Plasma physics

2023 winter s. 2/1 , C+Ex

prof. Juraj Glosík, doc. Radek Plašil

- Langevin theory of ion – molecule collisions
- Elementary processes in plasma: excitation, ionization

Chemical kinetics

$A + B \rightarrow Products$

number of collisions $\cdots\ \sigma_{AB}\, I_A\, n_B = \sigma_{AB}\, v_{AB}\, n_A\, n_B$

Energy distribution of reactants f

$$\frac{d[A]}{dt} = -\langle \sigma_{AB}\, v \rangle_f\, n_A\, n_B$$

$$\langle \sigma_{AB}\, v \rangle_f = \int \sigma_{AB}(v)\, v\, f\, dv$$

$$\frac{d[A]}{dt} = -k\, n_A\, n_B$$

$A \xrightarrow{k_1} Products$ $\quad k_1$: s^{-1}

$A + B \xrightarrow{k_2} Products$ $\quad k_2$: $cm^3 s^{-1}$

$A + B + C \xrightarrow{k_3} Products$ $\quad k_3$: $cm^6 s^{-1}$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

Rigid Spheres

$$\sigma_{RS} = \pi(r_A + r_B)^2$$

$$\langle \sigma_{AB}\, v_{AB} \rangle = \langle \pi(r_A + r_B)^2 \cdot v_{AB} \rangle = \pi b^2 \sqrt{\frac{8 k_B T}{\pi \mu}} = b^2 \sqrt{\frac{8 \pi k_B T}{\mu}}$$

Langevin collisional model

$$A^+ + B \rightarrow \textit{Products}$$

$$\alpha = \frac{|\vec{p}|}{|\vec{E}|} \quad \text{polarizability}$$

$$U = -\frac{1}{2}\frac{\alpha q^2}{r^4} + \frac{L^2}{2\mu r^2}$$

$$L = \mu v b_c \quad \text{angular momentum}$$

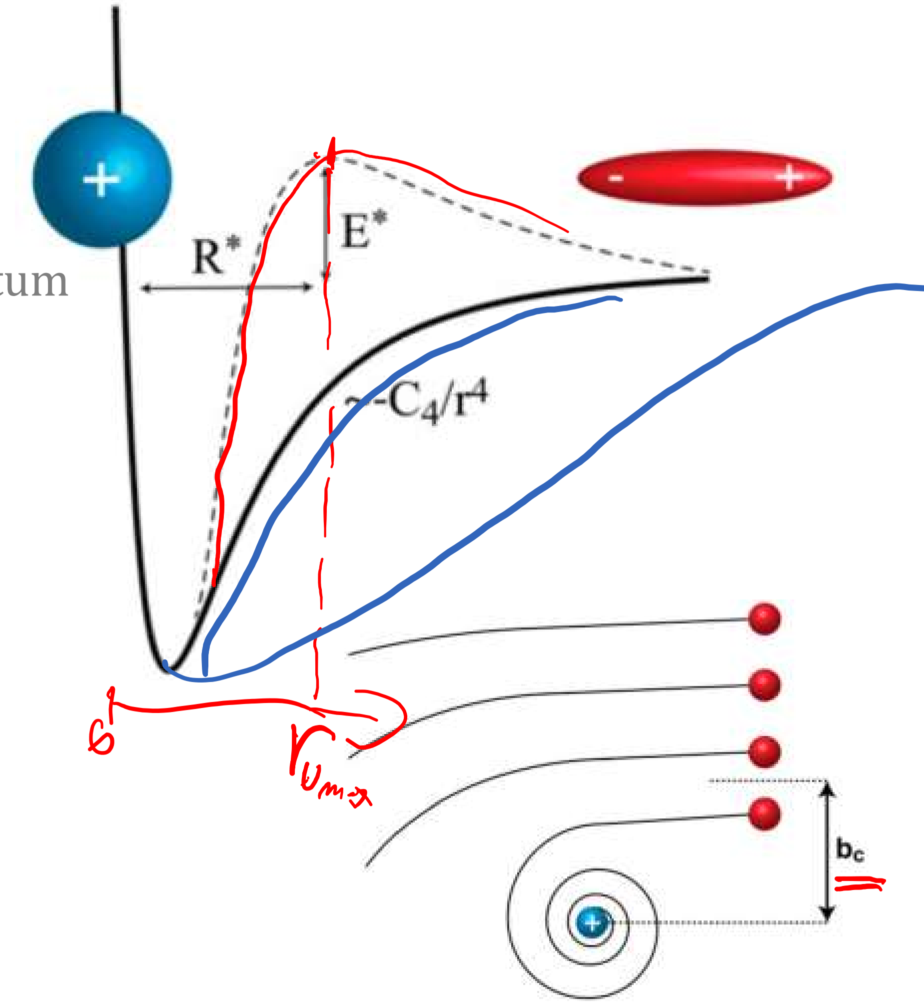
$$E_k = \tfrac{1}{2}\mu v^2$$

$$U = -\frac{1}{2}\frac{\alpha q^2}{r^4} + \frac{\mu^2 v^2 b_c^2}{2\mu r^2} = -\frac{1}{2}\frac{\alpha q^2}{r^4} + E_k\frac{b_c^2}{r^2}$$

