

Effect of the vibrational population of polyatomic molecules on the electron kinetics: the cases of CH₄ and CO₂

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The contribution of the vibrational population of polyatomic gases to the electron kinetics is discussed including inelastic as well as superelastic electron-vibration (e-V) collisions and multi-step excitation and ionisation collisions. To simplify the problem, the population of each vibrational mode is approximated by a simple harmonic oscillator (SHO) and the cross sections for e-V collisions computed in the framework of the distorted wave theory. These two approximations allow a substantial simplification on the e-V collision terms. The model is applied to study the electron kinetics in CH₄ and CO₂ mixtures assuming that the vibrational population is characterized by a temperature T_v .

The contribution of the vibrational population of diatomic gases in gas discharges has been extensively studied, with particular emphasis on mixtures with N₂ or O₂ [6, 5]. The treatment of polyatomic gases, however, is more complex, computationally demanding [2] and limited by the available cross sections. Frequently, models of discharges in mixtures with polyatomic gases (as in [1], CO₂) only consider the contribution of the lowest vibrational states even when higher vibrational states are populated.

Methane and carbon dioxide are two polyatomic gases that are being extensively studied in plasmas as energy or feedstock sources, chemical synthesis, environment protection or in planetary studies, to name just a few applications. In order to improve the modeling of these gases when the population of vibrational levels should be considered, a simplified model for the electron collision terms on the electron Boltzmann equation, has been developed. The starting assumptions are that each vibrational mode is independent and behaves as SHO, i.e. we neglect anharmonic contributions. Electron collisions however can promote both intra- and inter-mode transitions. In the framework of the distorted wave approximation for a SHO [7], the **intra-mode** cross sections involving two consecutive levels with vibrational number w of mode i , can be written as function of the cross section for the lowest transition as

$$\begin{aligned}\sigma_{w,w+1}^i(\epsilon) &= (w+1)\sigma_{0,1}^i(\epsilon) \\ \sigma_{w,w-1}^i(\epsilon) &= w\sigma_{1,0}^i(\epsilon)\end{aligned}\quad (1)$$

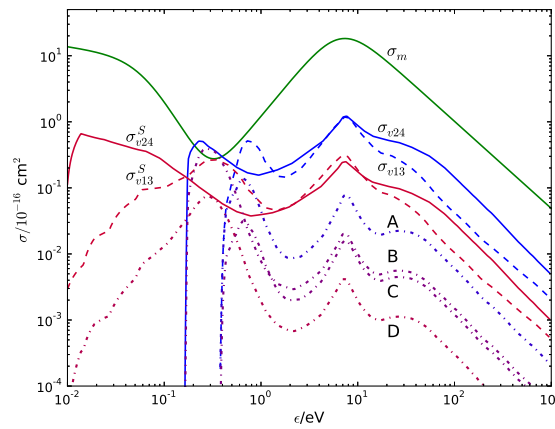


Fig. 1: Intra- and inter-mode vibrational cross sections for methane estimated from equations (1-2) – A: $\sigma_{0,1;0,1}^{ij}$, B: $\sigma_{1,0;0,1}^{ij}$, C: $\sigma_{0,1;1,0}^{ij}$, D: $\sigma_{1,0;1,0}^{ij}$. σ_m is the momentum transfer cross section and the index S identifies a superelastic cross sections.

The **inter-mode** transitions, for transitions involving two modes can be approximated

$$\sigma_{w,w\pm 1;p,p\pm 1}^{ij}(\epsilon) = \frac{\sigma_{ww\pm 1}^i(\epsilon)\sigma_{pp\pm 1}^j(\epsilon)}{\sigma_{0,0;0,0}(\epsilon)} \quad (2)$$

where $\sigma_{0,0;0,0}(\epsilon)$ is the elastic cross section. Thus, using equations (1), (2) and the detailed balancing principle, all vibrational cross sections can be obtained from the $\sigma_{0,1}^i$ cross section for each mode i and the elastic cross section. As an example, figure 1 shows the intra- and inter-mode vibrational cross sections for methane computed from equations (1-2).

The contribution of the vibrational population to multi-step electronic excitation and ionisation was estimated following the same procedure as in [3, 4].

Figure 2 shows the isotropic component of the calculated electron energy distribution function (eedf) in pure CH₄ for $E/N = 100$ Td and four values of T_v , assuming that all modes share the same vibrational temperature.

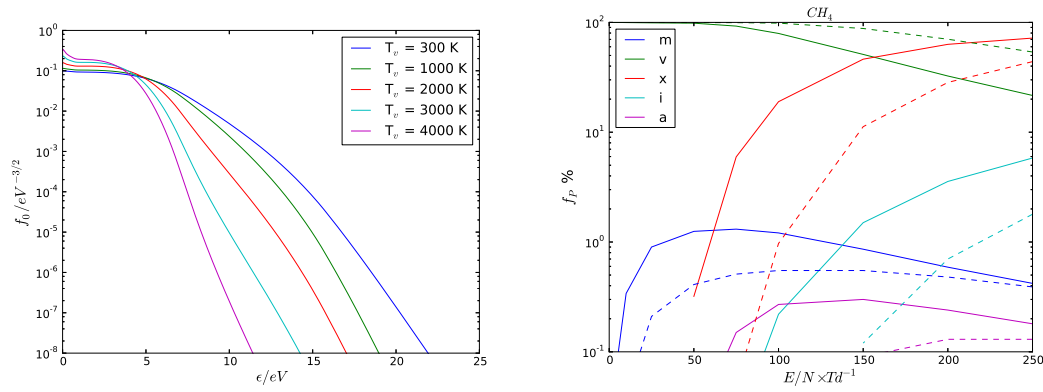


Fig. 2: Isotropic component of the eedf for different values of T_v (left) and fractional electron power losses for a) $T_v = 300$ K, (line) b) $T_v = 2000$ K, (dash) (right).

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