (b) mono-quantum transitions (000)→(100) and multi-quantum (000)→(10 0 0) at two different values of E/N (15 Td and 80 Td).

Let us consider now the effect of the different sets of e-V cross sections, introduced in the models 1-2, over the dissociation rates by DEM and PVM upper limit values. These rates have been already defined in details in previous works[16-18] and only a brief summary will be provided here.

Direct electron impact dissociation rates from ground state, $k_d(000)$, can be calculated by the following expression

$$k_d(000) = \int_{E_{thr}} f(\varepsilon)\sigma(\varepsilon)v(\varepsilon)d\varepsilon \qquad (4)$$

where $\sigma(\varepsilon)$ represents the dissociation cross section from ground state, E_{thr} the dissociation threshold energy, $f(\varepsilon)$ and $v(\varepsilon)$ the eedf and the electron velocity.

To take into account dissociation from excited vibrational levels, the following approximate formula has been introduced[16,44]

$$K_d(all) = \sum_i \exp\left[\frac{\varepsilon_i}{k_B}\left(\frac{1}{T_e} - \frac{1}{T_v}\right)\right] k_d(000) \qquad (5)$$

where ε_i are the excited vibrational level energies, k_B the Boltzmann constant, T_e and T_v the electron and vibrational temperatures, respectively. Eq. 5 is a consequence of different assumptions (see [16-18,44]): 1) the dependence of the cross sections on the principal quantum number is obtained by shifting the threshold energy by the appropriate energy[45]; 2) a Boltzmann distribution is considered for the vibrational levels; 3) a Maxwell distribution function is considered for electrons at the same energy of the actual eedf. This last approximation can be open to question under non-equilibrium conditions, as shown in this paper, as well as earlier by Petrovic et al.[46].

The PVM upper limit values of dissociation rates can give an estimation of dissociation induced by vibrational excitation, avoiding detailed vibrational kinetic model calculations. As a first approximation, we can suppose that e-V resonant

energy exchange processes introduce vibrational quanta at the bottom of the vibrational ladder, transported by vibration-vibration (V-V) up pumping mechanism[47] and then are dissipated by the dissociation process[48,49].

Considering only monoquantum transitions from ground state in the asymmetric mode, we can get the following expression[16,48]

$$K_d^{(ulPVM)} = \frac{1}{v_{max}} k_{eV}(0 \rightarrow 1) \qquad (6)$$

where $k_{eV}(0 \rightarrow 1)$ is the rate of the resonant $(000) \rightarrow (001)$ vibrational excitation process and v_{max} the number of vibrational quanta of the asymmetric mode, up to the dissociation limit (i.e. $v_{max}=21$).

On the other hand, considering the effect of excited vibrational levels, we can obtain the following formula, where the sum is performed to all eV available cross sections from ground state

$$K_d^{(ulPVM)}(all) = \frac{1}{v_{max}} \sum_i \frac{\varepsilon_i}{\varepsilon_{a_1}} k_{eV}(v_0 \rightarrow i) \qquad (7)$$

Note that in Eq. (7), we include the contribution of all the vibrational levels of the model, thus also symmetric and bending modes, but their vibrational quanta (ε_i) are normalized to the first asymmetric mode energy level (ε_{a_1}). This approximation to a given extent reduces the influence of the symmetric and bending modes, which present lower excitation threshold energies as compared with the asymmetric mode.

It is not easy to quantify the accuracy of Eqs. (6) and (7), which largely depends on the interplay of V-V and V-T energy exchange processes along the different vibrational modes. We can roughly estimate an accuracy up to a factor 5 for the asymmetric mode (i.e. Eq.(6)), since, in this case, V-V rates exceed the V-T ones, a situation discussed for different diatomic systems[48,49]. On the other hand a much

lower accuracy is expected for Eq. (7), which includes the symmetric and bending modes contribution due to the strong V-T deactivation rates along them.

In Fig. 8 and 9, the dissociation rate by electron impact of eq. (4) and (5) and the PVM upper limit values of eq. (6) and (7) are compared, as a function of the vibrational temperature T_2, for models 1 and 2 and for different E/N values, by including or not e-e collisions.

The differences in the relevant values from models 1 and 2 depend on the eedf differences, as well as, on the adopted cross sections for the vibrational excitation of the symmetric mode. The last point is responsible of the change in the $K_d^{(ulPVM)}(all)$ values in the two models, which persist in all the considered cases. On the other hand, the DEM values, in the two models, differ especially at low E/N and T_2 values, following the eedf behaviour.