U_{max}

$$\frac{dU}{dr} = 0 = +\frac{4}{2}\frac{\alpha q^2}{r^5} - 2E_k\frac{b_c^2}{r^3} \quad \Rightarrow r_{U_{max}} = +\frac{q}{b_c}\sqrt{\frac{\alpha}{E_k}}$$

$$U_{max} = -\frac{1}{2}\alpha q^2\frac{b_c^4 E_k^2}{q^4\alpha^2} + E_k b_c^2\frac{b_c^2 E_k}{q^2\alpha} = \frac{1}{2}\frac{b_c^4}{\alpha}\frac{E_k^2}{q^2}$$



Härter, A. and J. Hecker Denschlag, *Contemporary Physics* **55** (2014) 33.
doi:10.1080/00107514.2013.854618

Langevin collisional rate coefficient

$$U_{\max} = \frac{1}{2}\frac{b_c^4}{\alpha}\frac{E_k^2}{q^2}$$

$$U_{\max} \leftrightarrow E_k \qquad b_c = \sqrt[4]{\frac{2\alpha q^2}{E_k}}$$

$$\sigma_L = \pi\, b_c^2 = \pi q \sqrt{\frac{2\alpha}{E_k}}$$

$$k_L = \int v\, \sigma_L\, f(v) \mathrm{d}v = \int v \pi q \sqrt{\frac{2\alpha}{\frac{1}{2}\mu v^2}} f(v) \mathrm{d}v = 2\pi q \sqrt{\frac{\alpha}{\mu}} \int f(v) \mathrm{d}v$$

