Anisotropic scattering in rotational collisions of electrons with CO molecules

L.L. Alves

llalves@tecnico.ulisboa.pt

Instituto de Plasmas e Fusão Nuclear
Instituto Superior Técnico, Universidade de Lisboa
Lisboa, Portugal
http://www.ipfn.ist.utl.pt
https://www.ipfn.tecnico.ulisboa.pt/nprime/

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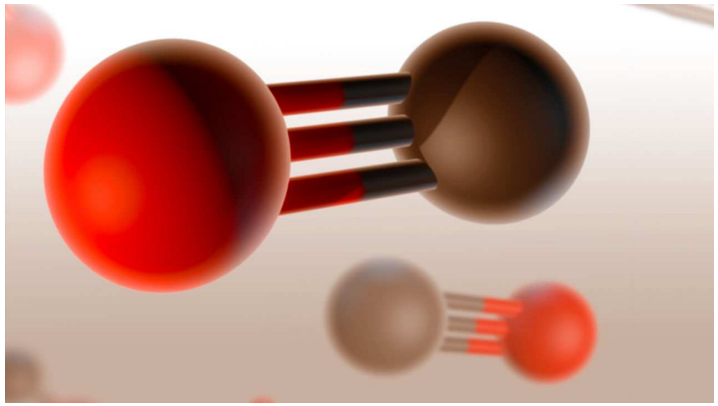
Anisotropic e-CO rotational collisions

Why CO ?



Planetology

- Earth, Mars, Jupiter (Cameron bands $a^3\Pi \rightarrow X^1\Sigma$)
- re-entry Physics

Astrophysics

- second most abundant gas in molecular clouds, after hydrogen

(rotational excitation of CO by photoelectrons and subsequent emission of radiation)

Plasma applications

- reforming of CO_2
- deposition: CO adsorption on surfaces

Anisotropic e-CO rotational collisions

Why e-CO rotational collisions ?

Reviews of electron-collision cross sections (CS) and swarm parameters

- Comprehensive reviews (no complete CS sets)
  Trajmar et al, *Phys. Rep.* 97 (1983)
  Brunger and Buckman, *Phys. Rep.* 357 (2002)
  Raju, *Gaseous electronics: theory and practice,* CRC Press (2005)
  Y. Itikawa, *J. Phys. Chem. Ref. Data* 44 (2015)

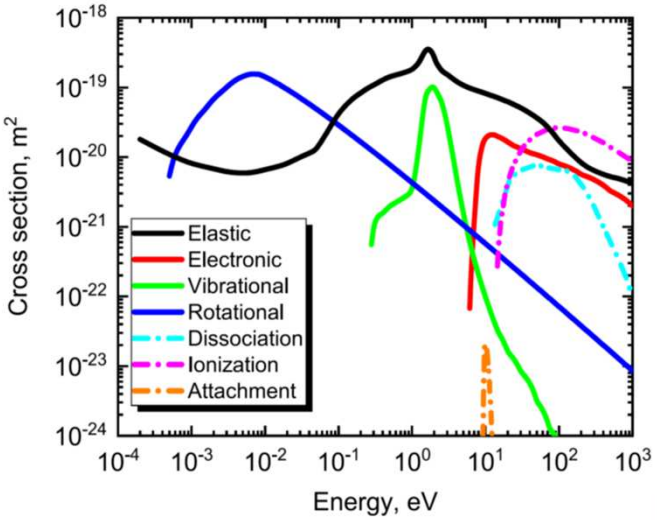
- Complete swarm-derived CS sets **(Phelps database on LXCat)**
  Hake and Phelps, *Phys. Rev.* 158 (1967)
  Land, *J. Appl. Phys.* 49 (1978)
  use of total momentum-transfer CS determined as sum of a dipole term, calculated as a dipole rotational with the Born approximation, and a nitrogen-like elastic CS

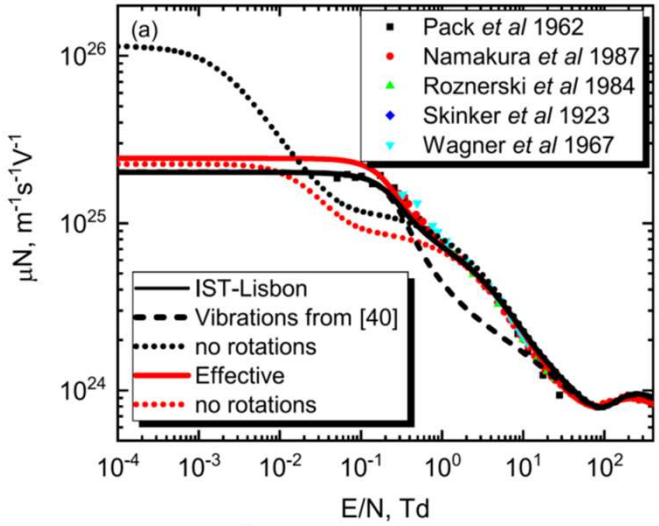
- Recent complete swarm-derived CS set **(IST-Lisbon database on LXCat)**
  P. Ogloblina et al, *PSST* (2015)
  - analysis of CS at low energies (predominance of electron-dipole rotational interactions)
  - proposal of elastic momentum-transfer CS obtained from an adjusted effective (total)

Two-term approximation calculations

Swarm-derivation of complete sets of cross sections

Complete sets of cross sections are those describing the total transfer of momentum and energy between electrons and the gas





