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Electron-impact induced ionization in CO molecules

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Abstract – The paper is focussed on the derivation of cross sections for the ionization processes induced by the collision of low-energy electrons with CO molecules either in the ground electronic state or in excited, vibrational or metastable electronic states. For the ionization from the ground state also partial, channel-dependent cross sections are presented. The BED and BEB theoretical approaches have been exploited, obtaining results in good agreement with available experiments for the ionization from the $v=0$ level of the ground state.

Keywords: interstellar cloud chemistry; electron-impact ionization; CO molecule; excited states

Riassunto – Il lavoro è incentrato sulla derivazione di sezioni d'urto per i processi di ionizzazione indotti dalla collisione di elettroni di bassa energia con molecole di CO sia nello stato elettronico fondamentale che in stati eccitati, vibrazionali o elettronici metastabili. Per la ionizzazione dallo stato fondamentale, sono presentate anche le sezioni d'urto parziali, dipendenti dal canale finale. Le sezioni d'urto sono state calcolate impiegando gli approcci BED e BEB, ottenendo risultati in buon accordo con gli esperimenti disponibili per la ionizzazione dal livello $v=0$ dello stato fondamentale.

Parole chiave: chimica nelle nubi interstellari; ionizzazione indotta da elettroni; CO; stati eccitati

1. Introduction

Among the future challenges of the modern *Astrochemistry* the construction of a *laboratory astrophysics* represents one of the most appealing, providing a virtual platform that, integrating the knowledge in spectroscopy gained in space observations, the accurate information in molecular structure and dynamics of elementary processes, and the advanced kinetic models including a state-to-state scheme and excited state kinetics, would allow to describe the evolution of the complex chemical network needed in the simulation of the interstellar dense molecular clouds, including the formation of complex prebiotic organic molecules [1, 2, 3].

The chemistry in interstellar gas clouds is efficiently driven by ion-neutral reactions, resulting in the formation of carbon chains and also small molecules, and this justifies the interest in the dynamical characterization of ionization processes. The photoionization mechanism is not efficient, being the UV light hindered in the penetration of the cloud by scattering in the outer regions, while the interaction of molecules with cosmic rays, mainly extremely high-energy protons originated from stars, represents the prevalent channel [4] producing secondary UV radiation and electrons. Therefore in addition to high-energy cosmic ray electrons also electrons of lower energies (from tens to hundreds eV) are present in the interstellar medium (ISM) making the ionization induced by electron-impact a relevant process in the chemical network.

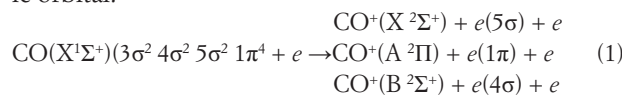
The CO is of large astrochemical interest being the second most abundant molecular species detected in the ISM and condensed on icy grains [1, 5]. Excited species of CO* can play a role in these environments, in fact molecules in rotational and vibrational excited levels are generated in the photo-fragmentation processes of organic molecules [6], and their emission spectra are the most important tracer of molecular gas within molecular clouds. Also electronic excited states can be formed either in the UV photodissociation of organic compounds or by direct excitation (electron or photon induced) of the CO ground state, or by conversion of vibrational energy to electronic excitation in CO collisions with heavy particles, an example being represented by the rapid conversion of highly vibrational excited CO molecules ($v > 40$) leading to the formation of the metastable $a^3\Pi$, also affecting the shape of vibrational distribution function of the ground state. The CO non-dissociative ionization channels have been object of numerous investigations and the CO⁺ emission of the first negative ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) and the comet tail ($A^2\Pi \rightarrow X^2\Sigma^+$) systems, well-characterized spectroscopically, allowed the indirect estimation of the electron-induced ionization cross sections, properly accounting for the cascade contribution [7].

In this paper the results recently obtained for the ionization of the CO molecule in collision with low-energy electrons are reviewed [8]. The theoretical framework is the binary-encounter model, in the dipole (BED) and Bethe (BEB) formulations, adopted for the derivation of channel-dependent and total cross sections. The investigation focussed on the role of excitation of the internal degrees of freedom, vibrational and electronic, in promoting the ionization process.

