

Calculated low-energy electron-impact vibrational excitation cross sections for CO₂ molecule

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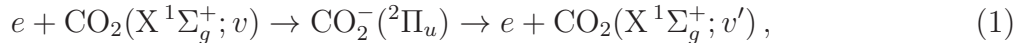
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Vibrational-excitation cross sections of ground electronic state of carbon dioxide molecule by electron-impact through the CO₂⁻ (²Π_u) shape resonance is considered in the separation of the normal modes approximation. Resonance curves and widths are computed for each vibrational mode. The calculations assume decoupling between normal modes and employ the local complex potential model for the treatment of the nuclear dynamics, usually adopted for the electron-scattering involving diatomic molecules. Results are presented for excitation up to 10 vibrational levels in each mode and comparison with data present in the literature is discussed.

One of the technological problems, connected with strategies for reduction of the global warming coming from the greenhouse effect produced by carbon dioxide, is represented by the capture at source and storage of the CO₂ gas, mainly based on the plasmolysis process leading to the splitting of CO₂ 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 CO₂ 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 CO₂ 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 state of carbon dioxide molecule useful in plasma kinetic modeling. The cross sections show two distinctive features observed experimentally: a ²Π_u shape resonance around 3.8 eV [8–10] and, at energies below 2 eV, an enhancement due to the presence of the ²Σ_g⁺ symmetry virtual state [11–13]. Both phenomena are explained in terms of a temporary CO₂⁻ system. For a general review on this topics see Itikawa paper [14] and references therein.

We present here the cross sections for the following process:



which occurs through the formation of the shape resonance generated by the electronic state ²Π_u of the CO₂⁻ ion. CO₂ in its ground electronic state, X ¹Σ_g⁺, is a linear molecule with 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 referred to, respectively, as the symmetric stretching, bending mode (doubly degenerate) and asymmetric stretching.

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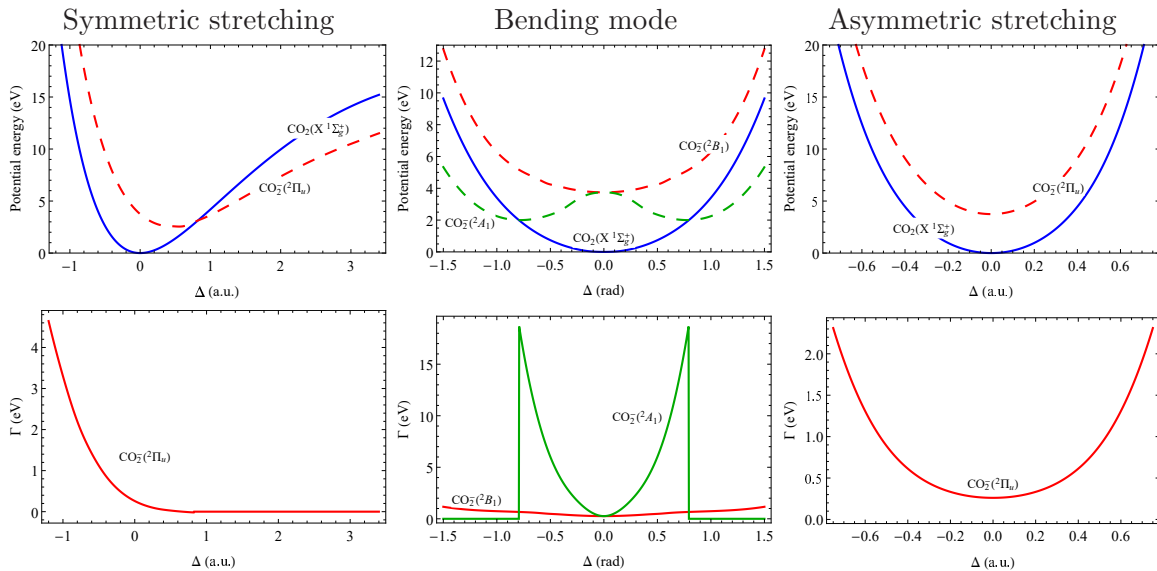


FIG. 1: Upper panels: Potential energy curves for the electronic ground electronic state $X^1\Sigma_g^+$ of CO_2 (full blue line) and for the resonant state CO_2^- (dashed red and green lines) for the three normal mode symmetric, bending and asymmetric. Lower panels: the corresponding resonance widths.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

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 approximately harmonic, 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 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 one mode only and does not affect at all the other two. Preliminary results for the symmetric stretch mode only, were given previously [19]. Here we present calculations on all the three normal modes of the molecule, for $0 \leq \nu_i \leq \nu_i' \leq 10$ ($i = 1, 2, 3$), and for electron collision energies from the threshold up to 10 eV.