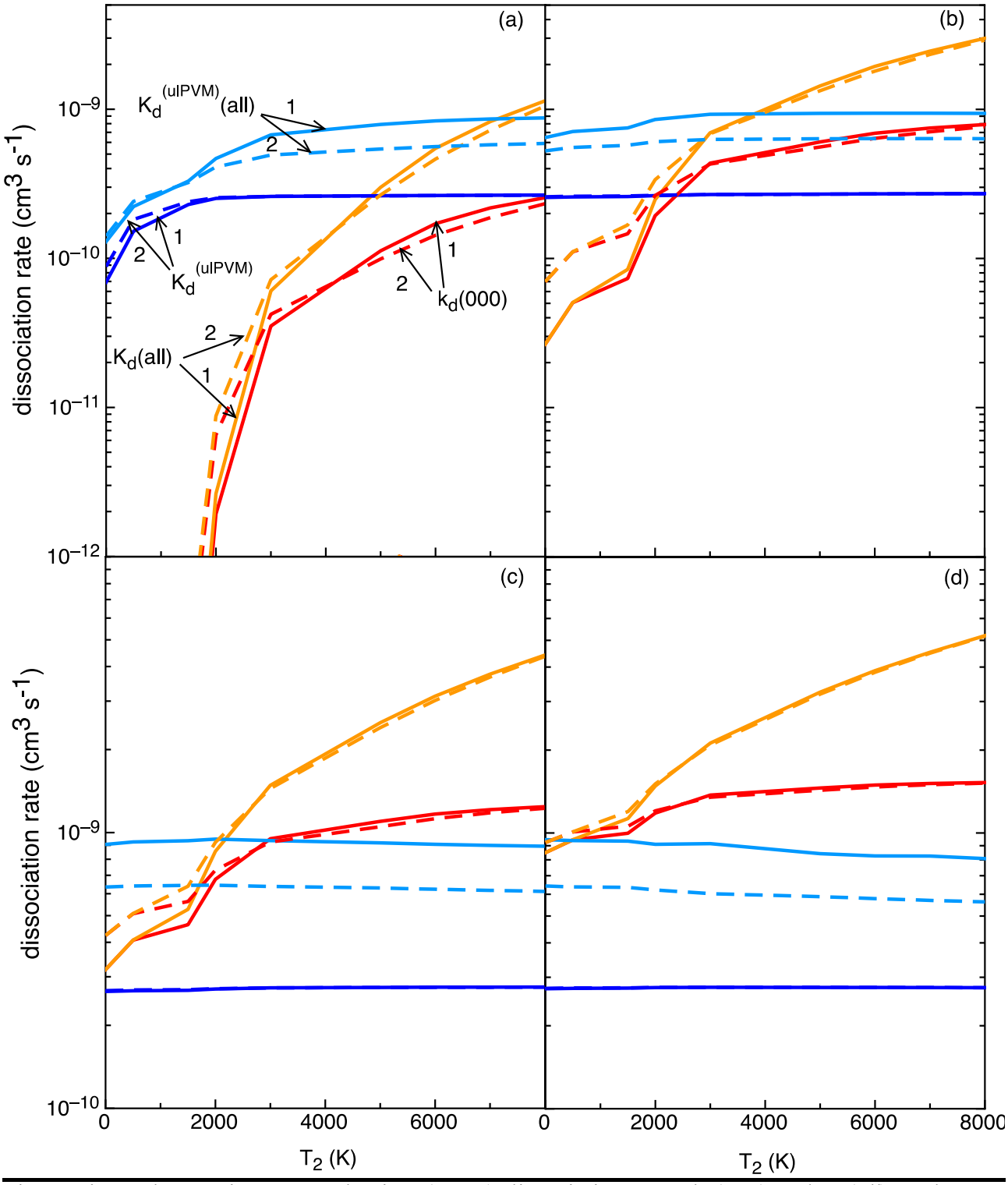

Fig. 8 Direct electron impact mechanism (DEM) dissociation rates, $k_d(000)$ and $K_d(all)$, and upper limit values of pure vibrational mechanism (PVM) dissociation rates, $K_d^{(ulPVM)}$ and $K_d^{(ulPVM)}(all)$, as a function of T_2, in the model 1 (full lines) and model 2 (dashed lines), under discharge conditions with (a) E/N=15 Td; (b) E/N=30 Td; (c) E/N=50 Td; (d) E/N=80 Td (with e-e collisions, ID=10^{-3}).

