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2016 Plasma Sources Sci. Technol. 25 06LT02

(http://iopscience.iop.org/0963-0252/25/6/06LT02)

Letters

IOP Publishing

Plasma Sources Science and Technology

Plasma Sources Sci. Technol. **25** (2016) 06LT02 (5pp)

doi:10.1088/0963-0252/25/6/06LT02

Letter

Calculated low-energy electron-impact vibrational excitation cross sections for CO_2 molecule

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Received 19 May 2016, revised 30 September 2016
Accepted for publication 4 October 2016
Published 27 October 2016

Abstract

Vibrational-excitation cross sections of ground electronic states of a carbon dioxide molecule by electron-impact through $CO_2^-(^2\Pi_u)$ shape resonance is considered in the separation of the normal modes approximation. Resonance curves and widths are computed for each vibrational mode. The calculations assume a decoupling between normal modes and employ the local complex potential model for the treatment of nuclear dynamics, usually adopted for electron-scattering involving diatomic molecules. Results are presented for excitation up to 10 vibrational levels in each mode and a comparison with data present in the literature is discussed.

Keywords: CO_2, cross sections, electron CO_2 scattering, CO_2 modelling

(Some figures may appear in colour only in the online journal)

One of the technological problems, connected with strategies for the reduction of global warming coming from the greenhouse effect of carbon dioxide, is represented by the capture at source and storage of CO_2 gas. This is mainly based on the plasmolysis process which leads to the splitting of CO_2 into CO molecules and atomic or molecular oxygen [1, 2]. The efficiency of the dissociation processes is strongly determined by the vibrational activation of the molecule. Models of CO_2 plasmas, aimed to optimize and clarify this chemical conversion, have recently been constructed [3–7]. The main limitation of these models is the lack of information on electron-impact cross sections or rate coefficients for collisions inducing vibrational transitions in CO_2 molecules; as result, modellers usually resort to estimated rates or approximate scaling-laws [6].

In order to fill this void, in this Letter we present a preliminary data set of electron-impact cross sections for vibrational excitation of ground electronic states of carbon dioxide molecules useful in plasma kinetic modeling. The cross sections show two distinctive features observed experimentally: a $^2\Pi_u$ shape resonance around 3.8 eV [8–10] and, at energies below 2 eV, an enhancement due to the presence of the $^2\Sigma_g^+$ symmetry virtual state [11–13]. Both phenomena are explained in terms of a temporary CO_2^- system. For a general review on this topic, see Itikawa's paper [14] and references therein.

We present here the cross sections for the following process:

$$e + CO_2(X\,^1\Sigma_g^+; v) \rightarrow CO_2^-(^2\Pi_u) \rightarrow e + CO_2(X\,^1\Sigma_g^+; v'), \quad (1)$$

which occurs through the formation of the shape resonance generated by the electronic state $^2\Pi_u$ of the CO_2^- ion. CO_2 in its ground electronic state, $X\,^1\Sigma_g^+$, is a linear molecule with

