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AN OVERVIEW OF ELECTRON IMPACT CROSS SECTION REQUIREMENTS FOR LOW TEMPERATURE PLASMA MODELLING

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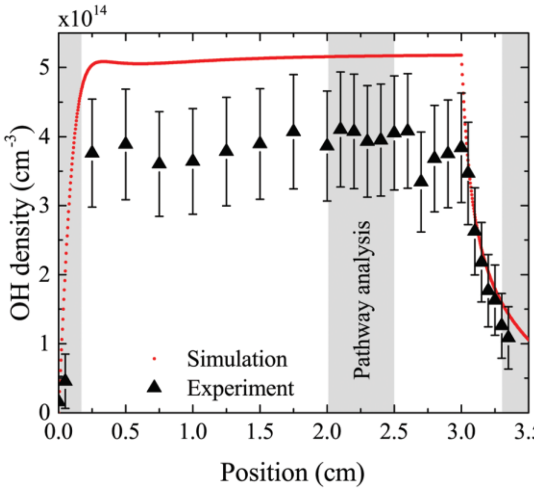
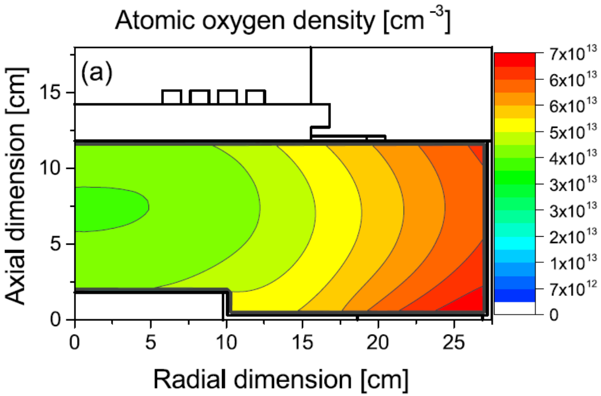
About this talk

- **My perspective**:
  - Applications of LTPs
  - Combining / comparing experiment and simulation
    - Focus on simulations
  - Accuracy of input data is crucial – does physical model or input data cause differences between simulation and experiment?
- **Aims**:
  - Introduction to LTP simulations from perspective of input data
  - My perspective on what kind of data is needed





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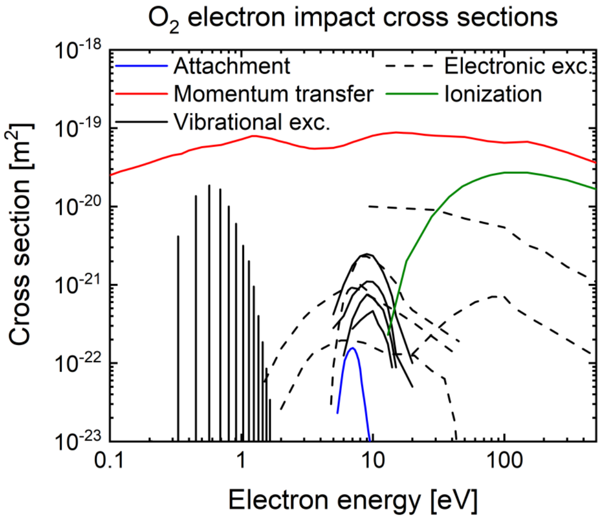
Applications of LTPs

Application	Typical feed gases used	Typical active species
Material processing	Ar, He, O_2, N_2, H_2, Cl_2, HBr, CF_4, SF_6 etc.	Radicals e.g. O, Cl, F Positive ions
Chemical conversion	O_2, N_2, H_2, CO_2, H_2O, CH_4, C_xH_y etc.	Radicals, excited states (vibrational, electronic)
Medicine	Ar, He, O_2, N_2, H_2O	Reactive oxygen and nitrogen species
Agriculture	O_2, N_2, H_2O	Reactive oxygen and nitrogen species

Ingredients of a LTP simulation

$$\frac{dN_i}{dt} = G_i - L_i \qquad \frac{dT_i}{dt} = G_{\varepsilon,i} - L_{\varepsilon,i}$$