Cross sections

Boltzmann solver

- **Monte-Carlo algorithm**
- **differential EBE**

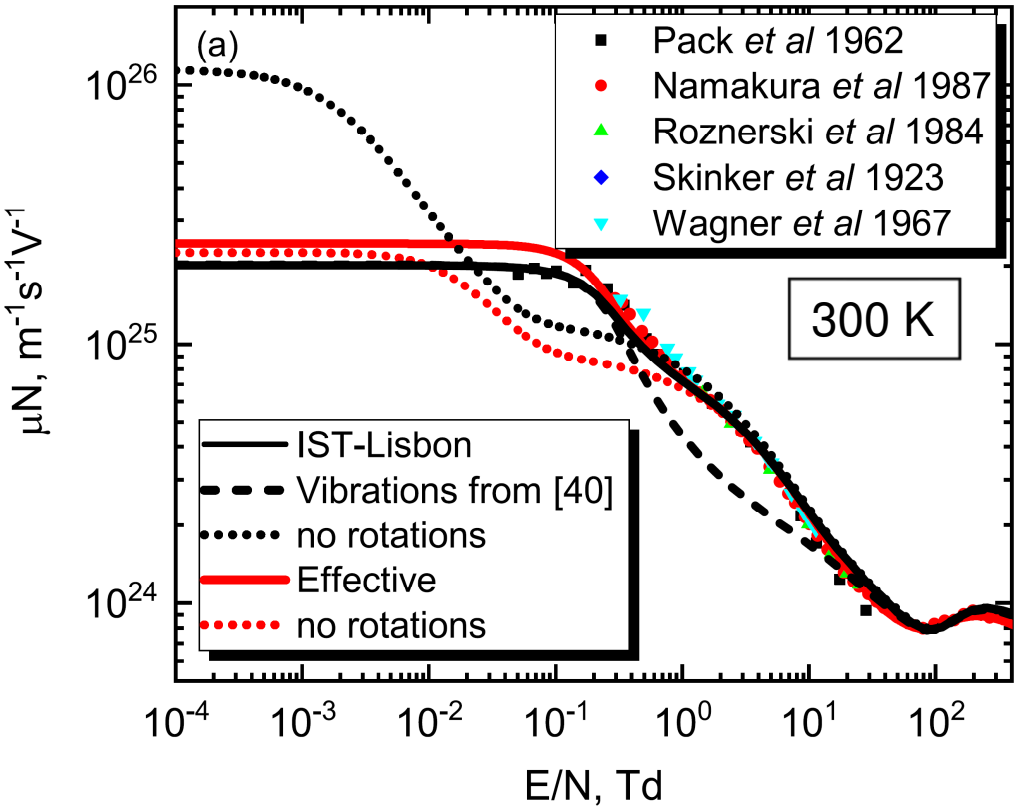
Swarm parameters

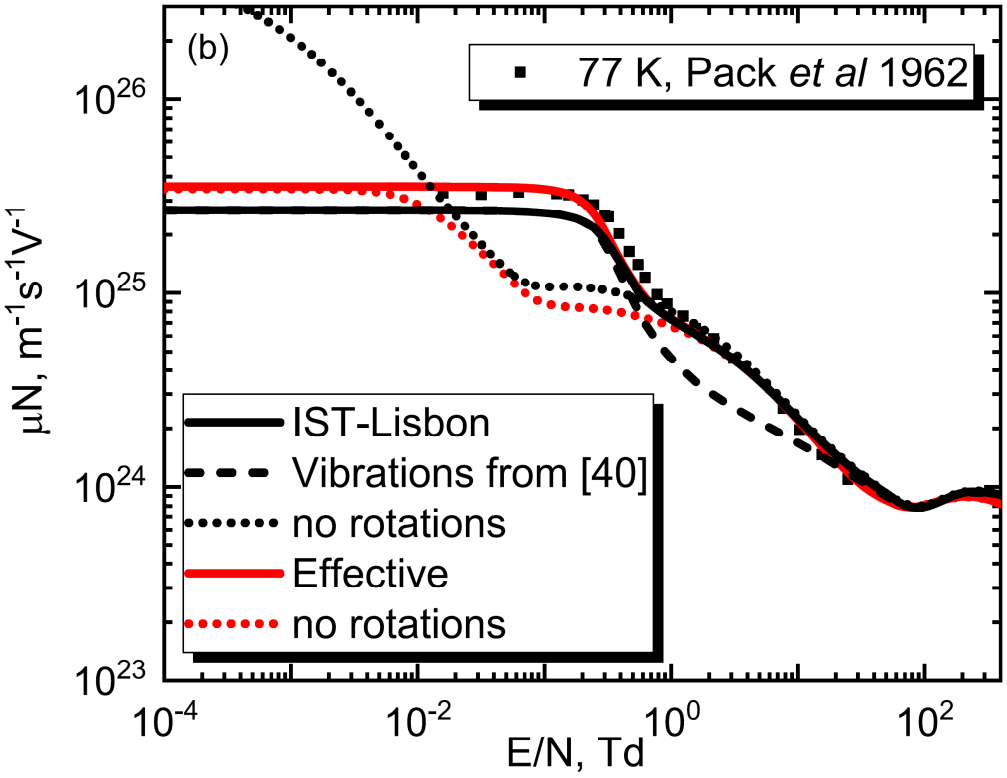
Comparison with experiment

Adjust cross sections

Anisotropic e-CO rotational collisions

Why e-CO rotational collisions ?





< 20% disagreement !

P. Ogloblina et al, *PSST* 29 (2020)

There is room for improving swarm predictions

Anisotropic e-CO rotational collisions

Why anisotropic effects ?

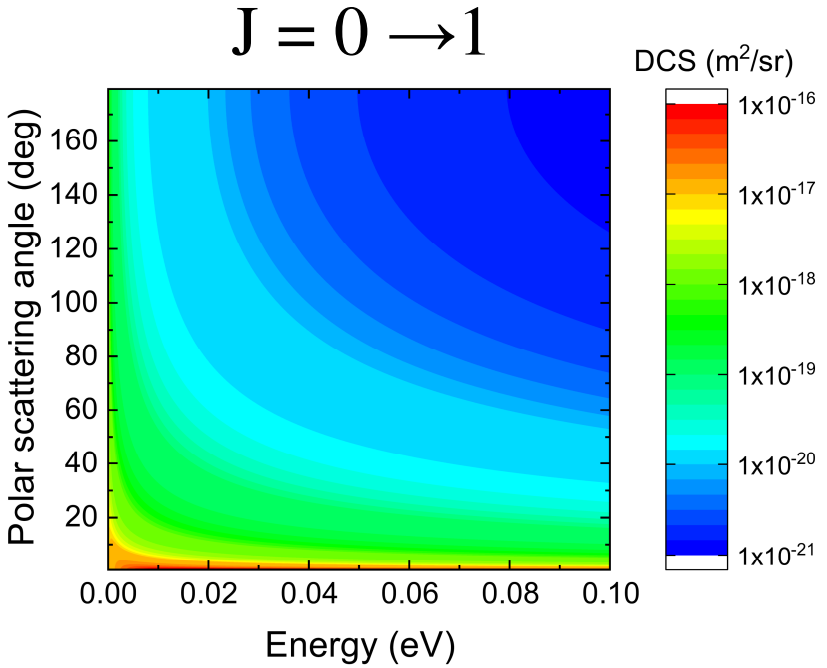
The differential cross section (DCS) for polar molecule CO
(Born approximation combined with point dipole interaction, for low energy region)