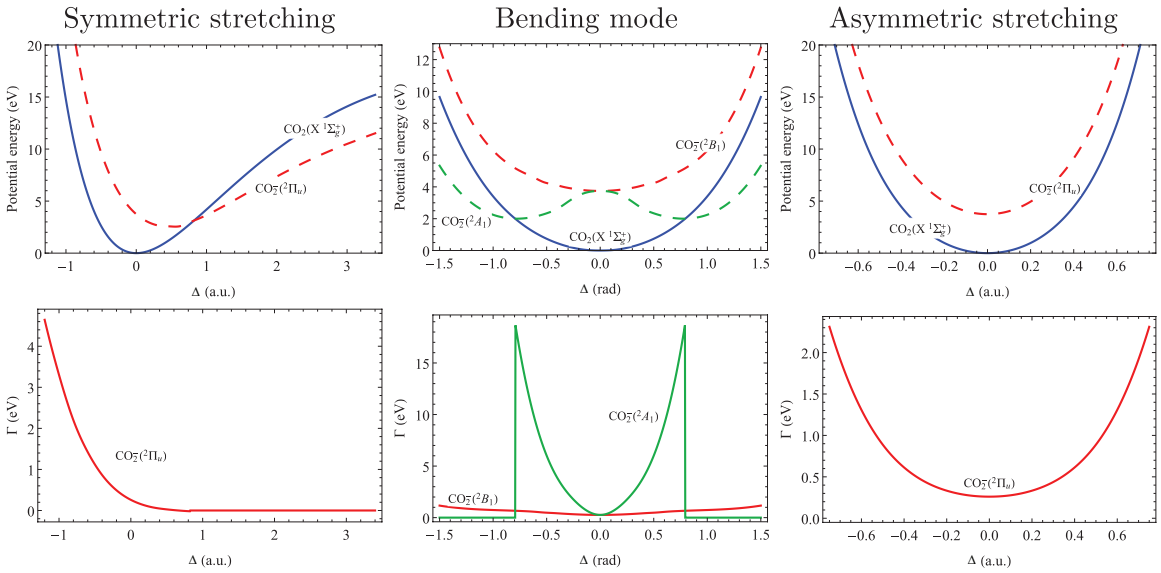

Figure 1. Upper panels: potential energy curves for the electronic ground electronic state $X\,^1\Sigma_g^+$ of CO_2 (full blue line) and for the resonant state CO_2^- (dashed red and green lines) for the three normal mode symmetric, bending and asymmetric. Lower panels: the corresponding resonance widths. Δ represents the displacement from the equilibrium geometry.

its C–O equilibrium distance $R_{eq} = 2.19\ a_0$ characterized by three normal modes of vibration, denoted in the following by $v = (\nu_1, \nu_2, \nu_3)$ and are respectively referred to as symmetric stretching, bending mode (doubly degenerate) and asymmetric stretching.

In principle, scattering involving polyatomic molecules needs a multidimensional treatment of the potential energy surface and of the nuclear motion, in order to take into account the non-adiabatic coupling between different vibrational modes [15]. However, as we are limiting ourself to the lowest vibrational levels, where the potential energy is approximatively harmonic, it is possible to adopt the assumption of separation of the modes and split the CO_2 potential into three one-dimensional independent modes. This allows one to compute the cross sections by employing the local model of resonant collisions as formulated for diatomic vibrational excitation [16–18]. In the uncoupled vibrational mode approximation, each mode is considered as independent. This implies that the scattering processes involves only one mode and does not affect the other two. Preliminary results for only the symmetric stretch mode were previously given in [19]. Here, we present calculations on all the three normal modes of the molecule, for $0 \leqslant \nu_i \leqslant \nu_i' \leqslant 10$ ($i = 1, 2, 3$), and for electron collision energies from the threshold up to 10 eV.

A peculiar aspect of the doubly degenerate $^2\Pi_u$ symmetry of CO_2^- ion is that it splits, upon bending, into two (Renner–Teller) $^2A_1$ and $^2B_1$ components. It is no longer degenerates due to the breaking of linear geometry ($D_{\infty h}$ symmetry to C_{2v} symmetry of bending mode) [20–22]. A second aspect, that derives from the stretch-bend coupling that is possible in polyatomic molecules, is an accidental degeneracy of vibrational levels belonging to different modes, known as the Fermi resonance [14, 22]. In the case of CO_2, a quasi-degeneracy occurs between the pure stretch (1 0 0) and the pure bending (0 2 0) levels (Fermi dyads) that result in a near 50:50 mixing of the two states; this occurence is well-known experimentally [10]. Here, we neglect this stretch-bend coupling; it is at least arguable that including it will only result in redistribution of flux in the excitation cross sections rather than radically different excitation rates.

Table 1. CO_2 vibrational levels ϵ_{ν_i} in the three normal modes refer to the energy of the corresponding ground vibrational levels whose value is $\epsilon_{\nu_i=0}$, with respect to the minimum of the potential energy curve, is given in the last row.

ν_i	Symmetric stretching $i = 1$	Bending mode $i = 2$	Asymmetric stretching $i = 3$
0	0.	0.	0.
1	0.1676 (0.172)	0.0764 (0.082)	0.2973 (0.291)
2	0.3345	0.1585 (0.159)	0.5996
3	0.5007	0.2415	0.9052
4	0.6661	0.3246	1.2138
5	0.8309	0.4081	1.5252
6	0.9949	0.4919	1.8396
7	1.1583	0.5760	2.1569
8	1.3208	0.6604	2.4771
9	1.4827	0.7450	2.8000
10	1.6439	0.8299	3.1257
$\epsilon_{\nu_i=0}$	0.0840	0.0357	0.1469

Note: The parenthesis show the experimental values from [22]. All entries are in eV.