A peculiar aspect of the 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, no longer degenerate, due to the breaking of linear geometry (D_{2h} symmetry to C_{2v} symmetry of bending mode) [20–22]. A second aspect, that derives from the stretch-bend coupling possible in polyatomic molecules, is an accidental degeneracy of vibrational levels belonging to different modes, known as Fermi resonance [14, 22]. In the case of CO_2 a quasi-degeneracy occurs between the pure stretch (100) and the pure bending (020) levels (Fermi dyads) that result in a near 50:50 mixing of the two states which 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.

The CO_2 potential energy curves were computed using the *ab-initio* quantum chemistry code MOLPRO [23], by adopting a aug-cc-pVQZ basis set and the coupled-cluster

	Symmetric stretching	Bending mode	Asymmetric stretching
ν_i	$i = 1$	$i = 2$	$i = 3$
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

TABLE I: CO₂ vibrational levels ϵ_{ν_i} in the three normal modes referred to the energy of the corresponding ground vibrational levels whose value $\epsilon_{\nu_i=0}$, with respect to the minimum of the potential energy curve, is given in the last row. In parenthesis are shown the experimental values from Ref. [22]. All entries are in eV.

(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 CO₂, were utilised to calculate the complex potential energy curve for CO₂⁻. The *R*-matrix calculations were performed on a grid of fixed internuclear distances. The position and width of the resonant state were then calculated by fitting the corresponding eigenphases sum with a Breit-Wigner function [26].

The potential energy curves for CO₂ and CO₂⁻ species and for the three normal modes, are shown in Fig. 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 I 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:

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

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

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

In Eq.(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 the paper [27] and references

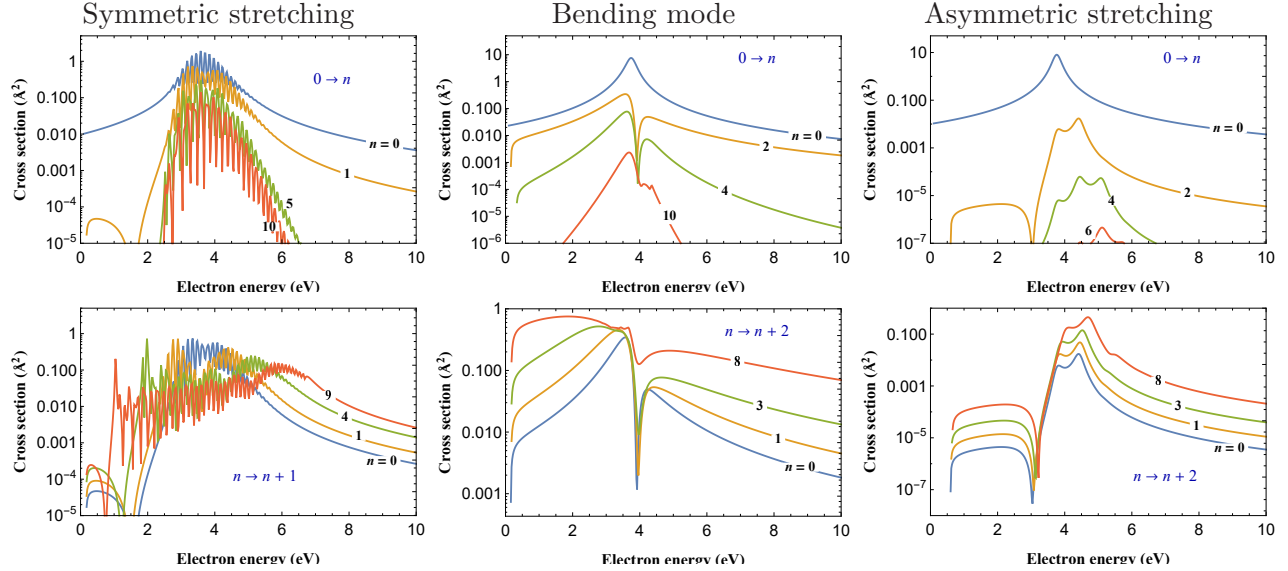


FIG. 2: Summary of the electron- CO_2 vibrational excitation cross sections as a function of the incident electron energy for the three normal modes. Upper panels: excitation cross section for processes starting from the lowest vibrational levels. Lower panels: mono-quantum (symmetric stretching) and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