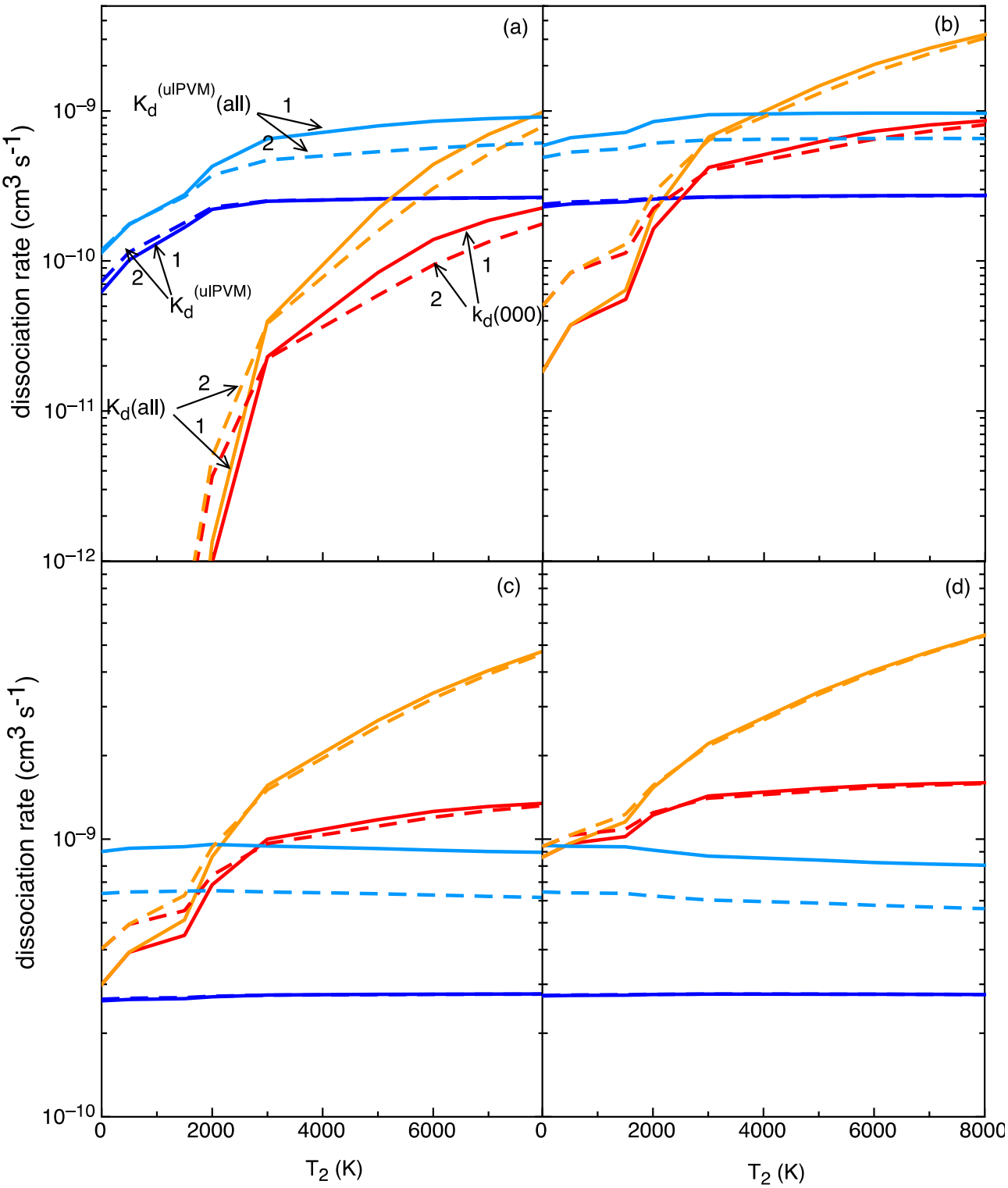

Fig. 9 Direct electron impact mechanism (DEM) dissociation rates, $k_d(000)$ and $K_d(all)$, and upper limit values of pure vibrational mechanism (PVM) dissociation rates, $K_d^{(ulPVM)}$ and $K_d^{(ulPVM)}(all)$, as a function of T_2, in the model 1 (full lines) and model 2 (dashed lines), under discharge conditions with (a) E/N=15 Td; (b) E/N=30 Td; (c) E/N=50 Td; (d) E/N=80 Td (without e-e collisions).

4. A NEW CHOICE OF THE ELECTRON IMPACT DISSOCIATION CROSS SECTION

As already anticipated, the electron impact dissociation cross sections, used in the previous section, as well as in refs.[16-18], correspond to a process considered in the deconvolution of swarm data by H-P database[13]. Such a cross section (H-P) is shown in Fig. 10, together with other CO_2 dissociation cross sections, reported in literature by different authors (Corvin and Corrigan[50], Itikawa[15], Fridman[7], C-H[26]). The H-P cross section shape is typical for forbidden transitions, i.e for the process

$$e^- + CO_2(X) \rightarrow e^- + CO_2(a^3\Pi) \rightarrow e^- + CO(X^1\Sigma^+) + O(^3P) \quad (8)$$

and is characterized by a threshold energy of 7 eV and a peak of about 0.6 10^{-16}cm^2 at 7.5 eV. The electron energy dependence of this cross section is in satisfactory agreement with the indirect measurements performed by Corvin and Corrigan[50], with a threshold energy of 6.1 eV and a peak of 0.35 10^{-16}cm^2 at 6.9 eV. Similar measurements performed by Smith and Austin[51] convalidate the results of Corvin and Corrigan[50].

On the other hand, Cosby and Helm[26] performed a more accurate determination of the dissociation process by electron beam interaction in the energy range 12.4 - 200 eV. The corresponding cross section (see Fig. 10) presents a threshold energy of 12 eV and a peak of 0.94 10^{-16} cm^2 at 27 eV and seems characteristic of the following transitions

$$e^- + CO_2(X) \rightarrow e^- + CO(X^1\Sigma^+) + O(^1S) \quad E_{thrs} = 9.539 \text{ eV} \quad (9)$$

$$e^- + CO_2(X) \rightarrow e^- + CO(a^3\Pi) + O(^3P) \quad E_{thrs} = 11.385 \text{ eV} \quad (10)$$

The same authors estimate a branching ratio of the reactions 79% for the first reaction and 21% of the second one. In Fig. 10, the dissociation cross section of Itikawa[15],

corresponding to reaction of eq. (10), is also reported. The corresponding cross section, while much lower than the C-H one, spans the same energy range.