1

$$k_L = 2\pi q \sqrt{\frac{\alpha}{\mu}}$$

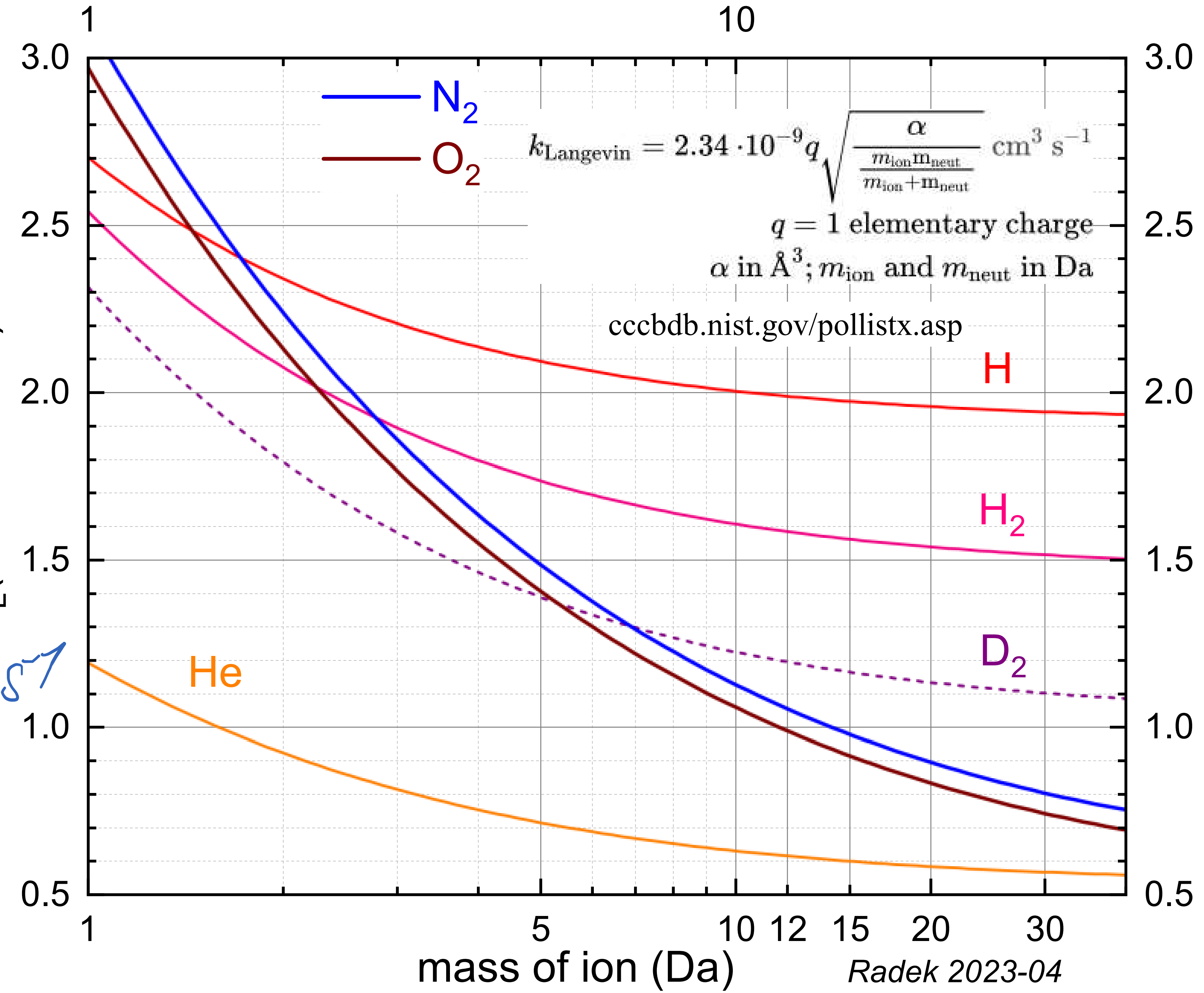
CGS

For once charged ions and molecules without a permanent dipole

$$k_L = 2.34 \cdot 10^{-9} \sqrt{\frac{\alpha(\text{Å}^3)}{\mu(\text{Da})}} \quad \text{cm}^3\text{s}^{-1}$$

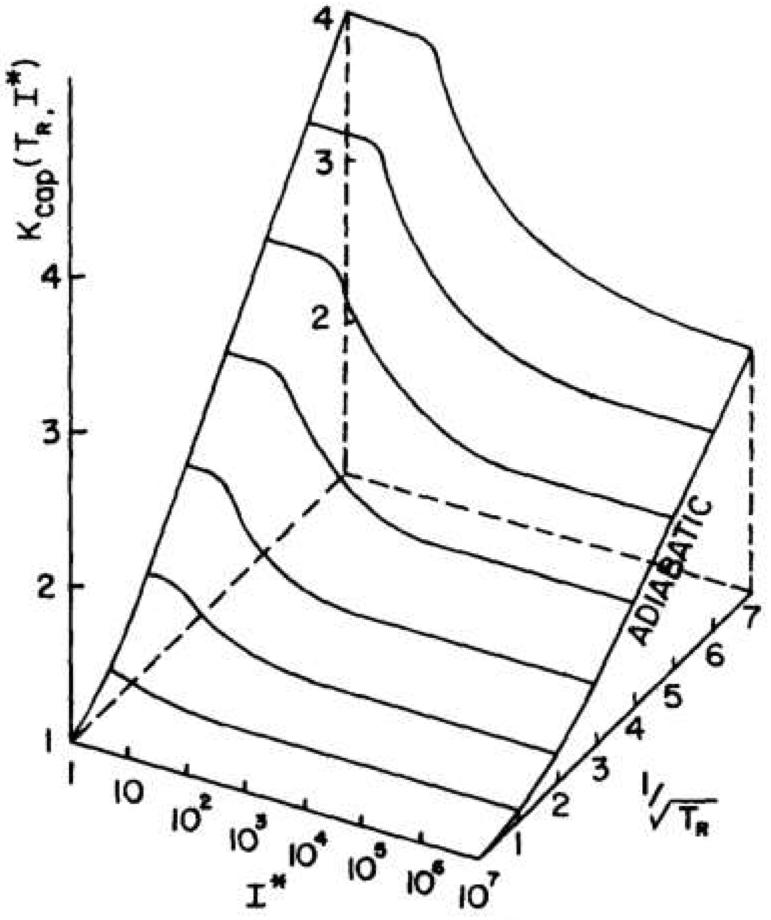
https://cccbdb.nist.gov/pollistx.asp

Langevin collisional rate coefficient



$10^{-9} \text{ cm}^3 \text{s}^{-1}$

Collisional rate coefficient – permanent dipole



$$K_{\mathrm{cap}}(T_{\mathrm{R}}, I^*) = \frac{k_{\mathrm{cap}}(T)}{k_{\mathrm{L}}}$$