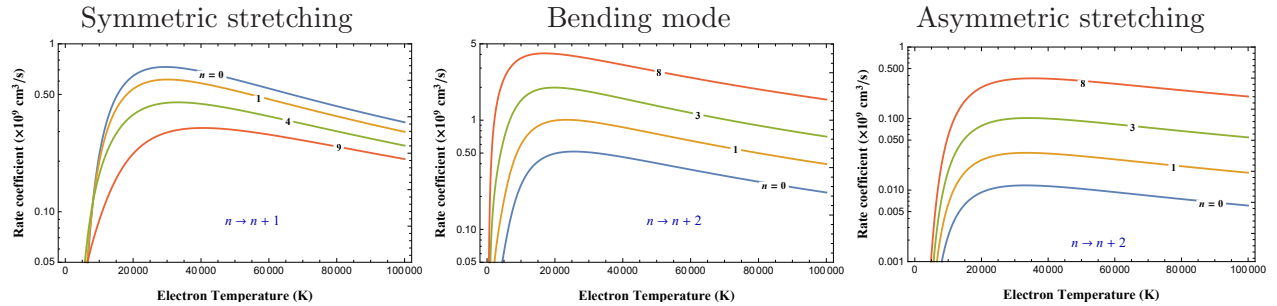


FIG. 3: Summary of selected electron- CO_2 vibrational excitation rate coefficients as a function of the electron temperature for the three normal modes.

therein. The cross section involving different modes (ν_1, ν_2, ν_3) is 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 n -th level of the three normal modes (upper panels). All cross section curves show a main 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. The inelastic cross sections decrease for increasing n , as expected, for all the three cases, also by orders of magnitude. The same figure (lower panels) also shows the cross sections for one-quantum transitions of the symmetric stretch

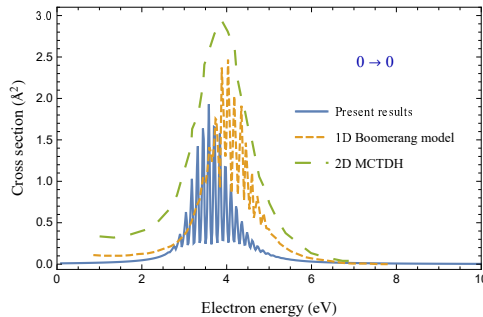


FIG. 4: Comparison between present result (solid blue curve) with the theoretical calculations of Rescigno *et al.* [20] (broken curves) for elastic symmetric stretching $0 \rightarrow 0$ cross section.

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, actually, show that this is not the case. This aspect however is not fully clarified in literature. In fact, a coupled model could produce non-zero bending cross sections for odd-parity transitions as showed in Estrada *et al.* [15] but also other processes, involving Feshbach resonances, could be important [28]. The cross sections shown in the lower panels of Fig. 2 refer to excitation process starting also 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 agreement 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, Fig. 5 shows very good agreement with experimental data available in literature for symmetric stretching cross sections. In the comparison for $0 \rightarrow 2$ bending mode transition cross sections, in Fig. 6, we find qualitative agreement with Kitajima *et al.* results [32] and disagreement with the estimated data presented by Campbell *et al.* [31]. These last data, as Campbell *et al.* state in their article, take into account also 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. Good agreement, with respect to the data reported in literature, is found for the symmetric stretching mode whereas for the bending and asymmetric modes further investigations, taking into account non-resonant contributions, are needed. Finally, the full set of data can be downloaded from the Phys4Entry database [33].