The CO_2 potential energy curves were computed using the *ab initio* quantum chemistry code MOLPRO [23], by adopting the aug-cc-pVQZ basis set and the coupled-cluster (CCSD(T)) and MCSCF models. Scattering calculations were performed using the UK polyatomic R-matrix codes [24, 25]. A static exchange plus polarization (SEP) model, and the same basis used for CO_2, were utilised to calculate the complex potential energy curve for CO_2^-. The *R*-matrix

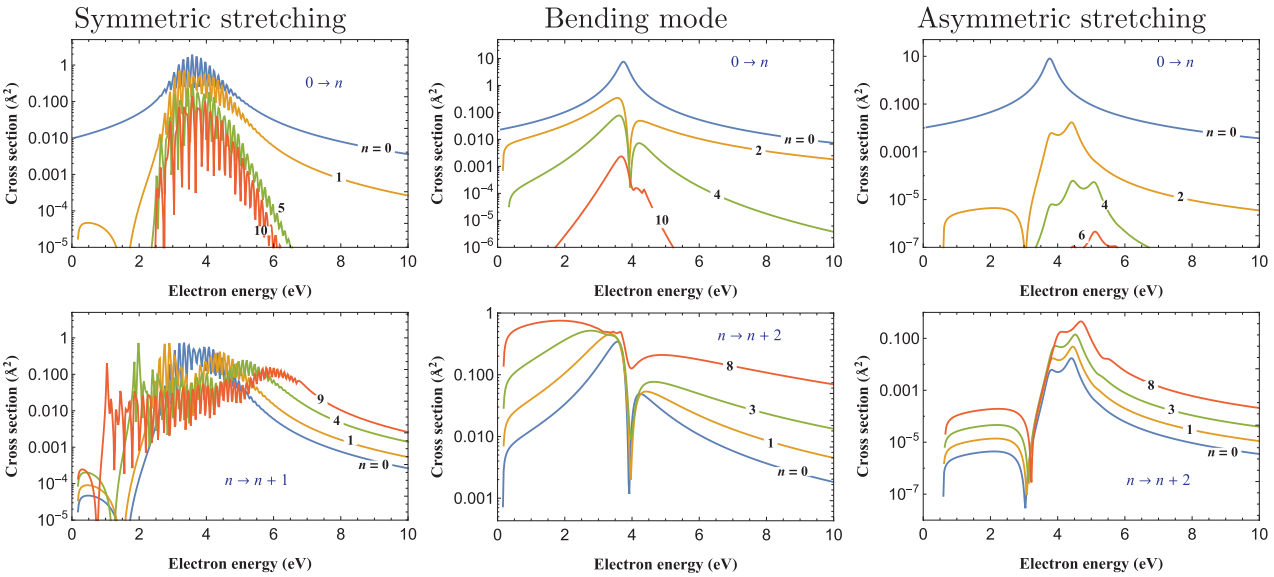

Figure 2. Summary of the electron-CO_2 vibrational excitation cross sections as a function of the incident electron energy for the three normal modes. Upper panels: excitation cross section for processes starting from the lowest vibrational levels. Lower panels: mono-quantum (symmetric stretching) and double-quantum (bending and asymmetric stretching) cross sections for processes starting also from vibrationally excited molecules.

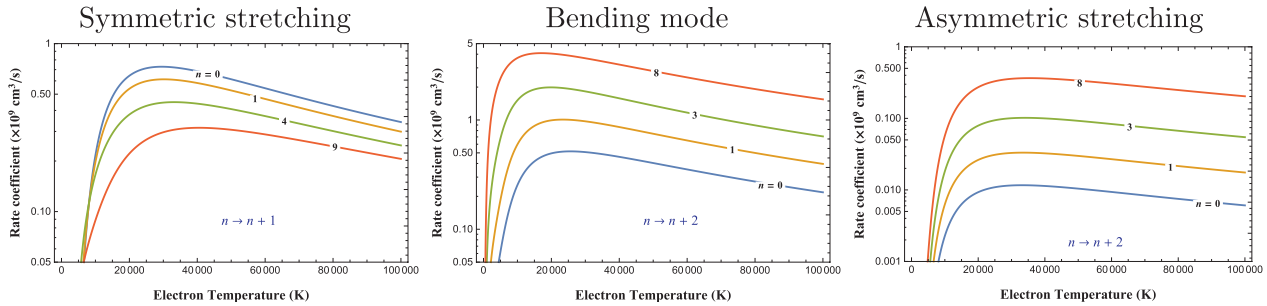

Figure 3. Summary of selected electron-CO_2 vibrational excitation rate coefficients as a function of the electron temperature for the three normal modes.

calculations were performed on a grid of fixed internuclear distances. The position and width of the resonant states were then calculated by fitting the corresponding eigenphases sum with a Breit–Wigner function [26].