$$T_{\mathrm{R}} = 2\alpha \frac{k_{\mathrm{B}} T}{\mu_{\mathrm{D}}^2}$$

$$I^* = \frac{\mu_{\mathrm{D}} I}{\alpha q \mu}$$

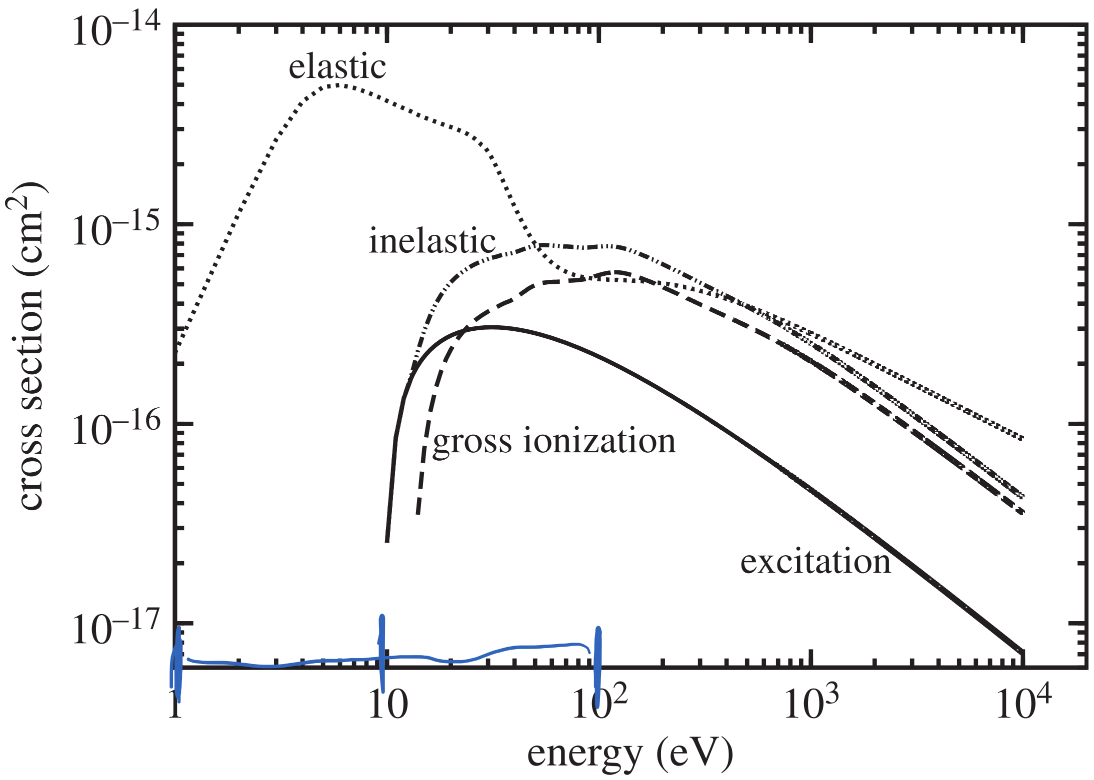
α Angle-averaged polarizability

μ_{D} Dipole moment

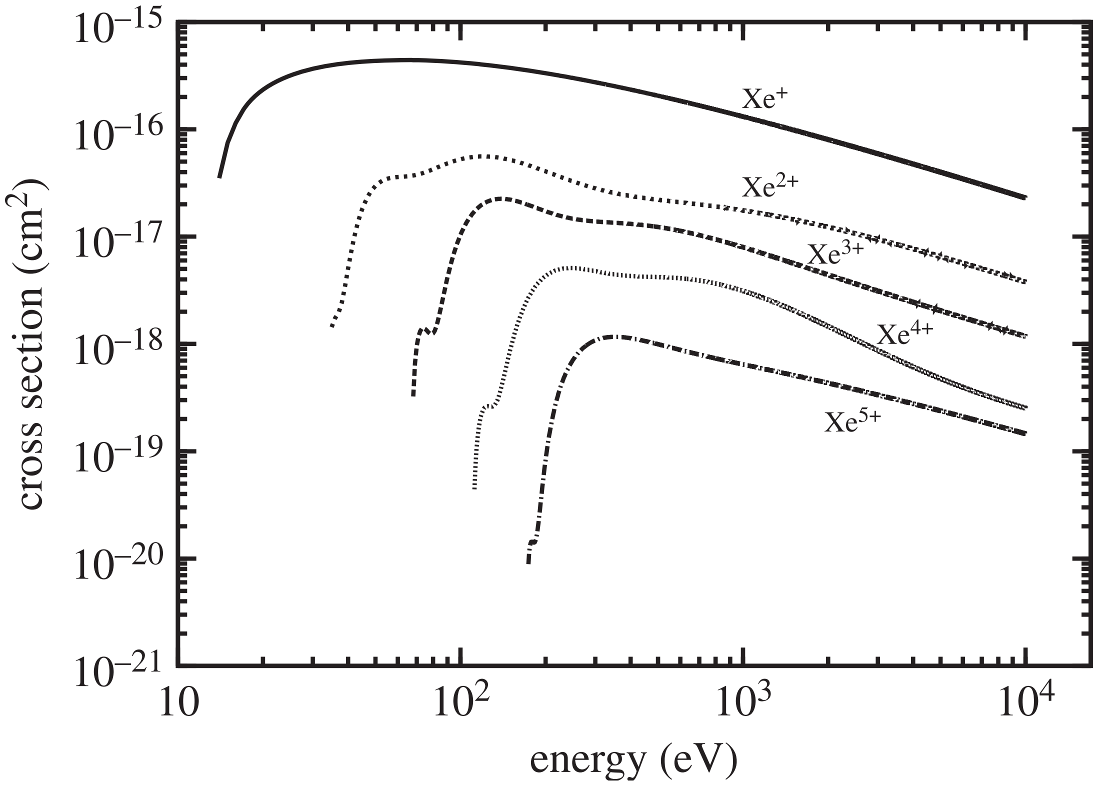
I Moment of inertia of the neutral

Parametrization of the ion-polar molecule collision rate constant by trajectory calculations
Su T., Chesnavich W. J. *J. Chem. Phys.* 76 (1982) 5183
doi: 10.1063/1.442828

Electron – Atom collisions



Electron impact cross sections for various elastic and inelastic processes of Xe.

