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Vibrational cross sections of methane: from individual cross sections to polyad groups

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Abstract: The fundamental vibrational frequencies of methane follow a simple relation leading to a vibrational structure with polyad groups. In this work, we extend the available electron vibrational cross sections to consider the polyad groups $P_1 – P_3$. Based on a swarm analysis relying on the solution of Boltzmann equation and a genetic algorithm [1], the new set of cross sections are fitted to the experimental transport parameters. The vibration excitation rates for the individual levels are computed from the polyad cross sections.

Keywords: Methane, vibrational cross sections, polyad groups

1. Introduction

Methane (CH_4) is present in many types of activities using plasma such as in technological applications (dry reforming, thin film applications or plasma-assisted combustion), fusion studies in tokamaks and the study of outer atmospheres, e. g. of Titan. The modeling of these plasmas depends on reliable electron collision cross sections (cs) for the gases involved.

CH_4, like the other spherical-top molecules (STM), has four fundamental frequencies of vibration, with degeneracies of, respectively, (1, 2, 3, 3). Due to the near coincidence between the frequencies of the bending modes, ν_2 and ν_4, on the one hand and of the stretching modes, ν_1 and ν_3, on the other, it has not been possible to experimentally separate the individual electron vibrational cs [2]. These cs are grouped in a bending, σ_{24}, and stretching, σ_{13}, cross sections.

The methane cross sections have been reviewed by Song et al [3], without recommending cs for neutral dissociation, and recently extended by Bouwman et al [4] with cs for neutral dissociation. The Song – Bouwman set includes a cs for momentum transfer, two for vibrational excitation, four for neutral dissociation, seven for ionization and two for dissociative electron attachment. This set is able to reproduce the measured values of transport parameters.

The rovibrational spectra of STM, however, show a complex structure of bands, the so-called *polyads*, which has motivated the development of high-resolution theoretical analysis of those spectra [5]. In the case of CH_4, the vibrational levels are grouped in *polyads*, P_n, with n satisfying the relation

$$n = 2v_1 + v_2 + 2v_3 + v_4 \tag{1}$$

where $v_i, i = 1, \ldots, 4$ are the number of vibrational quanta in each of the four modes.

Figure 1 shows the first six polyads of CH_4, the number of levels and sublevels and the compound degeneracy of states within each polyad.

The presence of polyads is also visible on the electron-energy loss spectrum [6, fig 2].

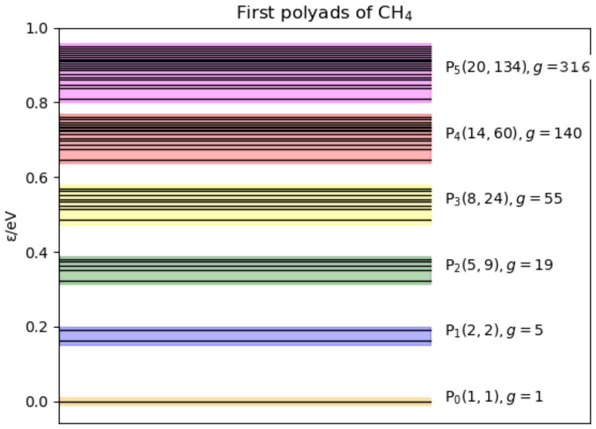

Fig. 1. First polyad levels of CH_4 and total number of states. In parenthesis, the number of levels and sublevels.

In light of this, the vibrational cs in [3,4] should be attributed to the polyads P_1 and P_2.

In this work we study the effect of including vibrational cs for higher polyad groups and propose an updated complete and consistent cs set.

2. Cross sections

We modified the Song – Bouwman cs set to consider polyad groups. Thus the σ_{24} and σ_{13} cs are replaced by σ_{P1} and σ_{P2}, respectively. While σ_{P1} corresponds to the excitation of the same modes and number of states as in σ_{24}, σ_{P2} corresponds now to the excitation of 19 states associated with the levels [1000], [0010], [0101], [0200] and [0002]. Note that the cs for superelastic collisions, obtained from the direct cs, depend on degeneracies. We have also introduced two extra vibrational cross sections for the P_3 and P_4 polyad groups with the same shape as σ_{P1} and σ_{P2}, and scaled the set of vibrational cs in order to fit the experimental swarm transport parameters. The selection of initial relative amplitude of these cs was guided by inspection of the electron-energy loss spectrum.