- Gain (G) and loss (L) terms required to simulate species densities and temperatures in LTPs
  - Determined by collision data
- Which collision data is required?
  - **Electron impact collision cross section sets**
    - Electron energy distribution function, electron transport coefficients
    - Rate coefficients for gain and loss of species and energy during electron impact collisions



Data from: Phelps Database, www.lxcat.net, retrieved on April 10, 2021, S. A. Lawton and A. V. Phelps, *J. Chem. Phys*. **69** 1055 (1978)

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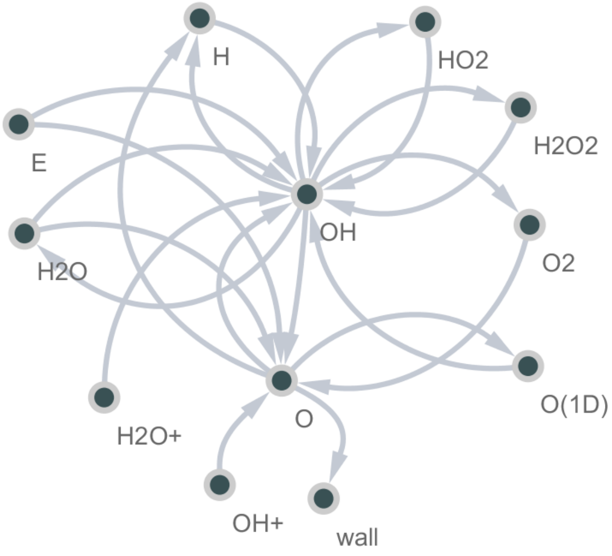
- Gain (G) and loss (L) terms required to simulate species densities and temperatures in LTPs
  - Determined by collision data
- Which collision data is required?
  - **Heavy (ion and neutral) particle collision cross sections / rate coefficients**
    - Gain and loss of species and energy during heavy particle collisions



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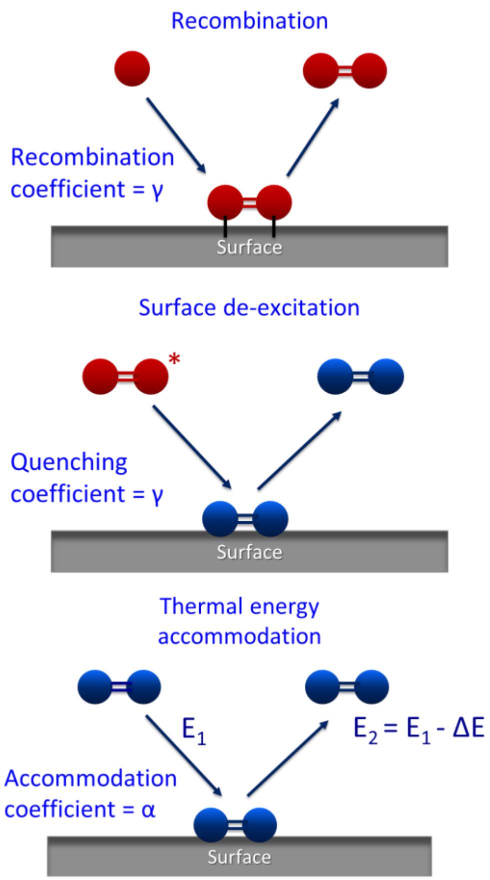

- Gain (G) and loss (L) terms required to simulate species densities and temperatures in LTPs
  - Determined by collision data
- Which collision data is required?
  - **Surface interaction probabilities**
    - Gain and loss of species and energy at surfaces