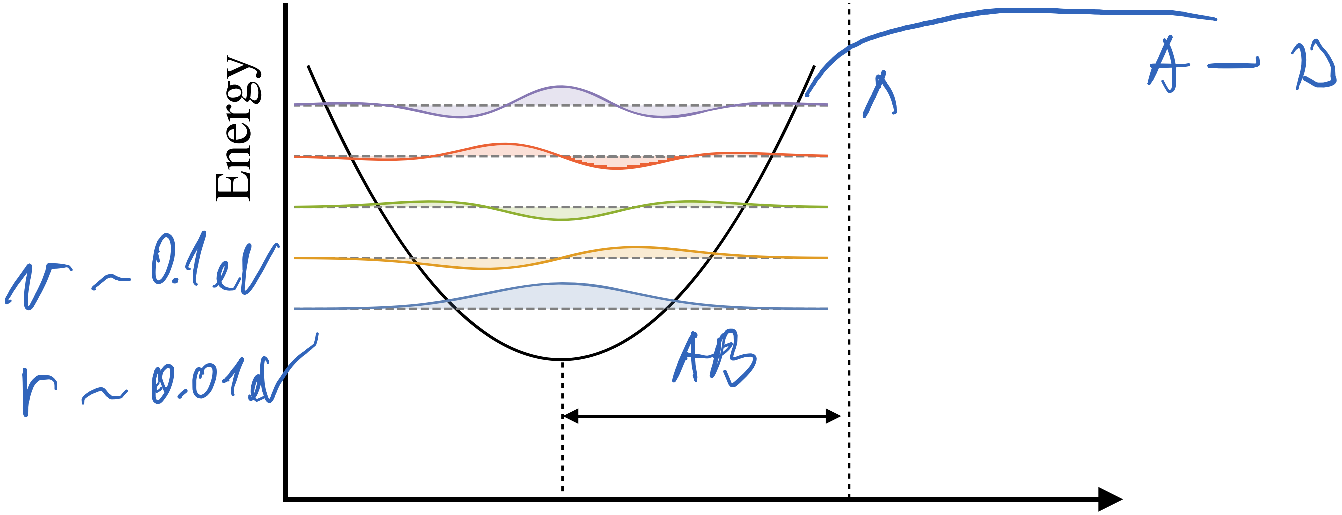


Electron impact ionization cross sections for Xe.

Mukundan V., Bhardwaj A. *Proc. R. Soc. A* 472 (2016) 20150727.
doi: 10.1098/rspa.2015.0727

Excitation collisions

- Photon
- Electron
- Molecule



Molecule A-B

Maguire H. et al. *Phys. Rev. Lett.* 123 (2019) 093601.
doi: 10.1103/PhysRevLett.123.093601

N_2 molecule – excitation by electron

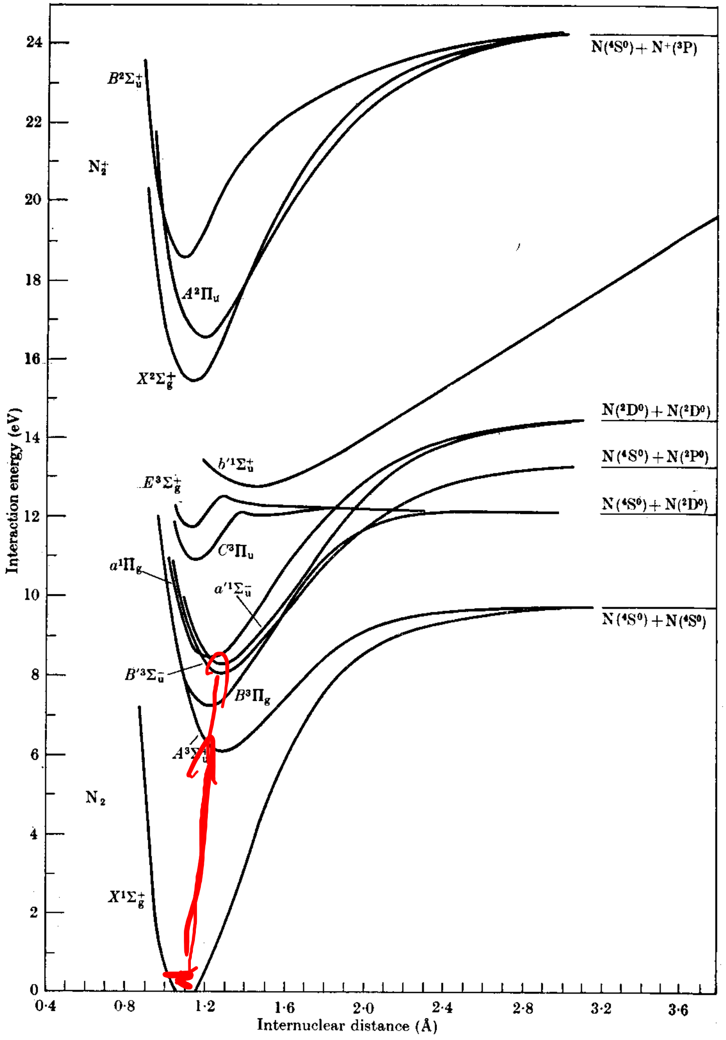


FIG. 13.46. Potential energy curves for some electronic states of N_2 and N_2^+.