The potential energy curves for CO_2 and CO_2^- species and for the three normal modes, are shown in figure 1 along with the corresponding resonance widths Γ. These curves are plotted as a function of the atomic displacements, Δ, calculated with respect to the equilibrium geometry for the three modes. Table 1 reports the vibrational energy levels ϵ_{ν_i} for each normal mode ($i = 1, 2, 3$).

The resonant cross section for the process in (1) of a single normal mode ν has been calculated [16, 19, 21], as a function of the electron energy ϵ, by:

$$\sigma_{\nu\to\nu'}(\epsilon) = \frac{4\pi^3}{k^2}|T_{\nu\nu'}|^2, \qquad (2)$$

where k is the incoming electron momentum and the scattering matrix, $T_{\nu\nu'}$, as a function of the total energy $E = \epsilon + \epsilon_\nu$, it is defined as:

$$T_{\nu\nu'}(E) = \langle\chi^*_{\nu'}|\mathcal{V}(\mathcal{H} - E)^{-1}\mathcal{V}|\chi_\nu\rangle. \qquad (3)$$

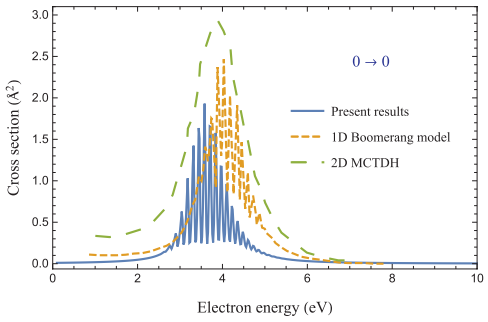

Figure 4. Comparison between present result (solid blue curve) with the theoretical calculations of Rescigno *et al* [20] (broken curves) for elastic symmetric stretching $0 \to 0$ cross section.

In equation (3), $\chi_{\nu(\nu')}$ is the wave function of the initial (final) vibrational level; $\mathcal{H} = T_N + V^- - \frac{i}{2}\Gamma$ is the Hamiltonian of the system, where T_N is the kinetics energy operator and $V^- - \frac{i}{2}\Gamma$ is the *complex optical potential* of the resonance; $\mathcal{V} = \sqrt{\Gamma/2}$ is the bound-continuum coupling matrix. Full details about the theoretical model can be found in [27] and references therein. The cross section involving different modes (ν_1, ν_2, ν_3) is

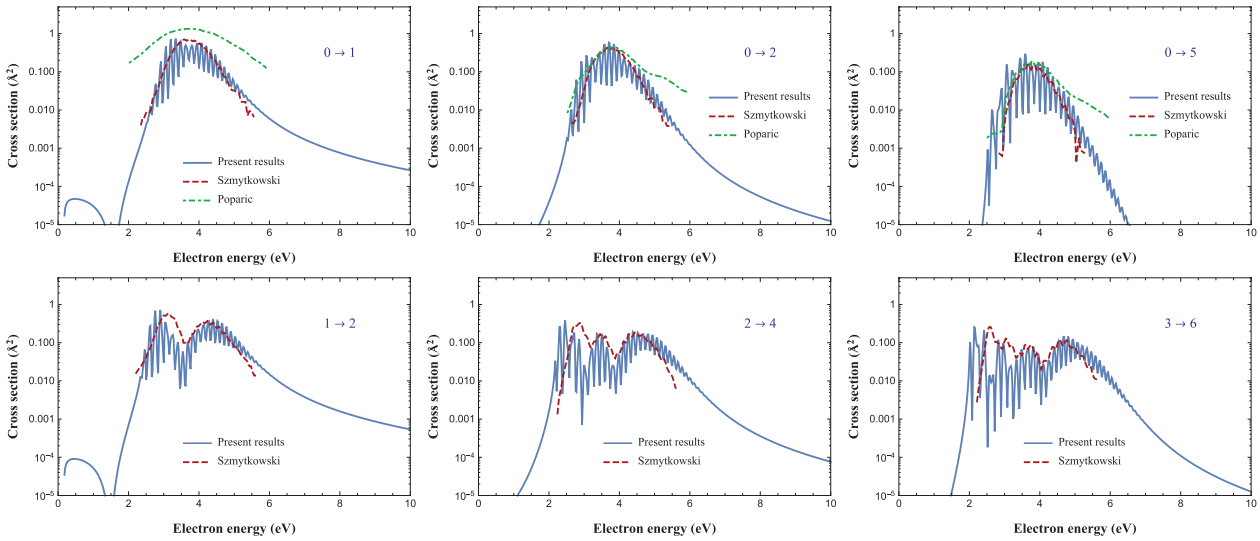

Figure 5. Comparison between the present results with available experimental data in [29, 30] for selected symmetric stretching cross sections.