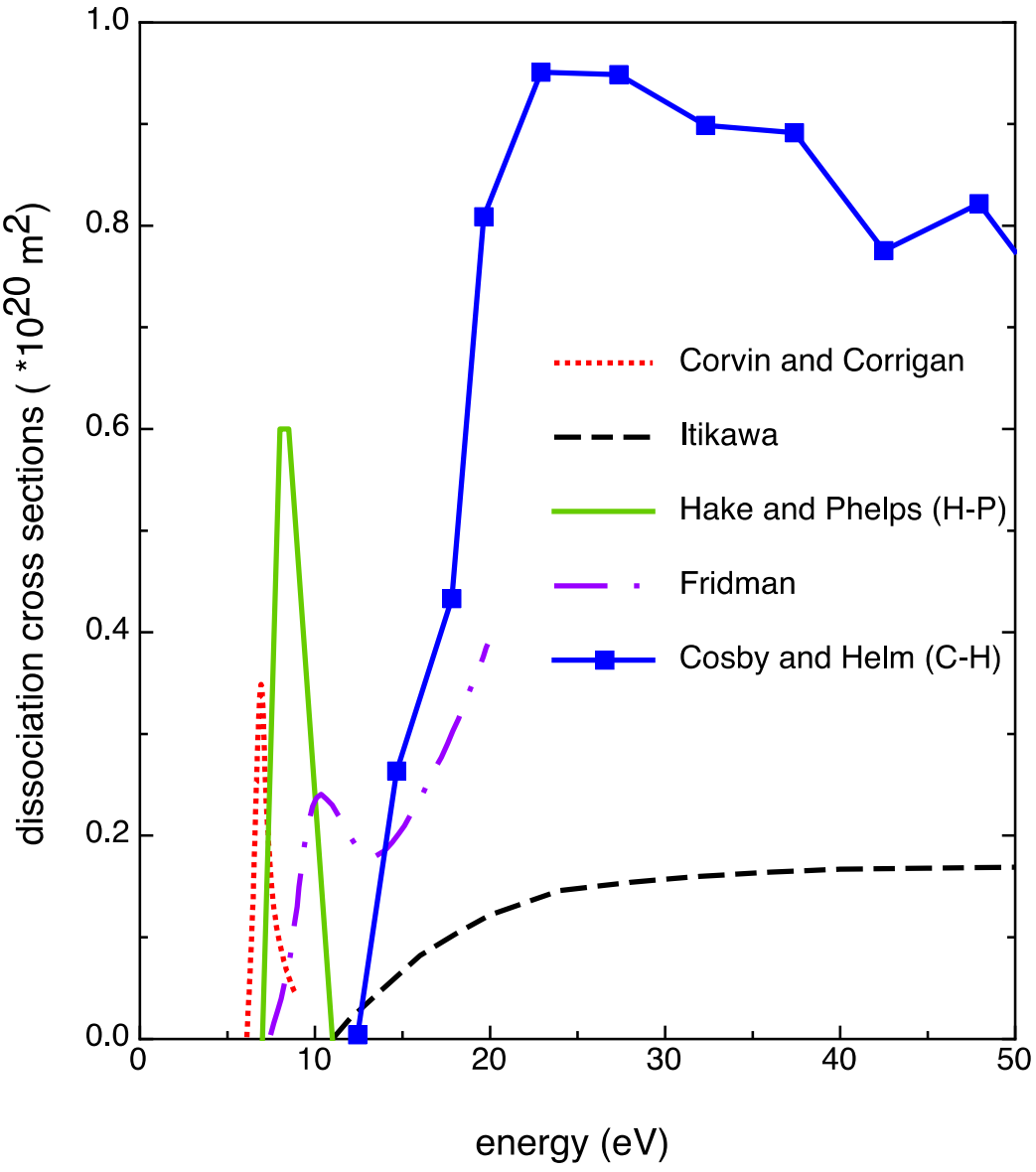

Fig. 10 CO_2 dissociation cross sections by different authors (Corvin and Corrigan[50], Itikawa[15], Hake and Phelps (H-P)[13], Fridman[7], Cosby and Helm (C-H)[26]).

Inspection of Fig. 10 shows that the indirect experimental results of Corvin and Corrigan[50], of H-P[13], as well as those of Smith and Austin[51], seem to indicate a dissociation channel at low energy, while the C-H one[26] indicates another high energy dissociation contribution. In Fig. 10, we report also the total dissociation cross section of Fridman[7], obtained by considering other independent choices, including

both a low energy threshold process and a high threshold energy one. A more complex theoretical and experimental work on CO_2 dissociation is needed to eliminate the existing large uncertainties, including the dependence of the electron impact dissociation cross section on the vibrational quantum numbers.

In this section, we want to understand how a different choice of dissociation cross sections affects our parametric results. In particular, in the Boltzmann solver, we add, to the H-P database, the C-H experimental cross section (model 3). Fig. 11 compares the stationary eedfs, obtained in model 1 and 3, under different discharge conditions (E/N=15, 30, 50, 80 Td) and several vibrational temperatures, neglecting e-e Coulomb collisions. Small differences appear only in the tails of the eedf distributions. In particular, the addition of the C-H dissociation channel is such to slightly decrease the eedf tail. Consideration of e-e Coulomb collision, up to an ionization degree of 10^{-3}, does not appreciably modify the qualitative and quantitative behaviour of eedf reported in Fig. 11. The low energy part of eedf, dominated by the e-V processes, which are the same in the two models, is practically unchanged in models 1 and 3. We should, therefore, expect no variations in the PVM rates. On the contrary, the DEM rates involving ground state and vibrational excited states should present differences in the two models, due to the large differences in the dissociation cross section. In particular, we should expect that the high threshold energy C-H dissociation rates should be much lower than the corresponding rates from H-P, these differences decreasing with the increase of E/N value and of the vibrational temperatures. These qualitative considerations are recovered in the relevant rates. Fig. 12 reports the relevant rates obtained in model 3.