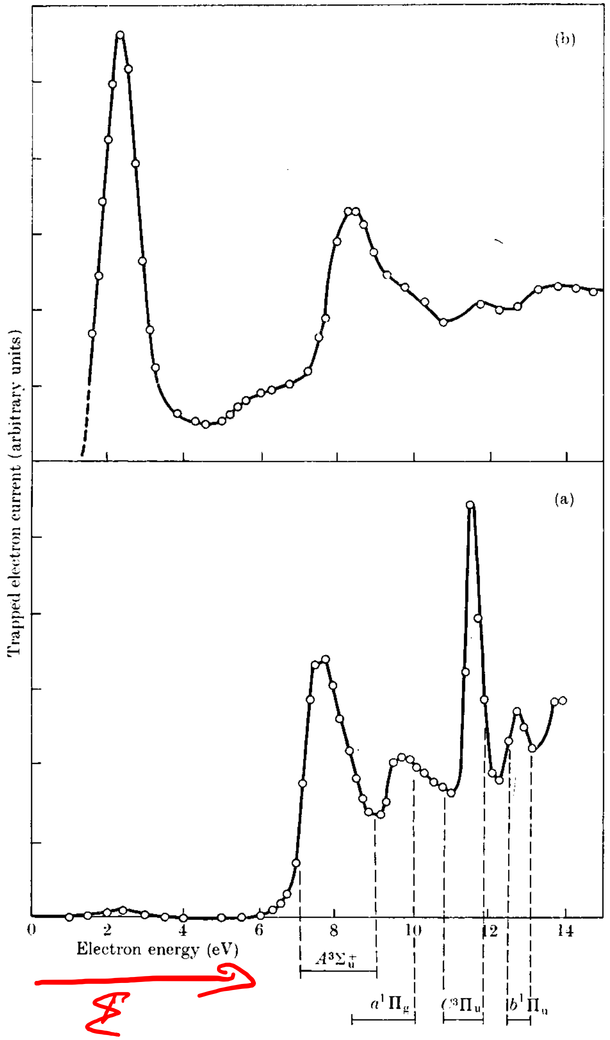
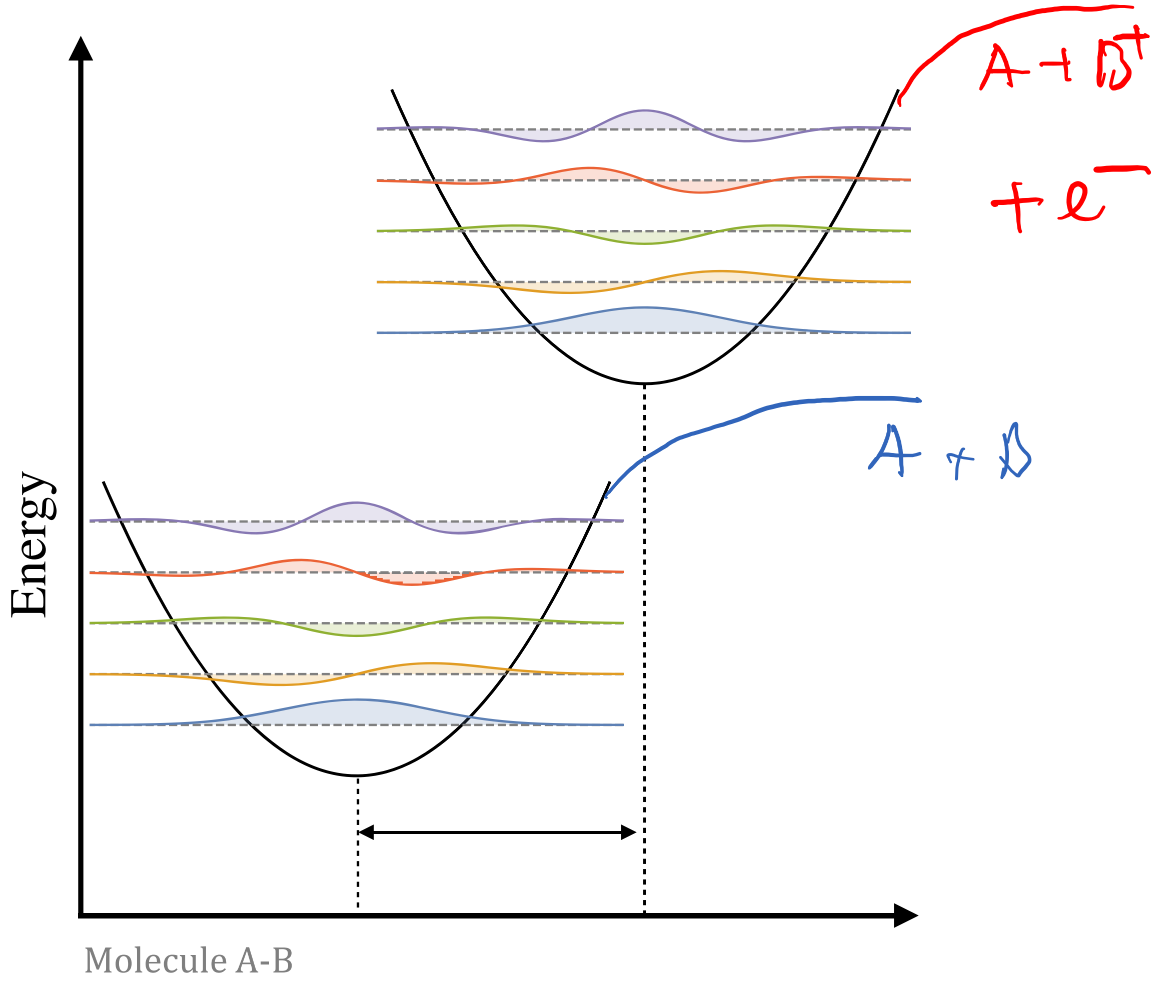


