The electron scattering database - Is it fit for purpose?

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Electron interactions pervade many areas of science and technology
Atmospheric physics and planetary atmospheres
Astrochemistry: Formation of molecules in Space
Semiconductor plasmas
Lighting industry
Radiation damage of DNA, cellular material and materials
Nanotechnology and surface engineering
Plasma modelling and database assessment
Thus to understand and model these processes you need cross sections....... Which requires a ‘database’
Data providers
* theory
* experiment

Data users in various application fields
* fusion science
* astrophysics
* industrial plasmas
* environmental physics
* medical (radiotherapy)

Data centers
data compilation
data evaluation (important but not easy)
dissemination and updating of database
retrievable online database
= easy to access, use, find data

International A&M data center network
IAEA, NIFS, A-PAN, KAERI, NIST, ORNL, GAPHIOR, VAMDC

Side by H Tanaka,
So how good is the data base?
Electron –atom scattering database

- Good database for electron scattering from the rare gases
- Data for electron scattering from light atoms (metals Na, Ca, Li) really quite good
- Data for electron scattering from some heavier atoms (e.g. Hg)
Electron – atom scattering database

- Data assimilated by mixture of experiments
  - Including coincidence \((e,2e)\) \((e,hv)\)
    experiments that characterise the scattering parameters
  - Such experiments benchmark theory
  - Eg R-matrix (K Bartschatt)
Elastic scattering and differential cross sections
Elastic Scattering - rare gases

Cho, McEachran, Tanaka, Buckman
JPB 37 4639 (2004)
Electron impact ionization

• Semi-empirical calculations (e.g. those of Deutsch-Maerk and Binary Encounter (BE) Kim) provide good estimates of the cross sections.

Thus calculations now used to populate databases and provide data for users e.g. for lighting industry.
Data needs for lighting

• Major sources are principally fluorescent lamps and metal halide discharge lamps
• **Rare earth metals** are commonly used in metal halide lamps to provide a white light spectrum similar to that of natural light.
• Three elements of interest are thulium, holmium and dysprosium.
Electron –molecule interactions

• (VERY) poor c.f. atoms
• Difficulty is complexity of molecular targets
• New scattering processes – dissociation – drives chemistry in many media (plasma chemistry)
Electron–molecule interactions

Total cross sections;
Experiments accurate to some 5%
(if we allow for forward scattering)
Lowest energies few meV!

Calculations using semi-empirical
(independent atom approximation) good
above 100 eV
Quantemol code for elastic low energy
Total cross sections for electron scattering

\[ I = I_0 \exp(-\sigma nl) \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃I</td>
<td>1.62</td>
</tr>
<tr>
<td>CH₃Br</td>
<td>1.81</td>
</tr>
<tr>
<td>CH₃Cl</td>
<td>1.87</td>
</tr>
<tr>
<td>CH₃F</td>
<td>1.85</td>
</tr>
</tbody>
</table>

- Plot of total cross section vs. electron energy for CH₃I, CH₃Br, CH₃Cl, and CH₃F.
- Equation I = I₀ exp(-σnl) is shown.
Electron–molecule interactions

Elastic cross sections;
Experiments accurate to some 10% - some cross sections make good standards
Angular range – can now measure whole angular range 0 to 180 using magnetic angle changer (Cho et al)

Can derive momentum transfer cross section data
- required for plasma studies
Elastic scattering - H₂O

Cho, Park, Tanaka, Buckman
JPB 37 625 (2004)
Electron – molecule interactions

Inelastic cross sections;

• Vibrational (correct for resolution and deconvolution)
• Excitation – very poor despite importance
• Allow for analyzer transmission effects
• Incorporation of rotational excitation in data…
Vibrational excitation

Energy loss spectra

![Graph showing vibrational modes in THF at 10 eV, 110° with CH₂, CH₂ bend, CH₂ twist + wag, C-C stretch, and CH₂ rock peaks indicated.](image)

Counts (×10³)

Energy loss (eV)
Vibrational excitation - HCOOH
Electron –molecule interactions

Excitation; Still a lot to be done but
Better expt data sets appearing from EELS

Theory – improving R matrix Schwinger etc
semi –empirical Kim (BEf)
Electron –molecule interactions

Ionisation;

Better data sets

(cf Theory – Kim (BE) and Deutsch Maerk)

Older experiments (<1980) contain some kinetic effects in the dissociative ionisation products.
At low energies electrons can do surprising things!