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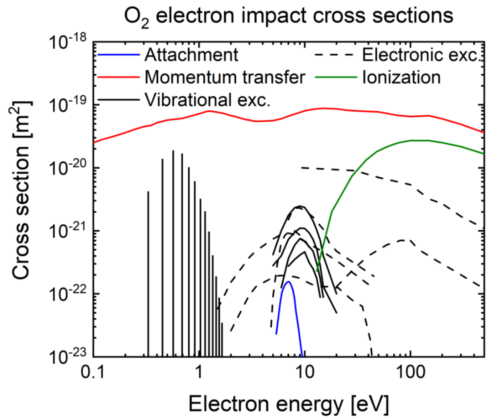
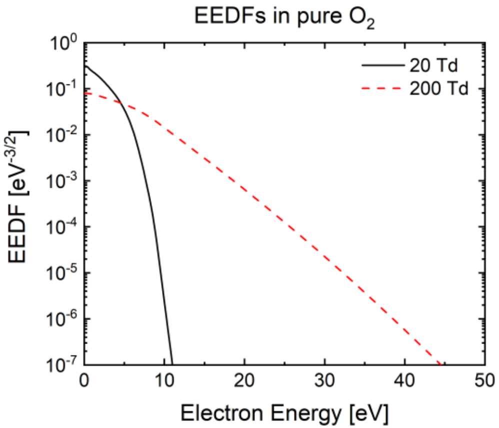
Electron energy distribution functions

- Typically non-Maxwellian
- Various approaches to calculate - simplified solutions of Boltzmann equation or Monte Carlo methods commonly used
- Solution from two-term approximation of Boltzmann equation (using Bolsig+ [2]) shown here.
  - Inputs:
    - Reduced electric field (E/N)
    - Electron impact cross section set
- Before use in plasma simulations, consistency of cross section set with experimental observations should be verified

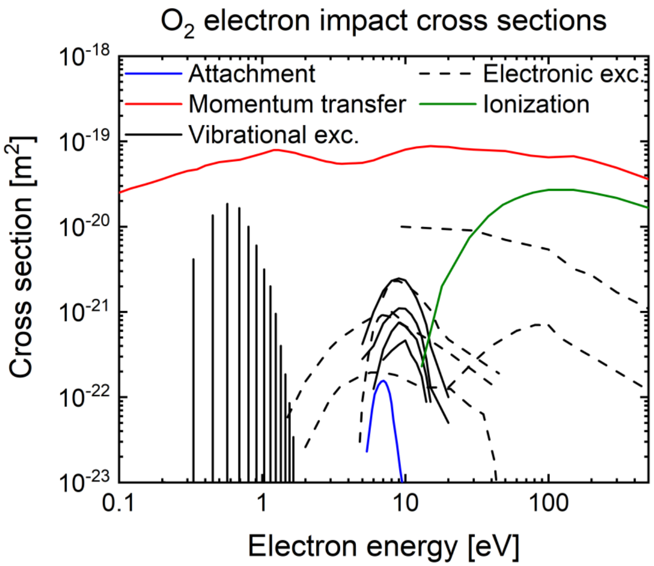




[1] **Cross sections** used in calculations from: Phelps Database, www.lxcat.net, retrieved on April 10, 2021, S. A. Lawton and A. V. Phelps, *J. Chem. Phys*. **69** 1055 (1978)
[2] **Calculations** carried out using Bolsig+: G. Hagelaar and L. Pitchford, *Plasma Sources Sci. Technol*. **14**, 722 (2005)

Cross section sets

- Cross section set from Phelps database for O_2 used as an example
- Derived from various cross section measurements with a number of assumptions
  - Certain cross sections typically used directly from original sources
    - Ionization, dissociative attachment, momentum transfer
  - Excitation cross sections not always used directly
    - Insights from different experiments used
  - **Goal**: cross section set should be consistent with experimentally measured electron transport coefficients



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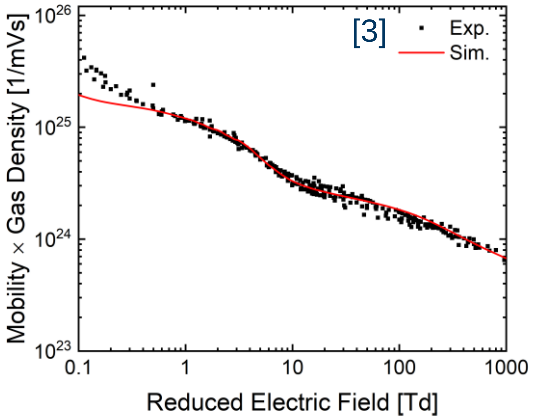
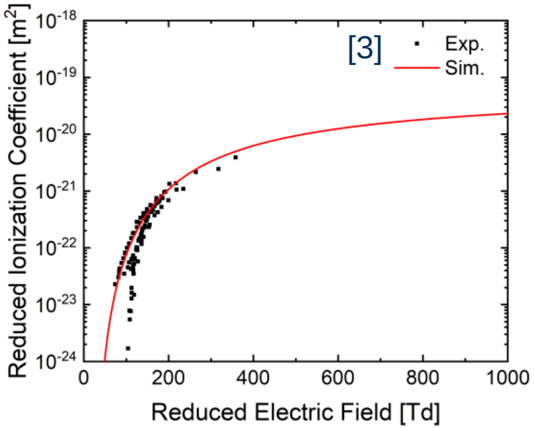
Transport / swarm parameters