Y. Itikawa, *J. Phys. Chem. Ref. Data* 44 (2015)

$$\frac{d\sigma(\epsilon,\theta)}{d\Omega} = \frac{4}{3}\frac{(a_0\mu)^2 R_\infty}{K^2}\sqrt{\frac{\epsilon'}{\epsilon}}\frac{J_>}{2J+1}$$

$$K^2 = |\mathbf{k}' - \mathbf{k}|^2 = \epsilon' + \epsilon - 2\sqrt{\epsilon\epsilon'}\cos\theta$$

$$J_> = \max(J, J')$$



The scattering distribution is highly anisotropic

Outline

Anisotropic e-CO rotational collisions

L Vialetto et al, *PSST* 30 075001 (2021)

- **The e-CO cross sections**
  - Integral and momentum-transfer cross sections for rotational collisions
  - Complete sets of cross sections adopted; swarm derivation
- **Swarm calculations and results**
  - MC code (+ angular scattering model)
  - The two-term LisbOn KInetics Boltzmann solver (LoKI-B)
  - Swarm results
- **Improving the two-term solver LoKI-B**
  - Implementation of anisotropic rotational cross sections
  - Swarm results
- **Final remarks**

Apologies for some busy slides

The e-CO rotational cross sections

Integral cross section and momentum-transfer cross section

The integral cross section (ICS)

$$\sigma^{ICS}_{J,J+1}(\epsilon) = 2\pi \int_0^{\pi} \frac{d\sigma(\epsilon,\theta)}{d\Omega} \sin\theta d\theta = \frac{(a_0\mu)^2 R_\infty}{V_{J,J+1}} \frac{J+1}{2J+1} f(\epsilon/V_{J,J+1})$$

The momentum-transfer cross section (MT)

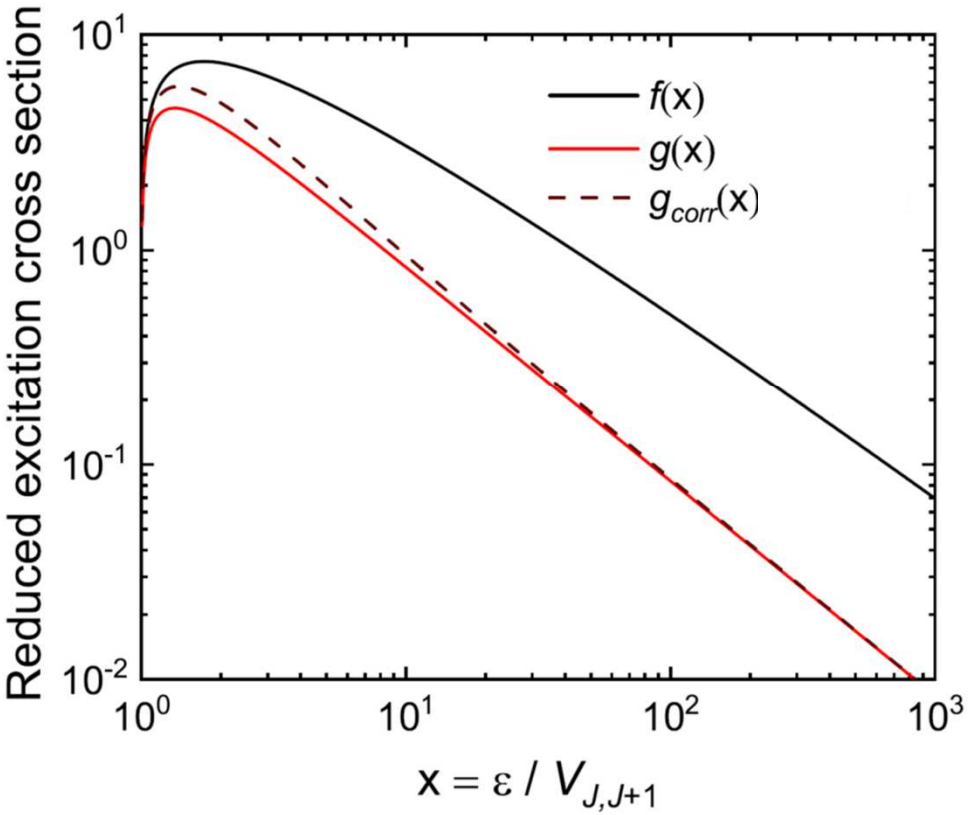
T. Makabe and R. White, *JPD* 48 (2015)