3. Boltzmann equation analysis

Two different methods were used to solve the Boltzmann equation (BE),

$$\partial_t f + \boldsymbol{v}\cdot\nabla_r f - \frac{\varepsilon_0}{m}\boldsymbol{E}\cdot\nabla_v f = C(f) \qquad (2)$$

for an electron swarm in a background gas with density N and acted upon a constant electric field, **E**. Here $f(\boldsymbol{r}, \boldsymbol{v}, t)$ is the electron velocity distribution function (evdf), m the electron mass e $C(f)$ the collision operator.

The first method expands the electron velocity distribution function on the density space gradients and solves BE for the expansion coefficients in a (v, θ) grid, where θ is the angle between ***E*** and ***v***, for either "time of flight" or "steady-state Townsend" conditions. Both flux and bulk swarm parameters are obtained. Further details can be found in [7].

The second method, implemented on the LoKI-B solver [8] solves a time and space independent form of BE under the two-term approximation.

In all BE methods, we assume isotropic electron scattering in all inelastic collision processes, a gas temperature of 293 K and that the kinetic energy available after each ionization event is shared equally between the two electrons.

To fit the cross section set to the experimental swarm parameters we have used a genetic algorithm [1]. The quality of the fitting was measured by a figure of merit, *S*, defined as the average of the square relative shift between the experimental values and the values obtained from the cs, for all published values and swarm parameters considered.

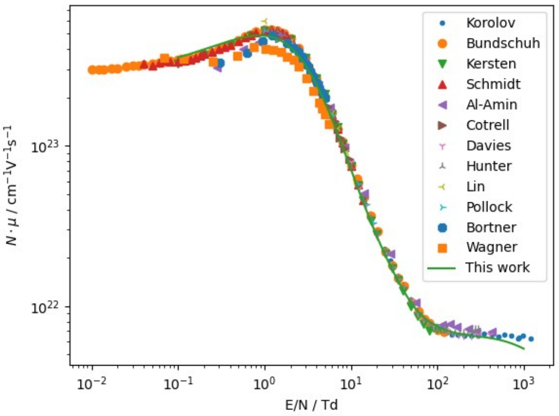

Fig. 2. Measured [9-20] and calculated values for the reduced mobility in pure CH_4 as function of the reduced electric field value, E/N.

4. Results and discussion

Following [4], we consider three swarm parameters: the bulk mobility, μ, the transverse characteristic energy, D_T/μ, and the effective Townsend coefficient, α_{eff} together with an extended selection of available experimental results.

Figures 2 – 4 compare the results for these swarm parameters obtained with the optimized cs set and the experimental measurements. The agreement is very good with the exception for the mobility for E/N > 600 Td and the transverse characteristic energy below 0.5 Td where deviations up to 10% are observed. The final cs set has a value of S = 0.010 while this value is S = 0.023 for the original set [4].

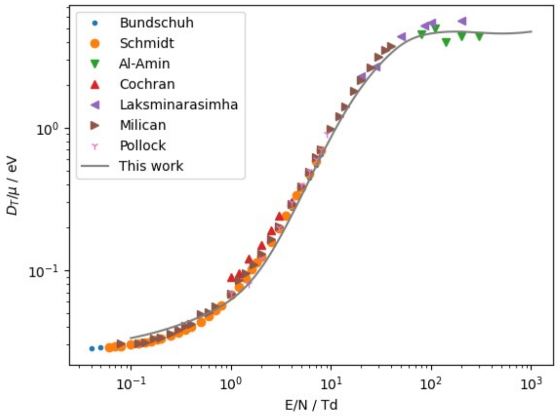

Fig. 3. Measured [10,12,13,21-24] and calculated values for the transverse characteristic energy in pure CH_4 as function of the reduced electric field value, E/N.