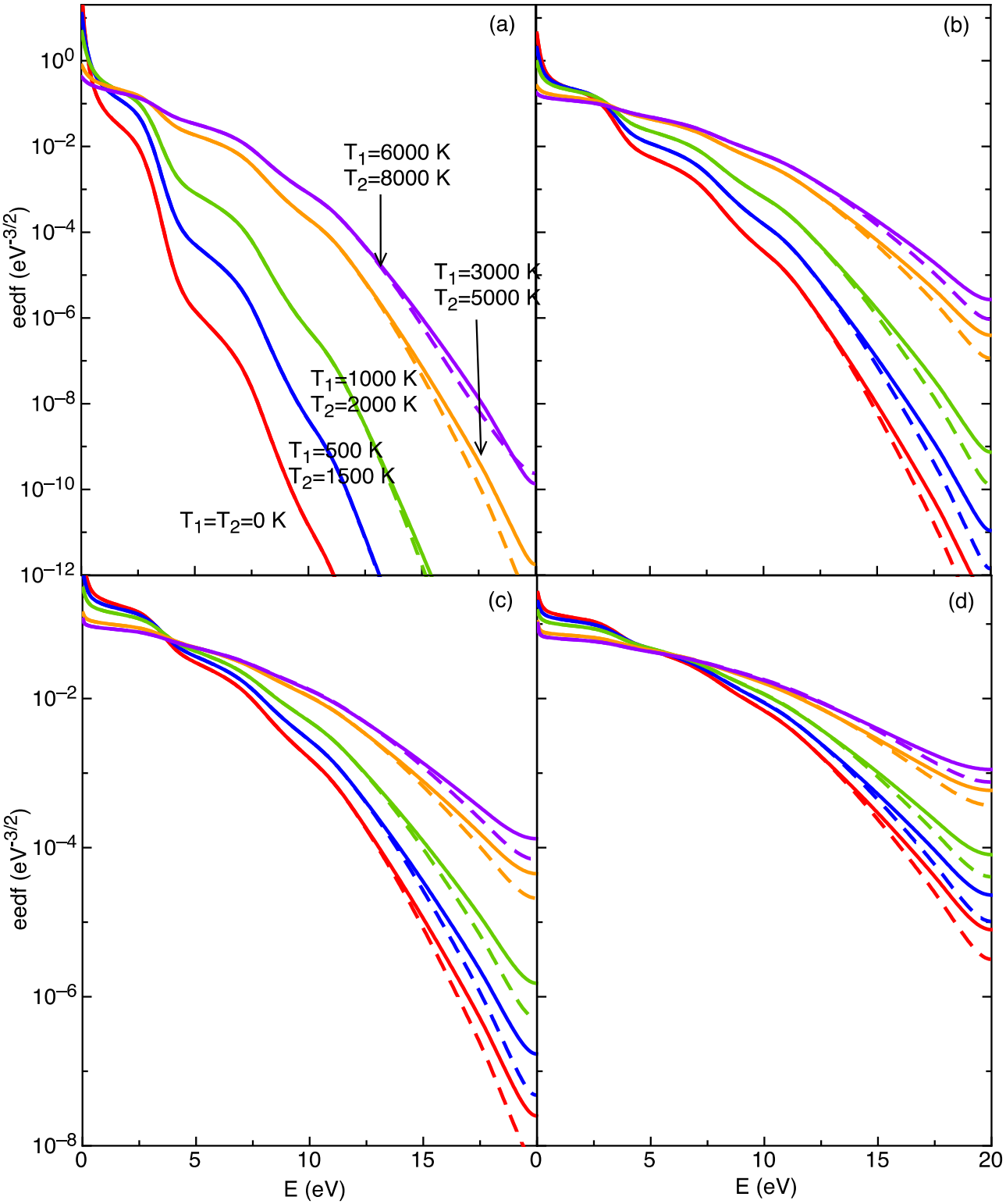

Fig. 11 Stationary eedf as a function of the electron energy in model 1 (full lines) and in model 3 (dashed lines) in discharge conditions without e-e collisions (a) E/N=15 Td; (b) E/N=30 Td; (c) E/N=50 Td; (d) E/N=80 Td for different couples of vibrational temperatures T_1, T_2.

