Electron-impact excitation cross sections for air kinetics

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Electron-impact induced vibronic excitation in N_2 to singlet states belonging the spectroscopic series $^1\Sigma_u^+$ and $^1\Pi_u$ have been calculated in the frame of a *similarity approach*, accounting for the non-adiabatic coupling of the electronic terms. State-to-state cross sections have been derived and compared with experimental results, emphasizing the irregular pattern of vibrational profile due to the non-adiabatic character of excitation transitions.

The realistic modeling of (re)-entry in Earth and nitrogen-rich planetary atmospheres relies on the accurate knowledge of the dynamics of N_2 molecule in collision with electrons, atoms, molecules and in the interaction with photons, accounting, in a state-to-state kinetic frame, for the energy stored in the internal (ro-vibrational) degrees of freedom. The excitation to the lowest three electronic terms of the $^1\Sigma$ and $^1\Pi$ spectroscopic series for N_2 system, received great attention since from the eighties [1, 2], being dipole-coupled to the ground state and representing the dominant contribution of the extreme ultraviolet spectrum of N_2 plasmas. These states, usually denoted as $b,c,o\,^1\Pi_u$ and $b',c',e'\,^1\Sigma_u^+$ exhibit a strong inter-state coupling, due to their mixed valence-Rydberg character, resulting in significant perturbation of vibronic bands. Moreover they are recognized to affect significantly the atomic budget, in fact the excitation process leads to dissociation, through predissociation mechanisms [3, 4].

It should be mentioned the pioneering work by Ermler *et al* [1], for the derivation of ab-initio potential energy curves and transition dipole moments of singlet terms of N_2 spectrum and the reference paper by Stahel *et al* [2], considering for the first time the electronic coupling, performing a complete and quantitative vibrational analysis. Spelsberg&Meyer [5] performed new ab-initio calculations, in the MRCI framework, for accurate potential energy curves of singlet terms, both adiabatic and diabatic representations, and also for the *R*-dependent coupling terms in the region of effective interaction, while recently Khakoo *et al* [6] investigated experimentally the electron-impact excitation of these states, deriving differential cross sections from energy-loss spectra.

Electron-impact excitation to these states have been considered in different theoretical approaches [7, 8] also deriving the vibrationally-resolved cross sections [9], however not accounting for vibronic coupling. The main consequence of vibronic coupling is that different electronic terms of the same symmetry loose their identity and should be treated as a complex of states, entailing the numerical solution of a system of coupled radial Schrödinger equations, here presented in a compact matrix formalism

$$\left[\hat{I}T + \hat{V}^d(R) - E \right] \hat{\chi}^d(R) = 0 \tag{1}$$

where $\hat{V}^d(R)$ is the symmetric interaction matrix, whose diagonal elements are represented by the diabatic potentials, while off-diagonal elements are the non-adiabatic coupling terms. The solution $\hat{\chi}^d(R)$ is a vector of of final-state radial wavefunctions, having a mixed character and containing information about all coupled electronic states.

The coupled-channel Schrödinger equation approach has been also successfully applied to the theoretical estimation of the linewidths and lifetimes of vibrational levels of the $b^1\Pi_u$ state, undergoing a strong predissociation [4].

Here the electron-impact induced vibronic transitions are considered, in the frame of the *similarity approach* [10], that allows a simplified expression for the state-to-state cross section, i.e.

$$\sigma_{v'v''} = \frac{2\pi e^4}{(\Delta E_{v'v''})^2} f_{v'v''}\varphi(x) \tag{2}$$

where $\Delta E_{v'v''}$ is the transition energy, $f_{v'v''}$ is the oscillator strength for the vibronic transition, φ is the so-called *similarity function*, a universal function of the reduced incident electron energy $x = E/\Delta E_{v'v''}$, describing the collision dynamics, optimized so as to fit experimental data.

The original formulation has been easily extended to include the vibronic coupling, going through the re-definition of the oscillator strength

$$f_{v'v''} = \frac{2}{3} \frac{g_{\text{excited}}}{g_{\text{ground}}} \Delta E_{v'v''} |\langle \hat{\chi}^d_{\text{excited}} | \hat{M}^d(R) | \chi_{\text{ground}} \rangle|^2 \tag{3}$$

where g represents the statistical weight of electronic terms.

The method, despite its simplicity, gives cross sections that compare satisfactorily with theoretical and experimental results in literature [6, 9, 11], succeeding in reproducing the irregular vibrational profile, characterizing these coupled systems, as shown in figure where the state-to-state excitation of b state are compared with experimental results by Zipf [11].
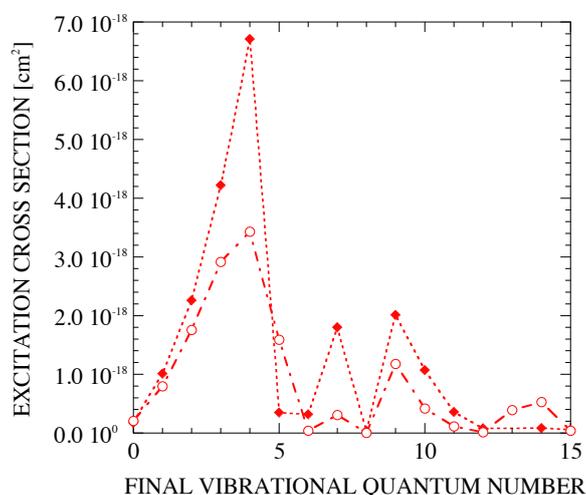

Fig. 1: Excitation cross section (open diamonds) from the $v''=0$ level of the ground state to the $b^1\Pi_u$ state of N_2 molecule, as a function of final vibrational quantum number v', at collision energy E=200 eV, compared with experimental results (closed diamonds) [11].

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