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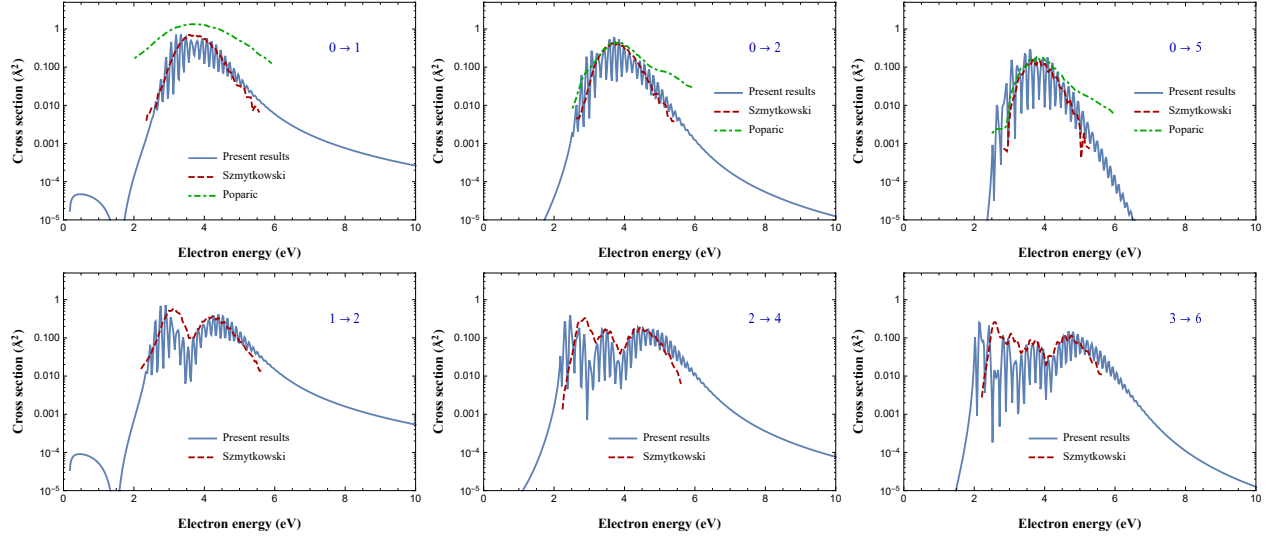


FIG. 5: Comparison between present results with available experimental data in Refs. [29, 30] for selected symmetric stretching cross sections.

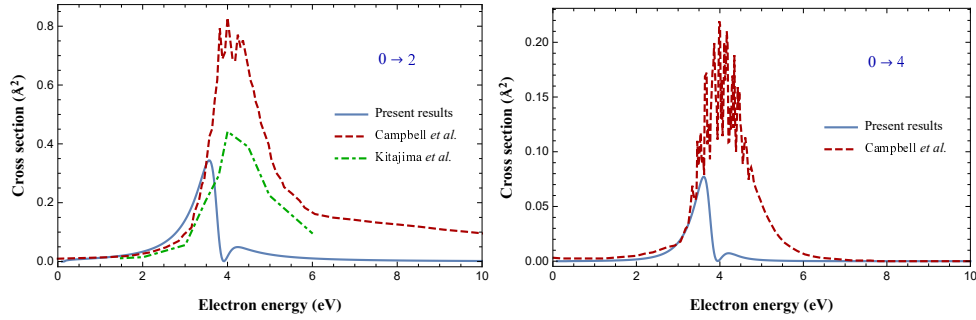


FIG. 6: Comparison between present results with available data in literature [31, 32] for bending stretching cross sections.

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References

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- [1] O Taylan and H Berberoglu. *Plasma Sources Sci. Technol.*, 24:015006, 2015.
 - [2] Adelbert P.H. Goede, Waldo A. Bongers, Martijn F. Graswinckel, Richard M.C.M van de Sanden, Martina Leins, Jochen Kopecki, Andreas Schulz, and Mathias Walker. *EPJ Web of Conferences*, 79:01005, 2014.
 - [3] L.D. Pietanza, G. Colonna, V. Laporta, R. Celiberto, G. D’Ammando, A. Laricchiuta, and M. Capitelli. *The Journal of Physical Chemistry A*, 120(17):2614–2628, 2016.