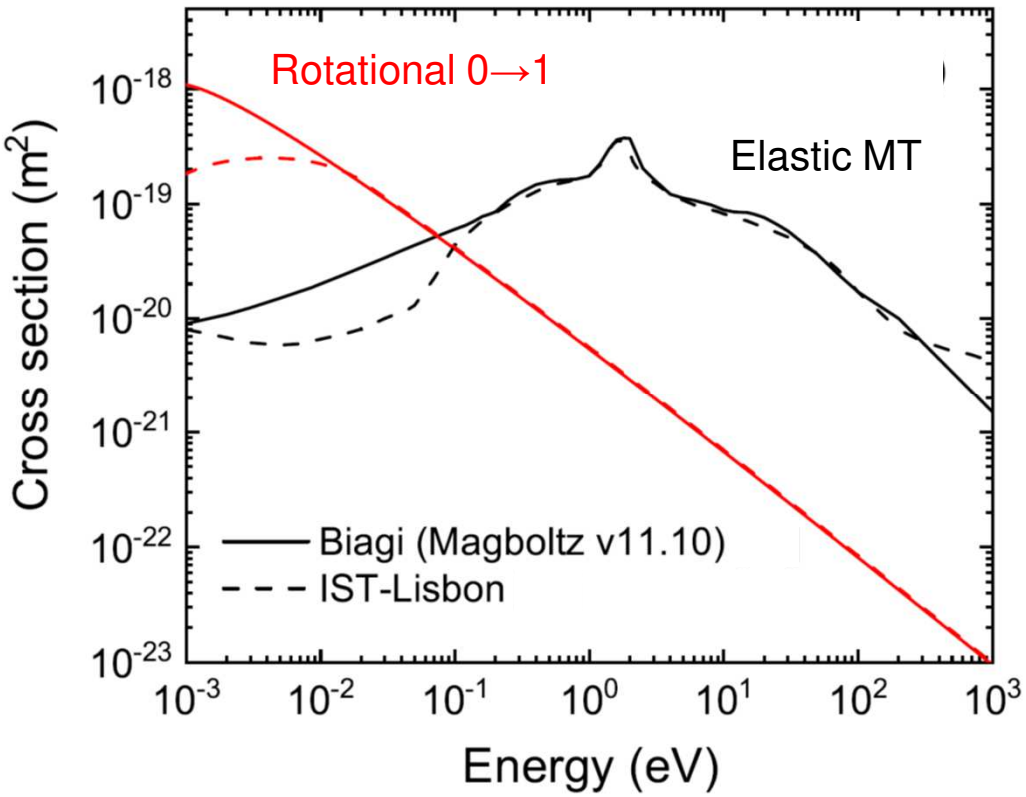
$$\sigma^{MT}_{J,J+1}(\epsilon) = 2\pi \int_0^{\pi} \frac{d\sigma(\epsilon,\theta)}{d\Omega} \left[1 - \left(1 - \frac{V_{J,J+1}}{\epsilon}\right)^{1/2} \cos\theta\right] \sin\theta d\theta$$

$$= \frac{(a_0\mu)^2 R_\infty}{V_{J,J+1}} \frac{J+1}{2J+1} g_{corr}(\epsilon/V_{J,J+1}) \rightarrow g(\epsilon/V_{J,J+1})$$

The e-CO rotational cross sections

ICS and MT: swarm-derivation of IST-Lisbon cross sections





Swarm-derivation of IST-Lisbon CS

Too small

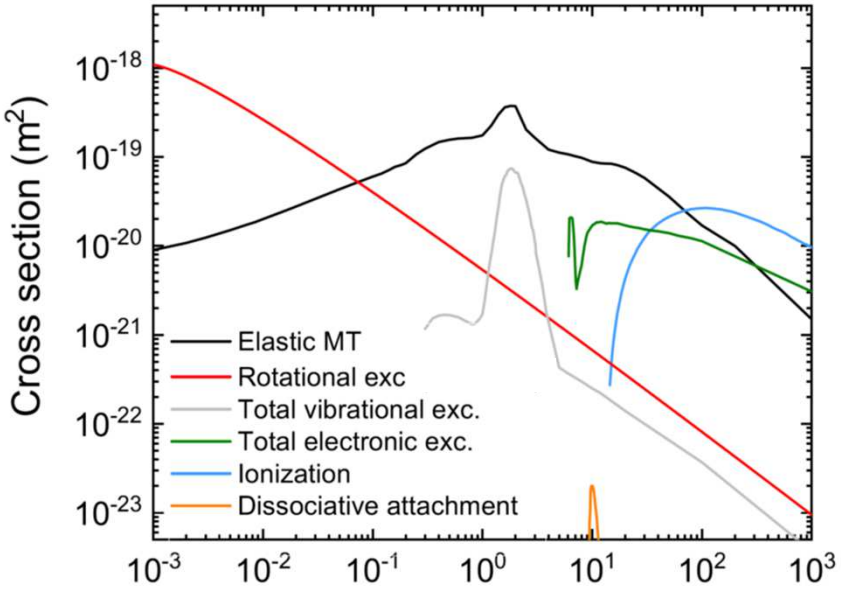
$$\sigma_{\text{elastic-MT}} = \sigma_{\text{effective}} - \sum_J \sigma_{J,J+1}^{MT}$$

Too large: adjust / reduce

Assuming isotropy

The e-CO cross sections

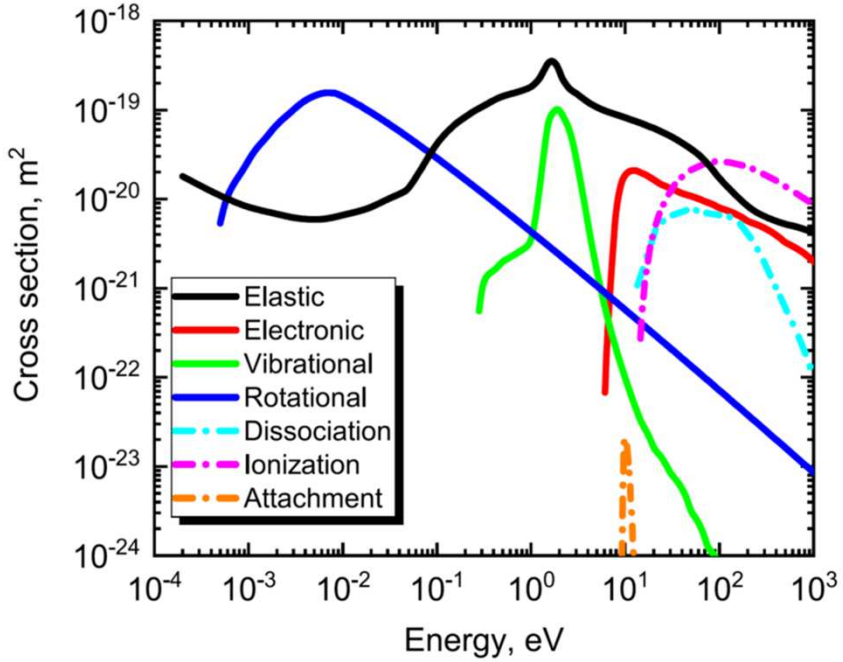
Complete sets of cross sections adopted



Biagi's Magboltz v11.10

http://magboltz.web.cern.ch/magboltz/

Vibrational excitations / deexcitations involving v=0-6
agree with Laporta et al, *PSST* 21 (2012), divided by 1.3
Electronic excitations (including diss attach & ionization)
mostly Sawada et al, *J. Geophys. Res* 77 (1972)
Rotational excitations / deexcitations involving J=0-26
with ICS from dipole-Born DCS
but adopting a different angular scattering model