- **Accuracy of cross section sets:**
  - Comparison between calculated and measured electron transport / swarm data e.g. electron mobility, ionization coefficient
  - ➢ Phelps cross section set is suitable for calculating electron transport properties (unsurprising!)
- **Some remarks on cross section sets:**
  - Not all application-relevant molecules have complete cross section sets available
  - Multiple combinations of cross sections can achieve agreement with swarm data
    - Individual cross sections within set may not be accurate





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[3] **Experimental data** from: J. Dutton, *J. Phys. Chem. Ref. Data*, **4**, 577, (1975) retrieved from lxcat.net on April 10, 2021

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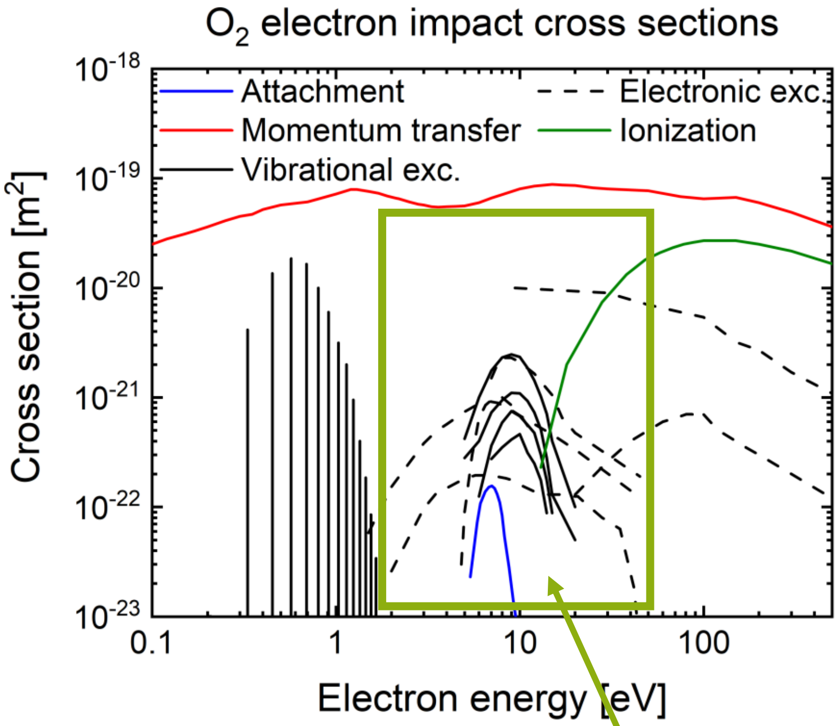
Electron impact rate coefficients

- For EEDF and transport coefficients, net energy loss is sufficient – can be achieved even if individual cross sections are not correct
- For species source terms (rate coefficients), cross sections for *specific processes* are required

Process	Data availability
$e + O_2 \rightarrow e + e + O_2^+$	☺
$e + O_2 \rightarrow O + O^-$	☺
$e + O_2 \rightarrow e + O_2(^1\Delta \text{ etc.})$	😐
$e + O_2 \rightarrow e + O + O$	☹