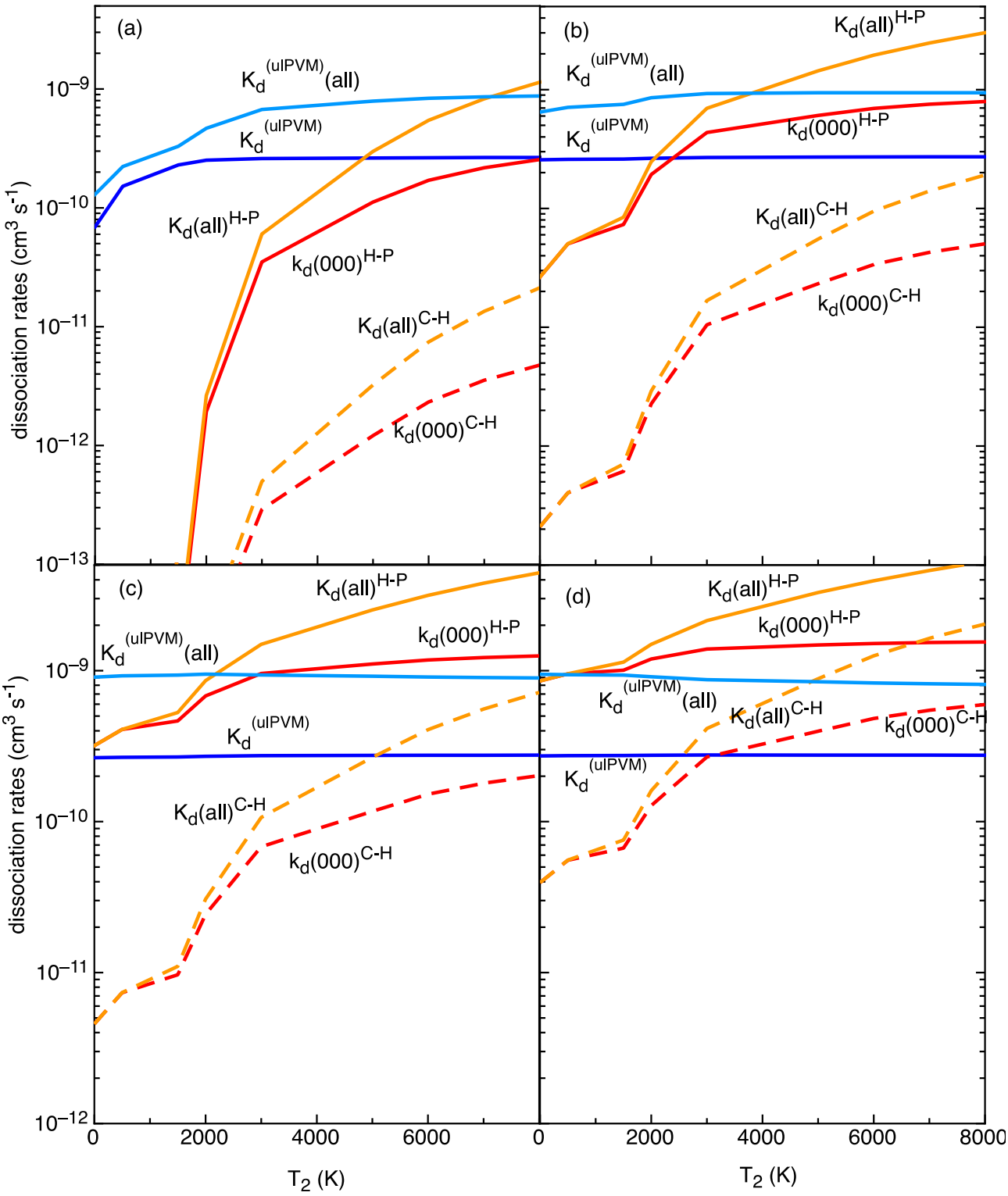

Fig. 12 Direct electron impact mechanism (DEM) dissociation rates of H-P, $k_d(000)^{H\text{-}P}$, $K_d(all)^{H\text{-}P}$, and C-H, $k_d(000)^{C\text{-}H}$, $K_d(all)^{C\text{-}H}$, and upper limit values of pure vibrational mechanism (PVM) dissociation rates, $K_d^{(ulPVM)}$ and $K_d^{(ulPVM)}(all)$, as a function of T_2 vibrational temperature, in the model 3, under discharge conditions with (a) E/N=15 Td; (b) E/N=30 Td; (c) E/N=50 Td; (d) E/N=80 Td (without e-e collisions).

The inclusion of C-H cross section to the H-P database adds another contribution to the total dissociation rate, which is much lower than the H-P dissociation one. However, the total dissociation rate, in model 3, is still governed by the H-P dissociation process, the C-H one starting to be important only at very high E/N values.

Of course, the situation completely changes if the addition of the C-H process in the H-P database is made by substituting it to the low energy threshold dissociation process of H-P (model 4). In this case, the eedf's are not sensibly modified because the low energy dissociation process is hidden in the Boltzmann equation by the e-V processes. However, the lack of the H-P dissociation process, substituted by the C-H one, decreases the importance of the dissociation channel in the relevant rates (see Fig. 13), increasing, at the same time, the importance of PVM mechanisms.

This result affects the fractional power losses in the CO_2 system (see ref.[17] for the relevant equations). In particular, use of C-H cross section, instead of H-P one, decreases the power losses through the dissociation channel, increasing, at the same time, the other channels, as it can be appreciated in Fig. 14.

The lack of the H-P dissociation cross section increases the eedf values in the range of the electronic excitation threshold energy (10.5 eV) and, as a consequence, promote the corresponding electronic excitation channel until a given reduced electric field value (for example, for T_1=500 K and T_2=1500 K, until 80 Td, see Fig. 14 a). For higher electric fields, the C-H dissociation cross section starts depleting the eedf for energies higher than 12 eV (see results of Fig. 11 d) reducing strongly the electronic excitation power losses (see results in Fig. 14 a at E/N=100 Td).