FIG. 13.47. Excitation spectrum of nitrogen obtained by Schulz using the trapped-electron method. (a) with well depth of 0·2 V. (b) with well depth of 0·8 V.

Ionization collisions

- Photon
- Electron
- Molecule



Maguire H. et al. *Phys. Rev. Lett.* 123 (2019) 093601.
doi: 10.1103/PhysRevLett.123.093601

Ionizations by electron impact

$$Ar + e^-(\varepsilon_0) \rightarrow Ar^+ + e^-(\varepsilon_1) + e^-(\varepsilon_2)$$

$$N_2 + e^-(\varepsilon_0) \rightarrow N_2^+(\varepsilon) + e^-(\varepsilon_1) + e^-(\varepsilon_2)$$
$$\rightarrow N^+(\varepsilon_1) + N(\varepsilon_2) + e^-(\varepsilon_3) + e^-(\varepsilon_4)$$

$$CH_4 + e^- \rightarrow CH_4^+ + e^- + e^-$$
$$\rightarrow CH_3^+ + H + e^- + e^-$$
$$\rightarrow CH_3^+ + H^- + e^-$$
$$\rightarrow CH_2^+ + H_2 + e^- + e^-$$
$$\rightarrow CH^+ + H + H_2 + e^- + e^-$$
$$\rightarrow CH^+ + H^- + H_2 + e^-$$
$$\rightarrow C^+ + H_2 + H_2 + e^- + e^-$$
$$\rightarrow C^{2+} + H_2 + H_2 + e^- + e^- + e^-$$

Ionizations near the threshold

$$\sigma(\varepsilon) = const\ (\varepsilon - \mathcal{E}_{\mathrm{Threshold}})^{\mu_{\mathrm{E}}/2 - 1/4}$$

$$\mu_{\mathrm{E}} = \frac{1}{2}\sqrt{\frac{100\,Z - 9}{4\,Z\ - 1}}$$

Z charge state of the final ion

$$\sigma(\varepsilon) = const\ (\varepsilon - \mathcal{E}_{\mathrm{Threshold}})^{1.127}$$

Single ionization of atoms

$$\sigma(\varepsilon) = const\ (\varepsilon - \mathcal{E}_{\mathrm{Threshold}})^{p}$$