2. Ionization of ground state CO molecule: the vibrational excitation

The electron-impact induced ionization of the ground state of CO molecule has been deeply investigated both experimentally [9, 10, 11, 12, 13] and theoretically [14], determining total and partial ionizations for the formation of the molecular ion in its ground and excited states, characterized by different lifetimes and branching ratios. The BED theoretical approach [14, 15], nowadays widely used in the literature for the estimation of total ionization cross sections also in the case of polyatomic molecules, has been successfully exploited for the derivation of partial cross sections to the relevant channels of ionization from the ground and from vibrationally excited molecules [8].

The ionization from the $v=0$ level of CO molecule is essentially a non-dissociative process leading to the formation of three different states CO⁺, namely $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$, and each ionization channel has been considered within a single-electron model. This is justified by the fact that the dominant configurations of these states can be generated from the configuration of the ground state by the removal of an electron belonging to a specific orbital.



The BED theory needs some specific shell parameters in its formulation for the ionization cross section, that are the orbital energies, the number of equivalent electrons participating in the ionization process and the average kinetic energy in the orbital. All these parameters can be obtained in a standard *ab-initio* electronic structure calculation step. In particular, EOMCC (equation of motion coupled-cluster) method implemented for ionization [16] in GAMESS package [17] has been exploited, using the basis set aug-ccpVTZ + Rydberg orbitals, to explore also the dependence of configurations, vertical energies and orbital parameters on the molecular geometry. On the other hand the so-called *continuum dipole oscillator strength*, describing the coupling of the bound electron in the molecule and the continuum in the channel-specific ionization process, it has been derived from photoionization experiments available in the literature [18] and it has been considered geometry-independent.

In Fig. 1 (a) the partial cross sections from the $v=0$ level of the ground state of CO molecule to the three ionization channels are reported, showing a dominant

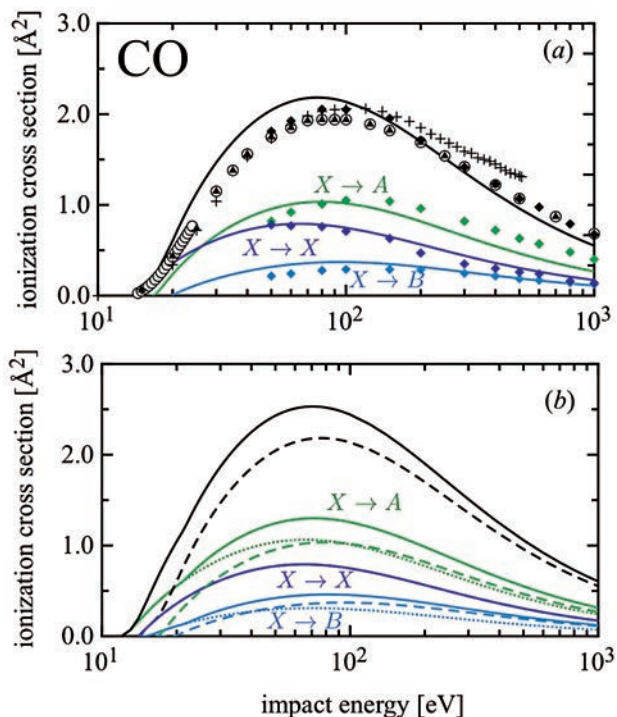


Fig. 1 (a) Total and partial BED nondissociative ionization cross sections from ground state of CO molecule [8] compared with experimental results in the literature. (diamonds) [11], (+) [12], (triangles) [13], (circles) recommended data [10]. (b) Total and partial BED cross sections for ionization from the fundamental, $\nu = 0$, (dashed line) and the excited vibrational level, $\nu = 40$, (solid line), non-dissociative contribution (dotted lines) [8].

role of the ionization to the $A^2\Pi$ state, despite a markedly energy dependence of the branching ratio [8]. The model reproduced the experimental results [11, 12, 13] quite well, except for the steeper behaviour at the threshold.

The ionization from excited vibrational levels of the CO molecule has been also estimated, resorting to the R -centroid approximation, considering the vertical nature of the transition, and considering the vibrational dependence described by the Franck Condon overlap integrals of coupled vibrational levels.