IST-Lisbon

P. Ogloblina et al, *PSST* 29 (2020)

Vibrational excitations / deexcitations involving v=0-10
Laporta et al, *PSST* 21 (2012)
Electronic excitations (including diss attach & ionization)
Sawada et al, *J. Geophys. Res* 77 (1972)
Itikawa, *J. Phys. Chem. Ref. Data* 44 (2015)
Rotational excitations / deexcitations involving J=0-16
adjusted ICS

Swarm calculations

Monte Carlo code

L. Vialetto et al, *PSST* 29 (2020)

- adopts null-collision method
- adopts a modified time-step technique
- includes the effects of the finite temperature of the background gas, with an exact Test Particle Monte Carlo technique
- describes e-neutral scattering events in the centre-of-mass frame
- uses a standard Time-Of-Flight method to calculate bulk transport parameters
- follows the trajectories of typically ~10^4 – 10^5 electrons
- defines the steady-state time t_{SS}, for a deviation of the mean kinetic energy < 0.1%
- improves statistics by averaging the bulk transport parameters in the interval [t_{SS}, 10 t_{SS}] with a sample time of 10^{-9} s

Swarm calculations

Monte Carlo code - angular scattering model

Angular distribution function

$$I(\epsilon,\theta) = \frac{1}{\sigma^{ICS}(\epsilon)} \frac{d\sigma(\epsilon,\theta)}{d\Omega}$$

Sampling of scattering angles

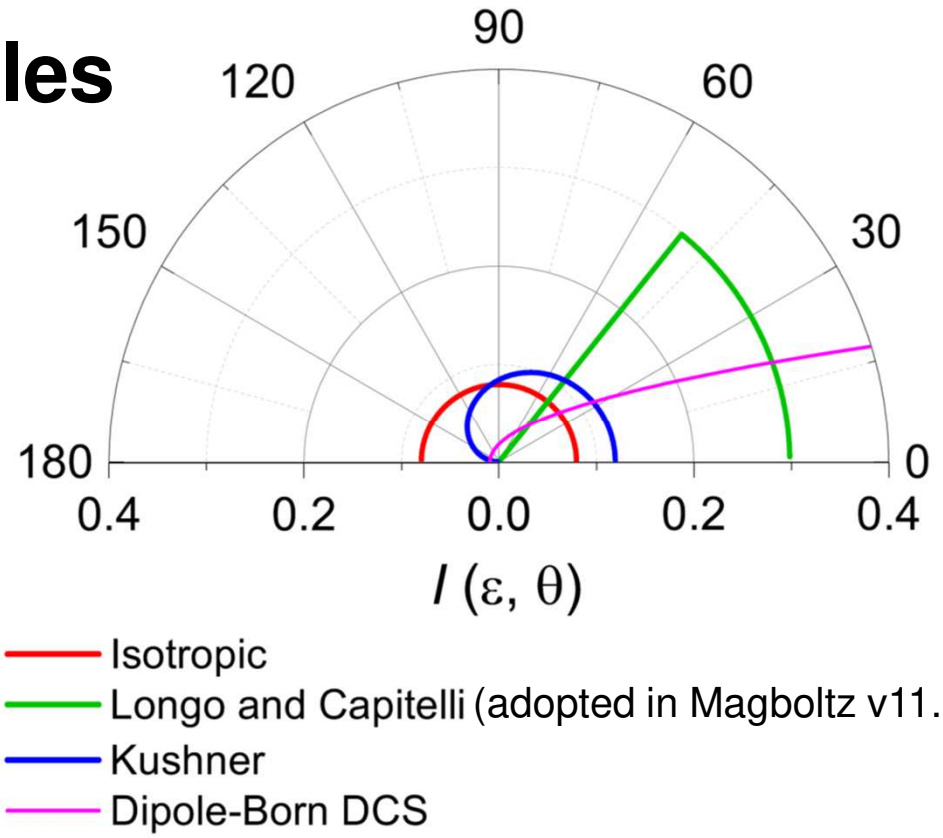
$$r_i = 2\pi \int_0^{\theta_i} I(\epsilon,\theta') \sin\theta' d\theta'$$

Dipole-Born DCS

$$\cos\theta_i = 1 + \frac{2\xi^2}{1-\xi^2}\left(1 - \xi^{-2r_i}\right)$$

$$\xi(\epsilon) = \frac{V_{J,J\pm1}}{\left(\sqrt{\epsilon \pm V_{J,J\pm1}} + \sqrt{\epsilon}\right)^2}$$

J=0→1 at ε = 0.01 eV



The LisbOn KInetics Boltzmann solver (LoKI-B)

(developed under MATLAB®)