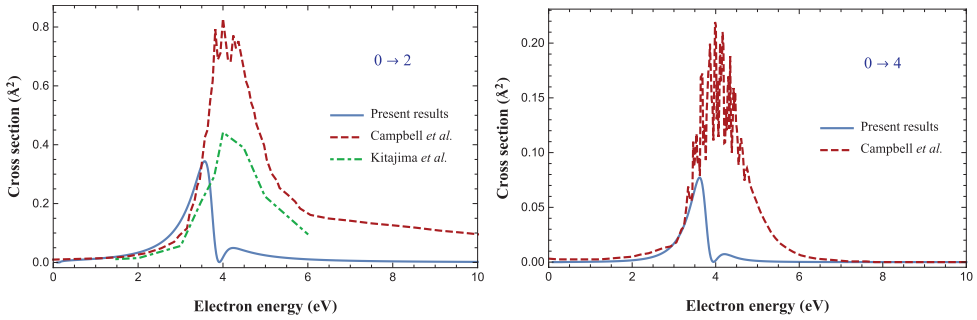

Figure 6. Comparison between the present results with available data in the literature [31, 32] for bending stretching cross sections.

given by the coherent sum over the cross sections for the three normal modes ν_i.

Figure 2 shows selected cross section results, as a function of the incident electron energy, for the vibrational transitions described in process (1), starting from the ground vibrational levels and exciting the nth level of the three normal modes (upper panels). All cross section curves show a pronounced peak close to 3.8 eV, which corresponds to the CO_2^- resonance threshold. The other secondary peaks correspond to the CO_2^- vibrational levels (boomerang oscillations). The figures show that the elastic cross sections ($n = 0$) for the bending and asymmetric stretching reach comparable values, an order of magnitude larger than those for the symmetric stretch. As expected, the inelastic cross sections decrease by orders of magnitude for increasing n for all three cases. The same figure (lower panels), also shows the cross sections for one-quantum transitions of the symmetric stretch motion, and two-quantum transitions occurring in the other two normal modes, for which the selection rule, $\Delta n = 0, 2$, holds. This is due to the symmetric shape of the potentials and widths in bending and antisymmetric modes, so that the Frank–Condon overlap between wave functions having opposite parity, is suppressed. Experimental investigations show that this is not the case. This aspect however is not fully clarified in the literature. In fact, a coupled model could produce non-zero bending cross sections for odd-parity transitions as shown by Estrada *et al* [15]. Notably other processes, involving Feshbach resonances, could also be important [28]. The cross sections shown in the lower panels of figure 2 refer to excitation process starting from vibrationally excited molecules. Figure 3 shows some series of the rate coefficients as a function of the electron temperature for the three normal modes.

Figure 4 shows the comparison with the theoretical calculations of Rescigno *et al* [20] for the elastic symmetric stretching $0 \rightarrow 0$ cross section. The present result, as well as Rescigno's 1D calculation, shows the well known resonant 'boomerang' structure and they are in general agrement with each other. The slight shift of the peak positions is due to the different potential energy curves used in the calculations. On the other hand, figure 5 shows very good agrement with the experimental data available in the literature for symmetric stretching cross sections. During the comparison for $0 \rightarrow 2$ bending mode transition cross sections, in figure 6 we find qualitative agreement with the results of Kitajima *et al* [32] and disagreement with the estimated data presented by Campbell *et al* [31]. These last data, as Campbell *et al* stated in their article, also take into account the Fermi dyad and triad coupling [21]. However, the disagreement between the theoretical and experimental cross sections shows that further

studies are needed to achieve reliable results for the excitation of bending modes.

In conclusion, in this Letter we presented a set of vibrational excitation cross sections for electron-CO_2 scattering in the separations of the mode approximation. In particular, we studied the role of the resonant contribution to the scattering. We find good agreement with respect to the data reported in the literature for the symmetric stretching mode, whereas, for the bending and asymmetric modes, further investigations are needed taking into account non-resonant contributions. Finally, the full set of data can be downloaded from the Phys4Entry database [33].

Acknowledgments

The authors wish to thank Prof M Capitelli (University of Bari, Italy) for useful discussions and Prof M Panesi (University of Illinois, IL) for careful reading of the manuscript. One of the authors (VL) would like to thank the Politecnico di Bari for the kind hospitality during the preparation of the present article. This work received funding from the project 'Apulia Space', PON 03PE-00067.6 from DTA Brindisi (Italy).

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