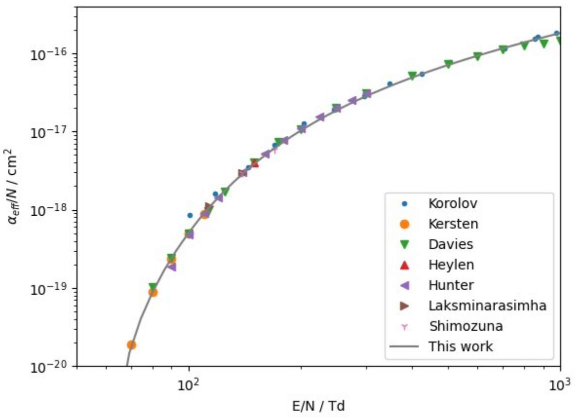

Fig. 4. Measured [9,11,15,25,16,22,26] and calculated values for the effective Townsend coefficient in pure CH_4 as function of the reduced electric field value, E/N.

Figure 5 shows the final cs set with the four polyad vibrational cs.

The rate coefficients for vibrational excitation of the polyad bands are shown in figure 6. Assuming that, in each band, the states are in thermodynamic equilibrium, the rate coefficients for vibrational excitation for each level, K_i, can be obtained from

$$K_i = K_P\, g_i \exp\left(-\frac{\varepsilon_i}{k_B T_{gas}}\right) / G \qquad (3)$$

where K_P is the rate coefficient for the corresponding polyad band, ε_i is the level energy and

$$G = \sum_{k=1}^{levels} g_k \exp\left(-\frac{\varepsilon_k}{k_B T_{gas}}\right) \qquad (4)$$

Figure 7 shows the rate coefficients for the P_1 and P_2 bands and the corresponding states of each bands.

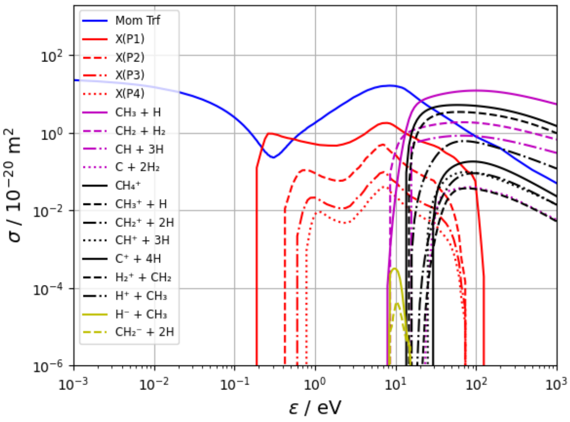

Fig. 5. Optimized cross sections set for CH_4. 🟦 - momentum transfer; 🟥 - vibrational excitation; 🟪 - dissociative excitation; ⬛ - ionization; 🟨 - attachment

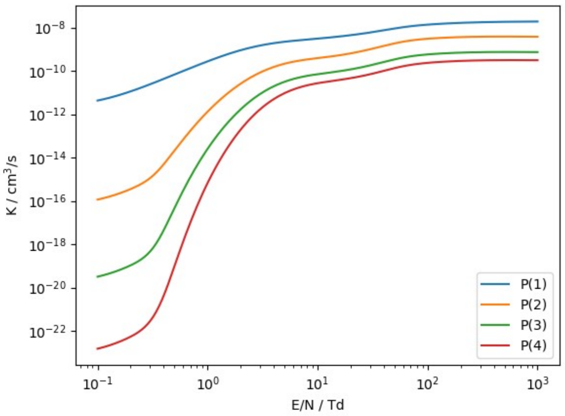

Fig. 6. Rate coefficients for vibrational excitation of the first polyad bands in pure CH_4 as function of the reduced electric field value, E/N.

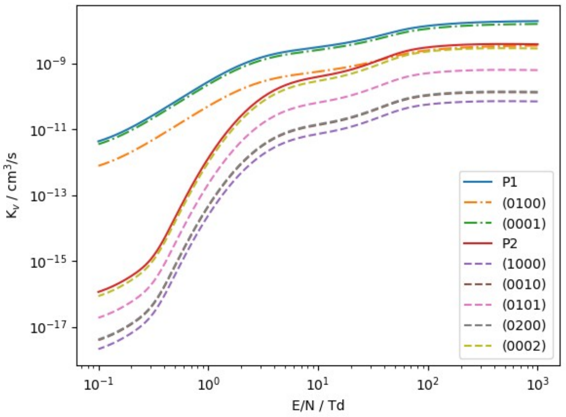

Fig. 7. Rate coefficients for excitation of P_1 and P_2 polyad bands and the corresponding states assuming thermodynamic equilibrium, as function of the reduced electric field value, E/N.

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