The total and partial ionization cross sections from the vibrational level $\nu=40$ are shown in Fig. 1 (b) together with those from $\nu=0$ level. The vibrational energy content of the target produces a modest enhancement of the process, relevant to the threshold shift to lower energy values, as already observed for N_2 [19, 20, 21]. More interesting is the evidence of a non-negligible contribution to the dissociative ionization, estimated as occurring at the inner turning point to the repulsive branch of the ionized state, when transition to the $A^2\Pi$ and $B^2\Sigma^+$

states are considered. This is largely due to the relative positions of potential energy curves of neutral molecule and the molecular ion that makes the overlap with the continuum of the two excited states quite broad.

3. Ionization of excited metastable state CO molecule: the electronic excitation

The relevant role of the metastable state of CO molecule, $a^3\Pi$, in the vibrational kinetics of non-equilibrium plasmas is well-assessed in the literature. The excited triplet state, not dipole-coupled to the ground state, could act as a reservoir of energy, sustaining, for example, the electron energy distribution function in post-discharge plasma conditions, pumping the CO vibrational distribution if collisionally quenched both in discharge and post-discharge [22, 23], or enhancing the rate of the mechanisms leading to the formation of CO_2 molecules, the *Boudouard reactions*, affecting the activation energy of the process [24]. The ionization process of the triplet has been investigated within the BEB method [8], thus assuming a form for the continuum dipole oscillator strength [15] and therefore the global ionization to all possible exit channels is actually estimated. The relevant parameters, i.e. orbital binding energy, occupation number and kinetic energy for the occupied orbitals, have been estimated again by performing *ab initio* unrestricted Hartree-Fock calculations at different molecular geometries, averaging the values for α and β orbitals. At the equilibrium geometry ($R_{eq} = 2.28 a_0$), which is relevant for the ionization of the fundamental vibrational level $\nu=0$ of the $a^3\Pi$ state, the dominant configuration is $3\sigma^2 4\sigma^2 5\sigma 1\pi^4 2\pi$, however elongating the internuclear distance the multi-configurational nature of the excited state makes more and more difficult to univocally identify the orbitals and assign the occupation numbers. In Fig. 2 the total ionization cross section for the $\nu=0$ level of the metastable state is displayed in a wide energy range, from the threshold (determined by the energy of the HOMO 2π orbital) up to 10^3 eV, and compared with the total ionization from the ground electronic state from $\nu=0$ and $\nu=40$. It is well evident how the electronic excitation of the molecular target, differently from the vibrational excitation, produces a significant enhancement of the ionization, not only increasing the peak value of the cross section but also reducing the threshold value and thus determining a huge increase of the corresponding rate coefficient in the low-temperature region. The effect of electronic excitation on the ionization has been observed also in the case of

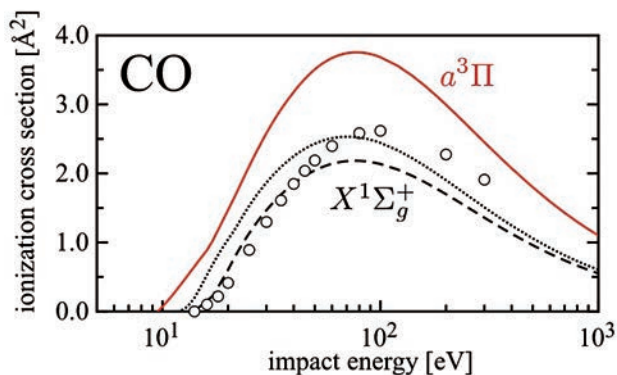


Fig. 2. BEB cross sections for total ionization (solid lines) of $a^3\Pi$ metastable and of the ground (circles) state [14] of CO by electron-impact. The ground state ionization cross sections from $v = 0$ (dashed line) and from $v = 40$ (dotted line) only to the X, A and B states of the CO^+ molecule are also reported.

the metastable state of N_2 molecule ($A^3\Sigma_u^+$) [8], results confirmed by calculations done with a different theoretical approach [25].

4. Concluding remarks

The ionization processes induced by low-energy electrons in CO molecule have been investigated in the frame of the binary encounter approaches (BED and BEB) obtaining total and channel-dependent cross sections for ionization initiated from a ground state molecule that are in good agreement with available experiments. The initial excitation of the molecule, either vibrational or electronic, has been considered and observed to produce an enhancement of the ionization, giving an indication of the importance of the inclusion of a comprehensive scheme of elementary processes for excited states in the kinetic codes in order to assess their role in the reactive chemistry of complex systems, as those of astrochemical interest.

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