- [4] Tom Kozk and Annemie Bogaerts. *Plasma Sources Science and Technology*, 24(1):015024, 2015.
- [5] Andrea Lombardi, Noelia Faginas-Lago, Leonardo Pacifici, and Alessandro Costantini. *The Journal of Physical Chemistry A*, 117(45):11430–11440, 2013.
- [6] Tom Kozk and Annemie Bogaerts. *Plasma Sources Science and Technology*, 23(4):045004, 2014.
- [7] Andr Janeco, Nuno R. Pinho, and Vasco Guerra. *The Journal of Physical Chemistry C*, 119(1):109–120, 2015.
- [8] Michael A. Morrison, Neal F. Lane, and Lee A. Collins. *Phys. Rev. A*, 15:2186–2201, Jun 1977.
- [9] I Cadez, F Gresteau, M Tronc, and R I Hall. *Journal of Physics B: Atomic and Molecular Physics*, 10(18):3821, 1977.
- [10] M. Allan. *Phys. Rev. Lett.*, 87:033201, Jun 2001.
- [11] L. A. Morgan. *Phys. Rev. Lett.*, 80:1873–1875, Mar 1998.
- [12] J. Tennyson and L. A. Morgan. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 357(1755):1161–1173, 1999.
- [13] Stephane Mazevet, Michael A Morrison, Lesley A. Morgan, and Robert K. Nesbet. *Phys. Rev. A*, 64:040701, Sep 2001.
- [14] Yukikazu Itikawa. *Journal of Physical and Chemical Reference Data*, 31(3):749–767, 2002.
- [15] H. Estrada, L. S. Cederbaum, and W. Domcke. *The Journal of Chemical Physics*, 84(1):152–169, 1986.
- [16] V Laporta, R Celiberto, and J M Wadehra. *Plasma Sources Science and Technology*, 21(5):055018, 2012.
- [17] V Laporta, D A Little, R Celiberto, and J Tennyson. *Plasma Sources Science and Technology*, 23(6):065002, 2014.
- [18] V. Laporta, R. Celiberto, and J. Tennyson. *Phys. Rev. A*, 91:012701, Jan 2015.
- [19] R. Celiberto, V. Laporta, A. Laricchiuta, J. Tennyson, and J.M. Wadehra. *The Open Plasma Physics Journal*, 2014, 7, (Suppl 1: M2) 33–47, 7, (Suppl 1: M2):33–47, 2014.
- [20] T. N. Rescigno, W. A. Isaacs, A. E. Orel, H.-D. Meyer, and C. W. McCurdy. *Phys. Rev. A*, 65:032716, Feb 2002.
- [21] C. W. McCurdy, W. A. Isaacs, H.-D. Meyer, and T. N. Rescigno. *Phys. Rev. A*, 67:042708, Apr 2003.
- [22] Gerhard Herzberg. *Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*. 1966.
- [23] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, et al. MOLPRO, version 2010.1, a package of ab initio programs, 2010.
- [24] Jonathan Tennyson. *Physics Reports*, 491(2-3):29 – 76, 2010.
- [25] J.M. Carr, P.G. Galiatsatos, J.D. Gorfinkiel, A.G. Harvey, M.A. Lysaght, D. Madden, Z. Mašin, M. Plummer, J. Tennyson, and H.N. Varambhia. *The European Physical Journal D*, 66(3):1–11, 2012.
- [26] Jonathan Tennyson and Cliff J. Noble. *Computer Physics Communications*, 33(4):421 – 424, 1984.
- [27] J N Bardsley and F Mandl. *Reports on Progress in Physics*, 31(2):471, 1968.
- [28] David C Cartwright and Sandor Trajmar. *Journal of Physics B: Atomic, Molecular and Optical Physics*, 29(8):1549, 1996.
- [29] G. B. Poparić, M. M. Ristić, and D. S. Belić. *The Journal of Physical Chemistry A*, 114(4):

- 1610–1615, 2010.
- [30] C Szmytkowski, M Zubek, and J Drewko. *Journal of Physics B: Atomic and Molecular Physics*, 11(12):L371, 1978.
 - [31] L. Campbell, M. J. Brunger, and T. N. Rescigno. *Journal of Geophysical Research: Planets*, 113(E8):n/a–n/a, 2008.
 - [32] M. Kitajima, S. Watanabe, H. Tanaka, M. Takekawa, M. Kimura, and Y. Itikawa. *Phys. Rev. A*, 61:060701, May 2000.
 - [33] Database of the european union phys4entry project, 2012-2016.