Often difficult to relate to specific excitation / dissociation processes

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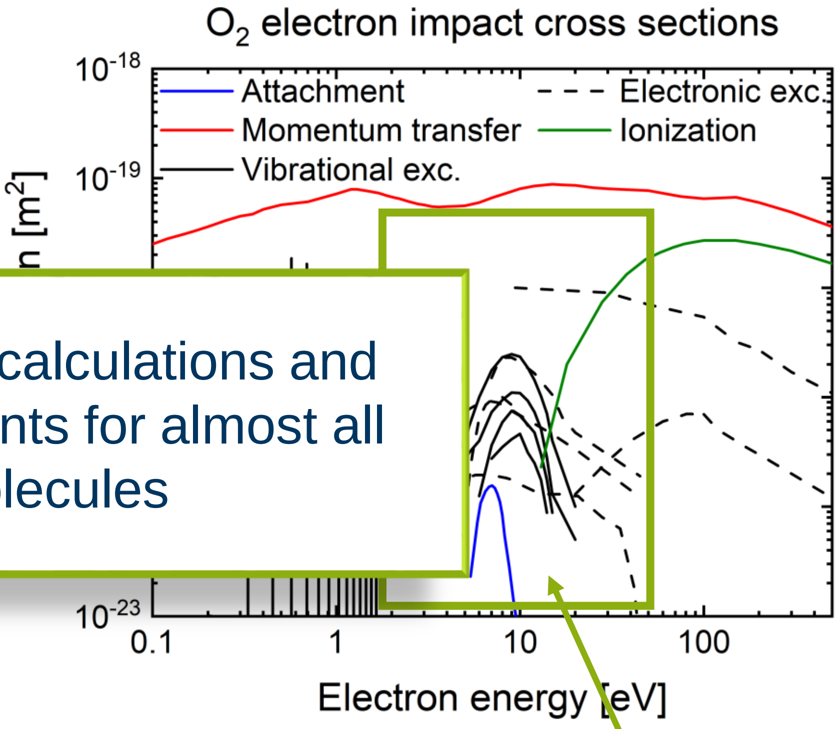
P	
e + O_2 –	
e + O_2 → O + O^-	☺
e + O_2 → e + O_2($^1\Delta$ etc.)	😐
e + O_2 → e + O + O	☹

Need for new theoretical calculations and experimental measurements for almost all LTP-relevant molecules



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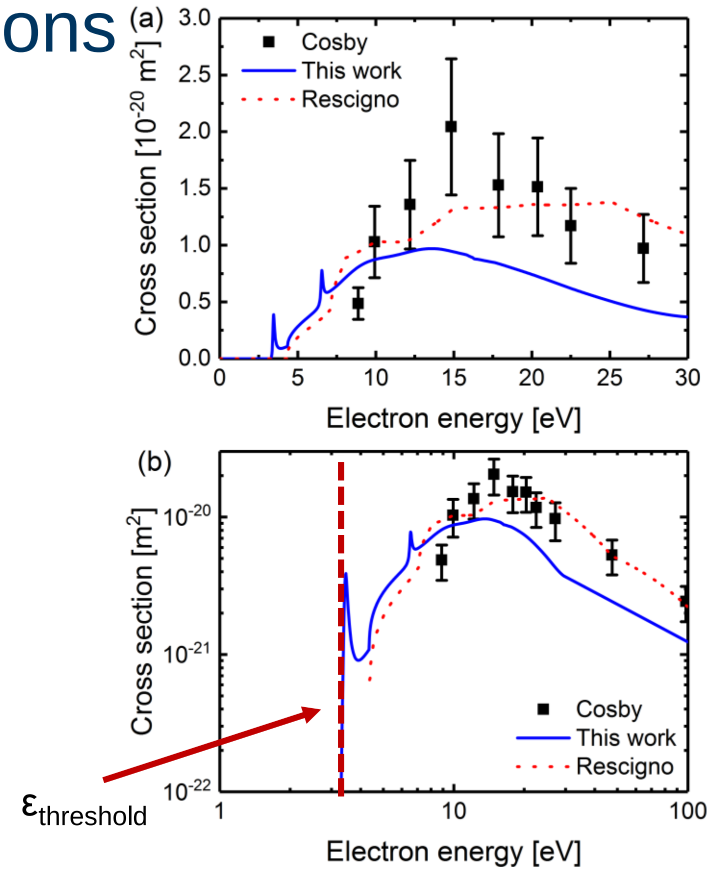
Dissociation cross section calculations