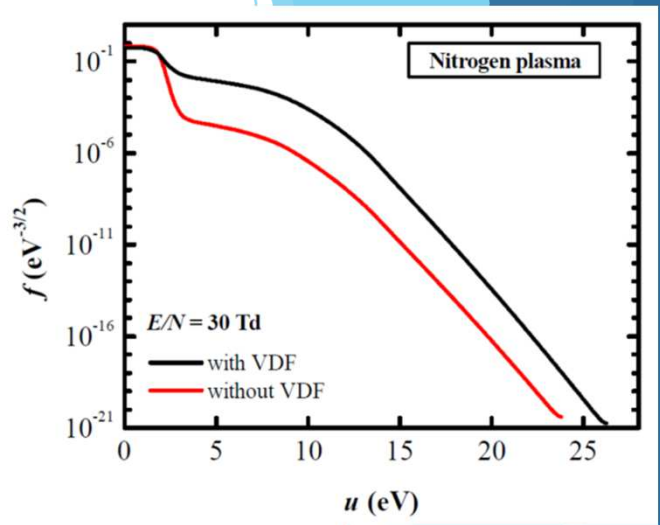
LisbOn KInetics

LoKI-B

OPEN SOURCE

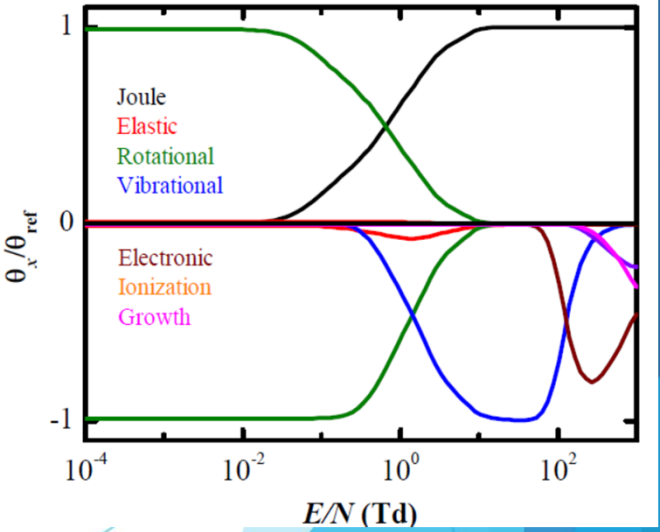
https://github.com/IST-Lisbon/LoKI

- solves the time and space independent form, or the time-dependent form, of the two-term electron Boltzmann equation
- includes e-e collisions, CAR operator, and growth models for the electron density.



The LisbOn Kinetics Boltzmann solver

was developed as a response to the need of having an electron Boltzmann solver easily addressing the **simulation of the electron kinetics** in **any complex gas mixture** (of atomic / molecular species), describing first and second-kind electron collisions with **any target state** (electronic, vibrational and rotational), characterized by **any user-prescribed population**.



A. Tejero-del-Caz *et al* Plasma Sources Sci. Technol. 30 (2021) 065008

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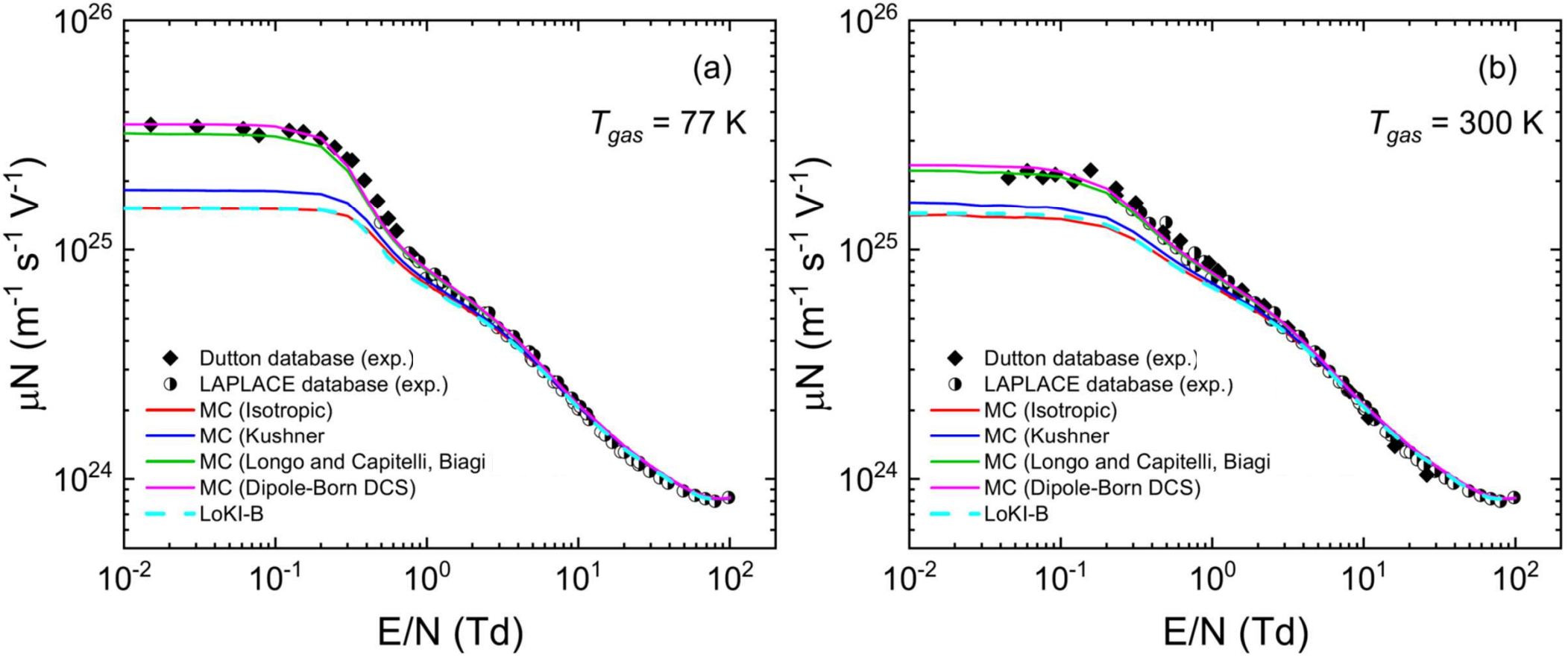
N PRiME