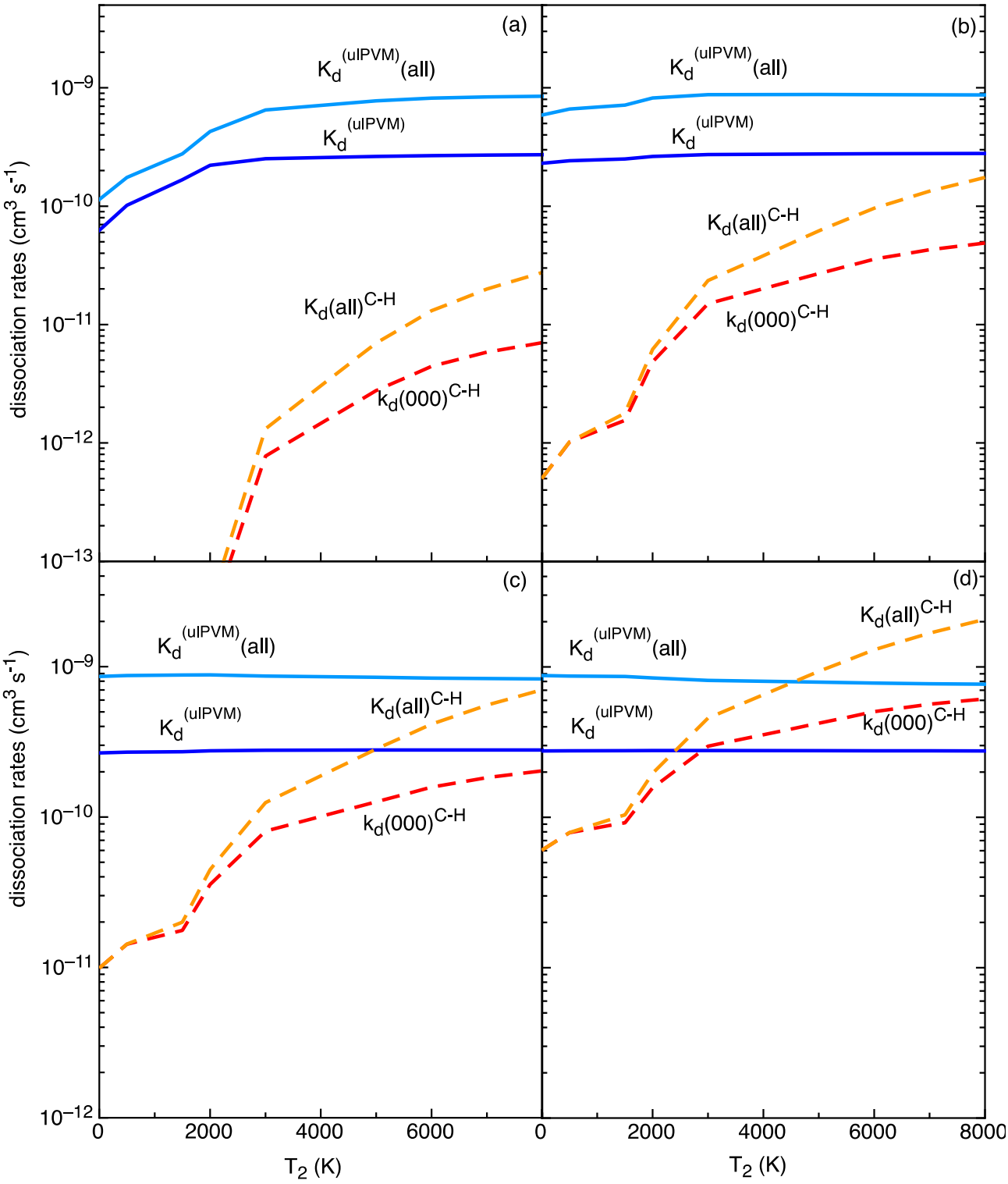

Fig. 13 Direct electron impact mechanism (DEM) dissociation rates of C-H, $k_d(000)^{C-H}$, $K_d(all)^{C-H}$, and upper limit values of pure vibrational mechanism (PVM) dissociation rates, $K_d^{(ulPVM)}$ and $K_d^{(ulPVM)}(all)$, as a function of T_2 vibrational temperature, in the model 4, under discharge conditions with (a) E/N=15 Td; (b) E/N=30 Td; (c) E/N=50 Td; (d) E/N=80 Td (without e-e collisions).