- They can ‘stick’ to the molecule
- To form a negative ion or ‘resonance’
- But only for a very short period of time (10^{-14} s)

- Then the electron detaches
- Leaving molecule excited or not (elastic scattering)
- But this process can also lead to the dissociation of the molecule

This is the process of **Dissociative Electron Attachment (DEA)**
Bond Selectivity using Electrons

Process of Dissociative Electron Attachment
Dissociative electron attachment therefore provides a method for breaking up molecules at low energies. Energies lower than the chemical bond energy!! Hence electrons can initiate chemistry.
Electron Induced chemistry

• Electrons used to ‘tune’ the products of a reaction

• Through selective bond dissociation different energy different pathways
Selective C-Cl bond cleavage at 0 eV

Selective C-F bond cleavage at 3.2 eV

Illenberger et al Berlin
Nucleophilic Displacement ($S_{N2}$) Reaction

e.g.: $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$
\[ e^- + CH_3Cl \rightarrow CH_3 + Cl^- \]

\[ \sigma < 10^{-23} \text{ cm}^2 \text{ (unmeasurably small)} \]
$S_N^2$ Reaction

Illenberger et al Berlin
$e^- \rightarrow CH_3Cl \rightarrow no \ ions$

$e^- \rightarrow (NF_3)_n \cdot (CH_3Cl)_m \rightarrow F^- \rightarrow Cl^-$
• Chemical **surface transformations** using electron induced reactions/

• DEA produces products that subsequently react on the surface

• E.g. Irradiate film of NF$_3$ and CH$_3$Cl
  • Form CH$_3$F
Negative ions in plasmas

• Many commercial plasma/etchant gases are electronegative

• E.g. The fluorocarbons, chlorine and oxygen (H₂ in fusion plasmas)

• Negative ions may be major negative charge carrier (> ‘free‘ electron flux) e.g. in CF₄ and oxygen plasmas 10x electron
Dissociative Electron Attachment

Question as to how establish cross section – RESOLUTION DEPENDENT

Kinetic effects in products

Zero energy peaks!

Few/no experimental standards to calibrate /standards
Innsbruck database

Theoretical calculations hard but developing…
DEA to $H_2$

- Long history

\[
H_2 \left( X^{1 \Sigma_g^+} + v \right) + e \rightarrow H_2^- \left( X^{2 \Sigma_u^+} \right) \rightarrow H^- + H
\]

- Applies to hydrogen isotopes HD and $D_2$. 
DEA to $\text{H}_2$

![Graph showing cross section versus electron energy for DEA to $\text{H}_2$. The graph includes data from Schulz 1959 and Rapp 1965, with distinct markers for each dataset.](image-url)
DEA to H$_2$

- So absolute cross sections do not agree

- Decided to remeasure using new apparatus

Use velocity map imaging to get angular distributions
Our results solid line Circles are Schulz (1959), triangles and squares – Rapp et al. (1965)
Need to correct for energy resolution
Compare with theory (Horacek et al., Prague)

**** Need to scale by 0.8 to fit
Electron–molecule interactions

Dissociation into neutrals particularly radicals

Detections of ground state products – in its infancy

Still testing methodologies

No standard

Kinetic effects in products
Electron–molecule interactions

Dissociation to excited states
Fluorescence– lots of data but
Detector calibrations
Role of cascade
Kinetic energy – Doppler broadening
The REAL TEST
Summation of independent cross sections to get total cross section
Few data sets analysed like this, none recently!!!!!

TETRAFLUOROMETHANE (CF4): "BEAM" vs SWARM

A cross section set composed of the "best" critically evaluated beam measurements may be significantly different from swarm derived cross sections which reproduce v(drift), ionization coefficient, etc.


"Assembling" cross sections, though necessary, is not always sufficient.......
SUMMARY

- Electron scattering database is ‘good’ for atoms theory ‘reliable’
- Electron molecule scattering ‘patchy’
  - Ionisation and total cross sections good
  - Elastic ok & theory improving
  - Inelastic poor
SUMMARY

• DEA cross sections  expt method emerging, theory improving
• Dissociation to neutrals poor

• And far more molecules need to be studied than size of community allows.
Then what to do with all this data?

- **Difficulties**
- Newest is not always best.
- Yours is not always best.
- Need to compare with standards / search for systematic errors.
- Theory vs experiment

- Need to have and maintain database
Any database on electron-molecule interactions must fulfill several basic pre-requisites.

- It should be comprehensive with a full listing of experimental and, where applicable, theoretical results.
Any database on electron-molecule interactions must fulfill several basic pre-requisites.

• Any database should provide a critical review of the presented data.
Any database on electron-molecule interactions must fulfill several basic pre-requisites.

- Any database that aims to be adopted by an applied community should include a list of recommended values.
Database needs

• Develop database that community has ownership of (eMOL)
• To work like journal editorial board for data review and analysis
• Access is easy for posting data
• Discussion is easy!
• Provides up to date summary of data and recommendations
The EU funded database and e-infrastructure now being developed through SUP@VAMDC to link VAMDC to other worldwide databases.
SUP@VAMDC

• Next talk ..................