loki@tecnico.ulisboa.pt

Swarm results - I

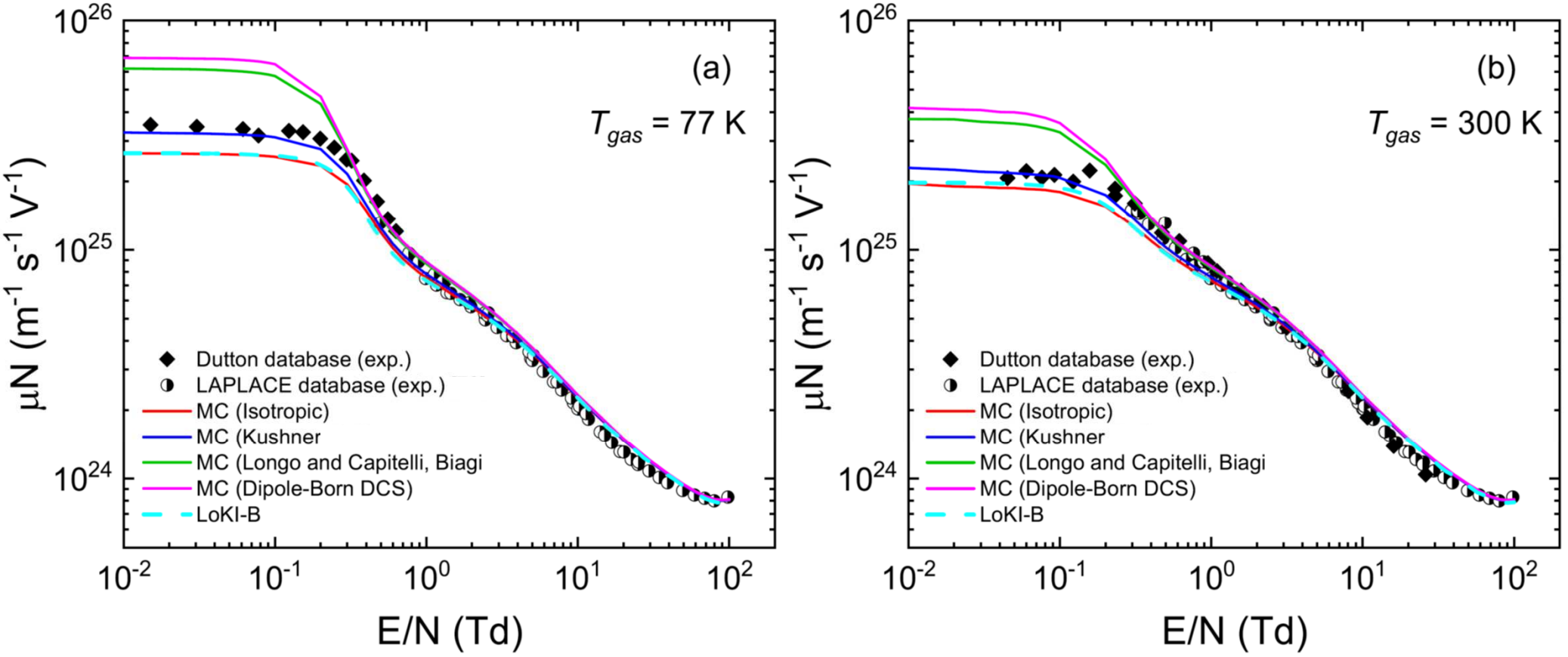
Biagi cross sections



- Excellent agreement between MC (isotropic) and LoKI-B
- 2% agreement between MC (dipole-Born DCS) and experiment
  - at 300 K
  - at 77 K for $E/N < 0.2$ Td, $E/N > 0.8$ Td (8% in other cases)

Swarm results - II

IST-Lisbon cross sections



- Between MC (isotropic) / LoKI-B and experiment
  - agreement below 1% at 300 K
  - up to 20% disagreement at 77 K
- Between MC (dipole-Born DCS) and experiment
  disagreement between 30% (300 K) and 50% (77 K), for this cross section set

Expanding the DCS in Legendre polynomials

Makabe and Petrovic, *Plasma electronics: applications in microelectronic device fabrication* (2014)

$$\frac{d\sigma_k(\epsilon,\theta)}{d\Omega} = \sum_{j=0}^{\infty} \frac{2j+1}{4\pi} \sigma_k^j(\epsilon) P_j(\cos\theta)$$

$$\sigma_k^j(\epsilon) = 2\pi \int_0^{\pi} \frac{d\sigma_k(\epsilon,\theta)}{d\Omega} P_j(\cos\theta) \sin\theta d\theta$$ … orthogonality relation

By truncating the expansion to the first order

$$\sigma_{J,J+1}^{ICS}(\epsilon) \simeq \sigma_{J,J+1}^{0}(\epsilon)$$

$$\sigma_{J,J+1}^{MT}(\epsilon) \simeq \sigma_{J,J+1}^{0}(\epsilon) - \sigma_{J,J+1}^{1}(\epsilon)$$

The angular distribution of scattering can be described using only ICS and MT cross sections

Improving the two-term solver LoKI-B

Implementation of anisotropic rotational CS

The updated first anisotropy equation

$$f_1(\epsilon) = -\frac{E}{N}\frac{1}{\Omega_c(\epsilon)}\frac{df_0(\epsilon)}{d\epsilon}$$

$$\Omega_c(\epsilon) \simeq \sum_i \delta_i \sigma^{MT}_{i,ela}(\epsilon) + \sum_{i,j>i}\left[\delta_i \sigma^0_{i,j}(\epsilon) + \delta_j \frac{g_i}{g_j}\frac{\epsilon + V_{i,j}}{\epsilon}\sigma^0_{i,j}(\epsilon + V_{i,j})\right]$$