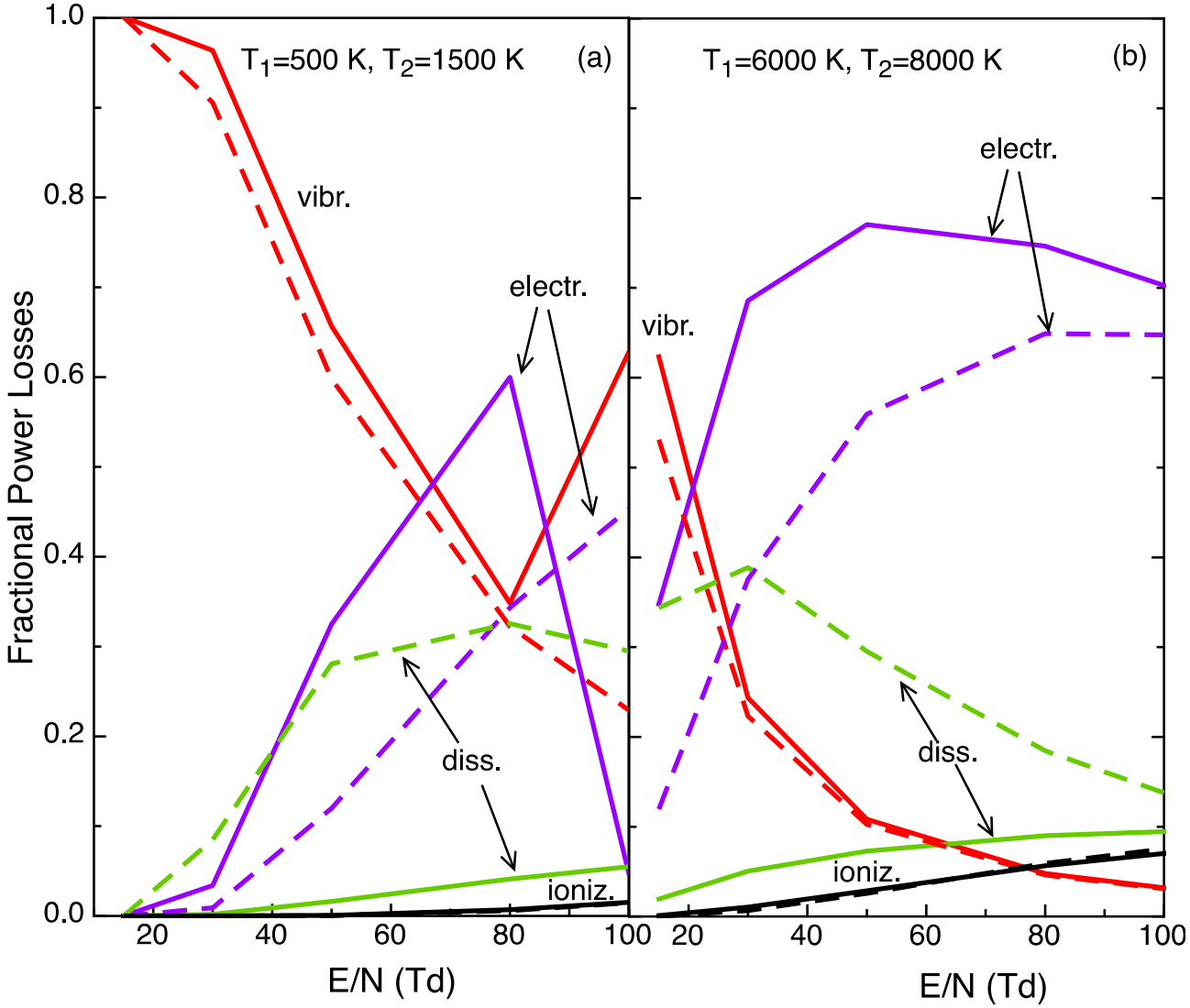

Fig. 14 Electron fractional power losses dissipated in the different channels (vibrational, dissociative, electronic excitation and ionization) as a function of the reduced electric field E/N for (a) T_1=500 K, T_2=1500 K; (b) T_1=6000 K, T_2=8000 K. The dashed lines correspond to results of model 1 (H-P dissociation cross section[13]) while the full lines correspond to results obtained in model 4, by substituting the H-P dissociation cross section with the C-H one[26].

5. CONCLUSIONS AND PERSPECTIVES

The main conclusions of the present paper deal with: 1) the role of electron molecule interactions on the symmetric mode of CO_2 in affecting eedf and the dissociation rates of PVM and DEM mechanisms; 2) the addition, to the H-P database, of the experimental C-H dissociation cross section.

The new results have been obtained by inserting new electron molecule vibrational excitation cross sections, linking the first ten vibrational levels of symmetric mode, through mono-quantum and multi-quantum transitions, whose cross sections have been calculated in the hypothesis of independent vibrational modes. Comparison with the H-P results, which to a given extent include intermode interaction, shows a satisfactory agreement on eedf and dissociation rates. This result can be important for the future improvement of CO_2 vibrational kinetics, indicating that, the hypothesis of independence of modes in electron molecule cross sections can represent a satisfactory alternative to the vibrational kinetics of CO_2, in the absence of complete sets of coupled mode cross sections. In any case, the coupled model is more accurate, but also more difficult to be realized. This result persists also considering a complete set of electron molecule vibrational excitation of the asymmetric mode of CO_2, the presence of which, more significantly, affects eedf and the dissociation rates[16,17].

The other important point discussed in the present paper is linked to the direct dissociation cross sections of CO_2. In our previous works, we have used a 7 eV threshold cross sections reported in the H-P database, while other authors use the Itikawa cross section with a threshold energy of 12 eV. The latter cross section can be improved with the corresponding experimental C-H cross section, which presents similar threshold energy. The choice of H-P and of C-H cross sections do not alter significantly eedf, having however an important role on the dissociation rates due to the threshold energy effects. It is very difficult, at this stage, to choose between H-P or C-H dissociation cross sections. Future work in this direction should take into account the dissociative electronic states of CO_2 in the electron energy range 6-12 eV. Alternatively, one could use the two sets of cross sections either separately or

together to reproduce macroscopic experimental dissociation rates of CO_2, even though this kind of comparison is strongly affected by the inaccuracy of the numerous elementary processes introduced in the kinetics.

The present results, as well as, those reported in our recent papers, indicate a road map to be followed in the construction of a self-consistent plasma chemical model to be used in a predictive mode for optimizing the activation of CO_2 under discharge and post discharge conditions. First of all, any kinetic model should be coupled with the kinetics of electronically and vibrationally excited states due to the importance of superelastic vibrational collisions in affecting eedf in discharge and post discharge conditions. In doing so, a lot of work should be done on the construction of new databases of electron-molecule and molecule-molecule cross sections, depending on the vibrational quantum number(s). To understand better the results, one should construct databases for both coupled and de-coupled oscillators taking, into account the work made in these years by Bogaerts[11,12] and Kustova and Armenise[52,53].

Particular attention should be paid to the direct electron impact dissociation process, including the influence of electron molecule vibrational and dissociation excitation cross sections of CO_2 on the electron energy distribution function and dissociation mechanisms in cold pure CO_2 plasmas, including its dependence on the vibrational quantum number(s). The assumption of a simple vibrational threshold shift of the dissociation cross section[11,12, 16-18, 45] should be eliminated. On the other hand, a new experimental determination of the dissociation cross section in the ground state in the range 6-30 eV is welcome to eliminate the present incertitude on this important process.

The other important point, to be included in future improvements, is linked to the introduction in the Boltzmann solver of all the vibrational levels belonging to the asymmetric normal mode, with their corresponding e-V cross sections going beyond the use of the Fridman scaling law.

In any case, a tremendous effort must be made in developing new databases for the CO_2 system, taking into account the dependence of the relevant processes on the

vibrational quantum numbers, following the approach used for characterizing the molecular plasmas of diatomic reacting molecules[39,54,55]. In this connection, new experimental determination of the dependence of e-V cross sections on gas temperature should are welcome, trying to increase the gas temperature range considered by Buckman et al.[56].

6. ACKNOWLEDGEMENTS

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