- Illustrating the importance of high resolution cross sections close to the energy threshold
- Chlorine is an essential molecule for plasma processing
  - Cl atoms used in plasma etching
  - Minimum electron energy of ≈ 3.3 eV required for Cl_2 dissociation
  - Limited data available particularly in the threshold region
- New calculations carried out to provide cross section close to threshold (Hamilton *et al*)



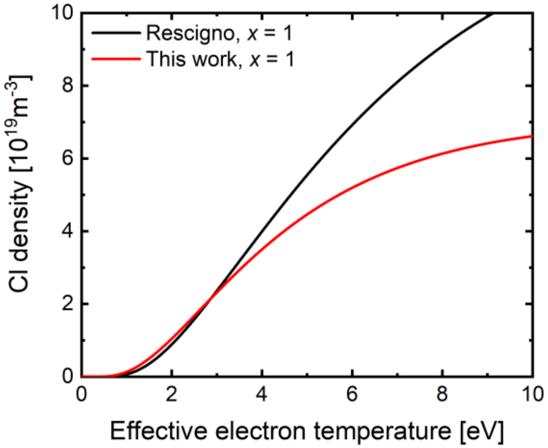
Figures reproduced from J. R. Hamilton *et al Calculated electron impact dissociation cross sections for molecular chlorine (Cl_2), Plasma Sources Sci. Technol*. **27** 095008 (2018) https://doi.org/10.1088/1361-6595/aada32 under CC BY 3.0
“Rescigno” data: T. Rescigno *Phys. Rev. A*, **50**, 1382 (1994)
“Cosby” data: P.C. Cosby H. and Helm 1992 Dissociation rates of diatomic molecules Technical Report WL-TR-93-2004 Aero Propulsion and Power Directorate, Wright Laboratory

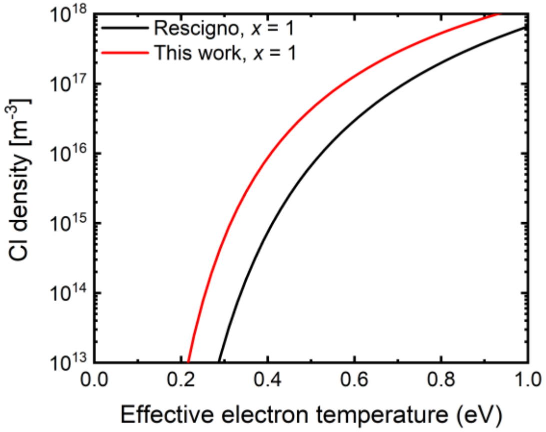
Simple model of Cl density

- Estimate Cl density accounting for gains due to dissociation and wall losses

$$n_{Cl} \approx \frac{2n_e n_{Cl2} k_{diss}}{k_{wall}}$$

- Assume typical values of low pressure industrial plasma reactor (e.g. inductively coupled plasma):
  - Pressure – 1 Pa
  - $n_e = 1 \times 10^{16}\ m^{-3}$
  - Cylindrical reactor: r = 10 cm, h = 5 cm
  - Surface recombination coefficient = 0.05





"Rescigno" cross section data used for calculations from: T. Rescigno *Phys. Rev. A*, **50**, 1382 (1994)
"This work" cross section data used for calculations from: J. R. Hamilton *et al Plasma Sources Sci. Technol*. **27** 095008 (2018)

Summary

Green = most important data known and accurate
Yellow = moderate amounts of important data still missing / more accurate data needed
Red = large amounts of important data still missing

Application	Typical feed gases used	Typical active species
Material processing	Ar, He, O_2, N_2, H_2, Cl_2, HBr, CF_4, SF_6 etc.	Radicals e.g. O, Cl, F Positive ions
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Agriculture	O_2, N_2, H_2O	Reactive oxygen and nitrogen species

- Needs:
  - Complete cross section sets where these are not available
  - Vibrational and electronic excitation (and dissociation cross sections)
  - Collisions between excited states, and collisions of excited states with surfaces

- General remarks:
  - LTP community always in need of new data for new applications using different molecules
  - Ongoing work in the area is enabling plasma simulations to be carried out with new levels of detail

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Institute for Electrical Engineering and Plasma Technology

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