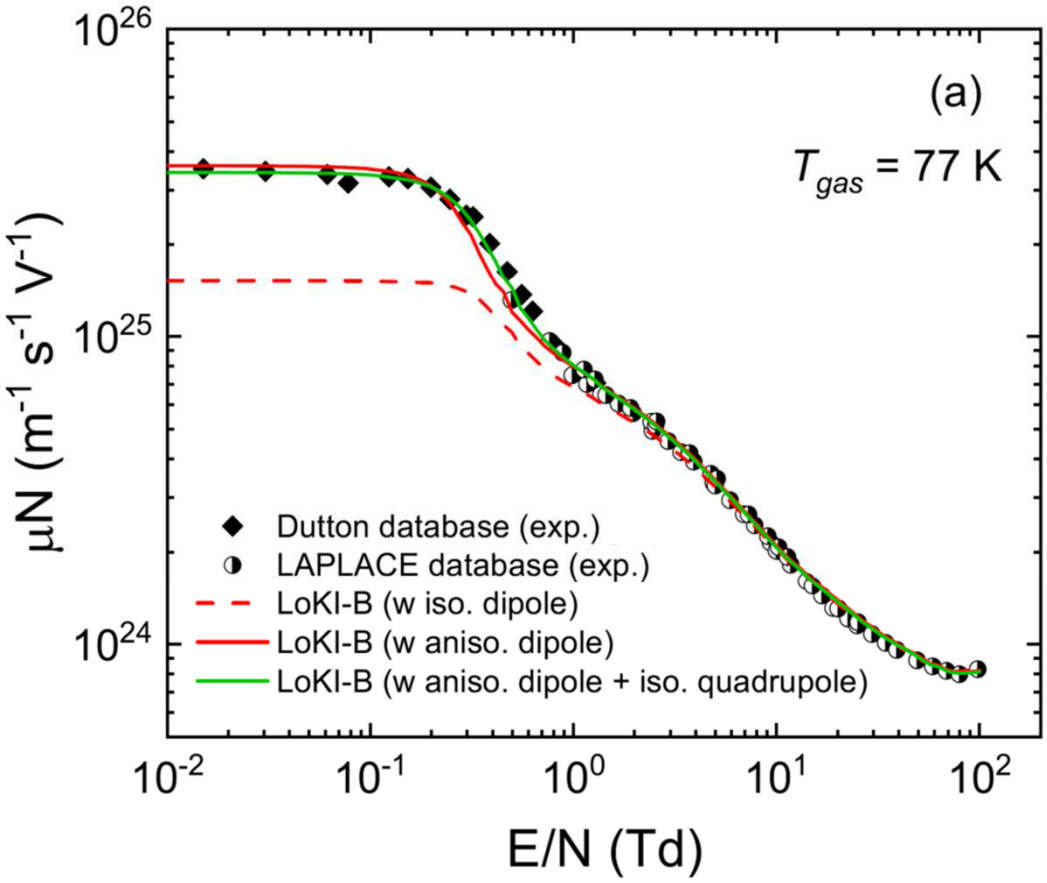
$$+ \sum_{J,J+1}\left[\delta_J \sigma^{MT}_{J,J+1}(\epsilon) + \delta_{J+1}\frac{g_J}{g_{J+1}}\sigma^{MT}_{J,J+1}(\epsilon)\right]$$

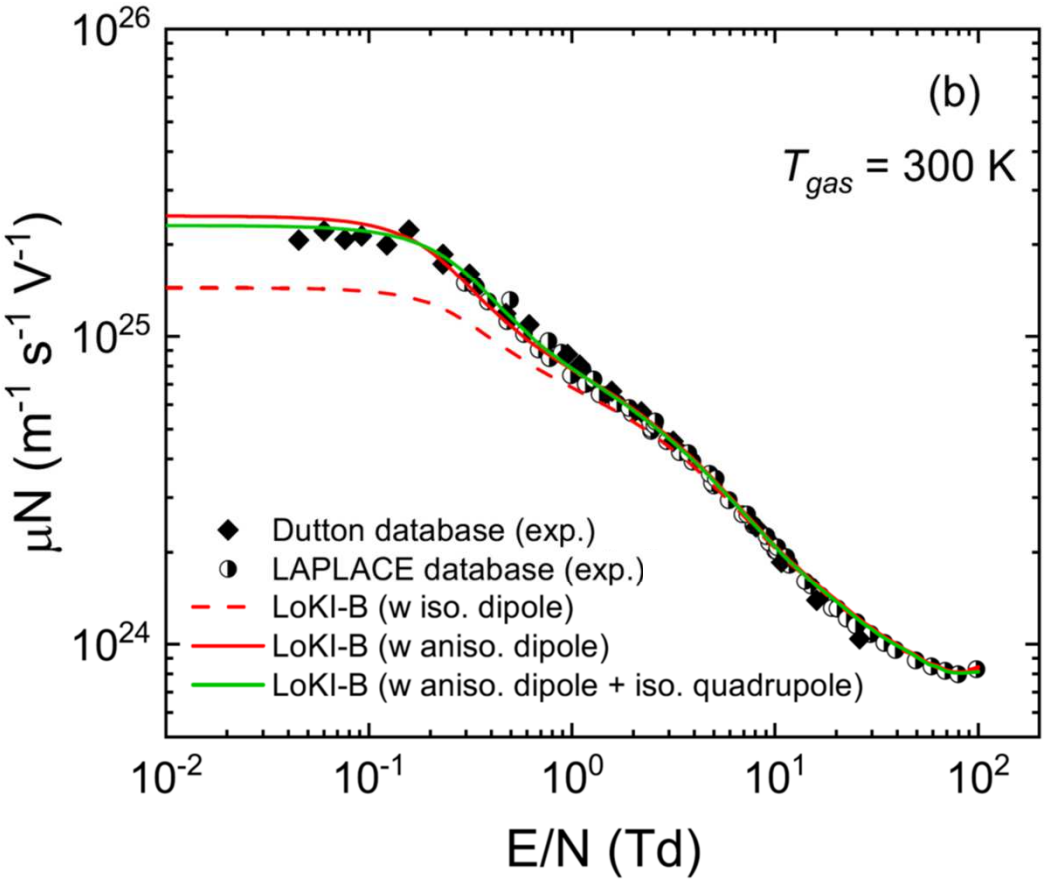
… for negligible $V_{J,J+1}$ energies

The improved treatment distinguishes between ICS and MT cross sections for rotational collisions

Swarm results - III

Improved LoKI-B with Biagi cross sections





Between improved LoKI-B and experiment

- agreement within 8% (at intermediate E/N values) with anisotropic dipole rotational collisions
- excellent agreement (below 2%) with anisotropic dipole rotational collisions + isotropic quadrupole rotational collisions

Final remarks

- **Investigation of the e-CO anisotropic scattering in rotational collisions**
  - swarm calculations and comparison with measurements
  - MC code and two-term Boltzmann solver (LoKI-B)
  - adopting Biagi's complete set of cross sections (Magboltz code v11.10) combined with ICS coherently deduced from dipole-Born DCS for rotations

- **Use of dipole-Born DCS for rotational collisions in CO**
  - allows proposing a novel forward-peaked model for MC simulations
  - enables implementing anisotropic dipole rotational collisions, in two-term solvers
  - leads to good agreement (within few percent) between simulations (MC and two-term) and measurements of swarm parameters in CO

    (improved agreement after including isotropic quadrupole rotational collisions)

- **Use accurate DCS in future research on electron swarms**
  - the calculation of swarm parameters is more influenced by the choice of the angular scattering model (deviations up to 50%) than the adoption of the two-term approximation
  - Extend the study to other collisional mechanisms (e.g. vibrations), even in two-term solvers (with partial cross sections derived from Legendre polynomials expansion of DCS)

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FOM

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