Wannier exponent

Wannier G. H. *Phys. Rev.* 90 (1953) 817.
doi: 10.1103/PhysRev.90.817

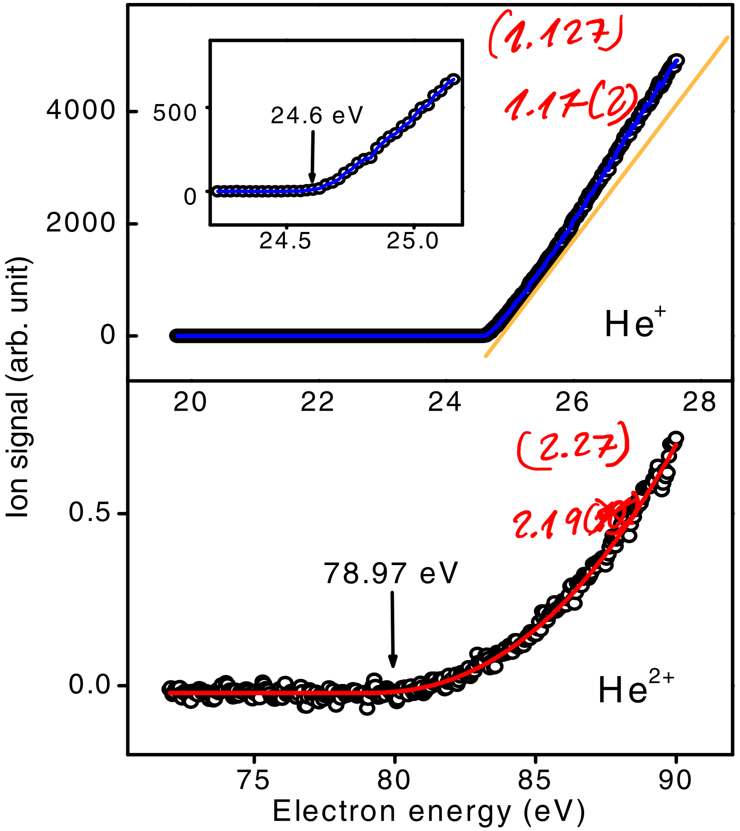
Multiple ionization

Different context

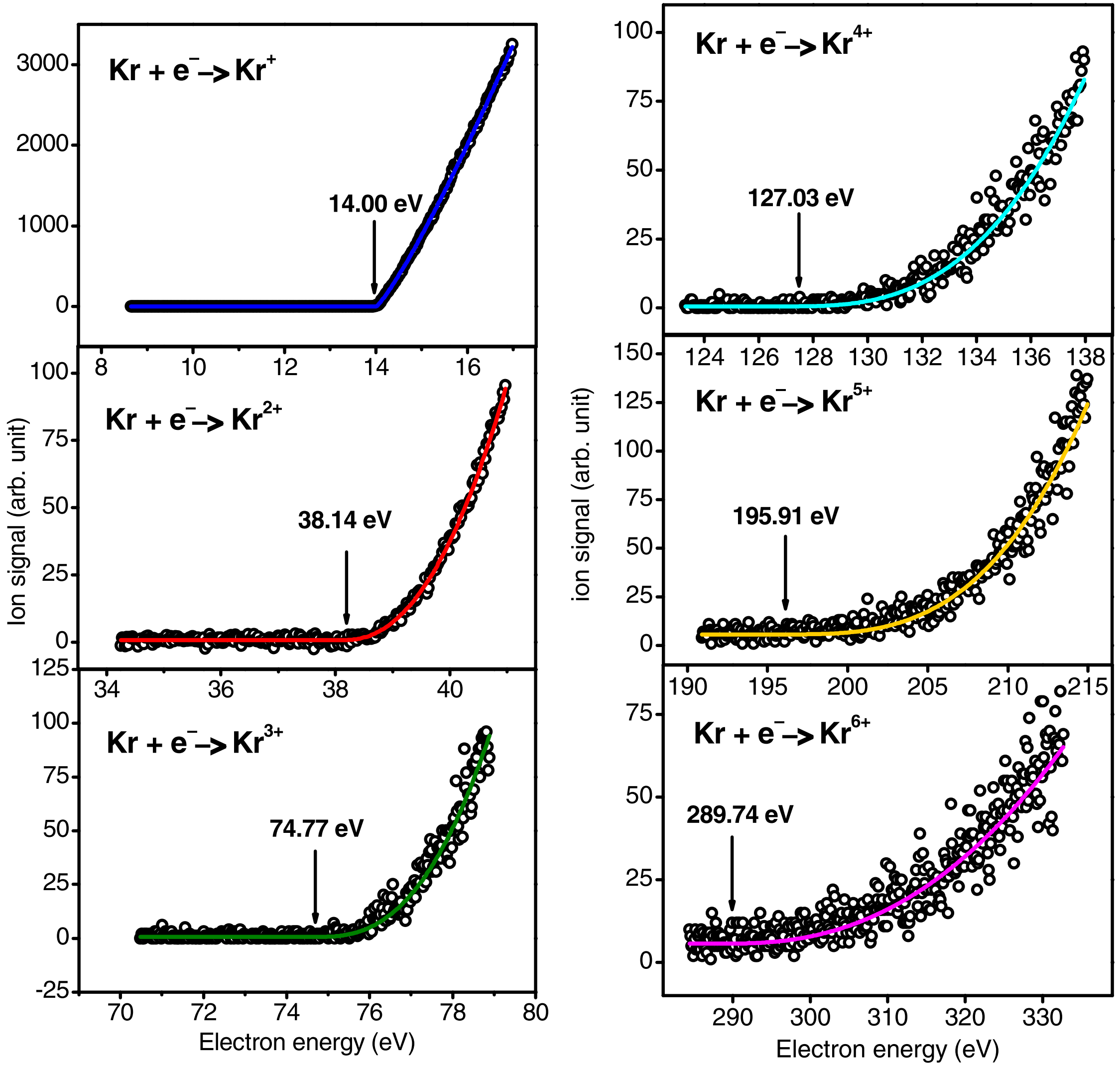
$$\sigma_{\text{Total}} = \sigma^{+} + \sigma^{2+} + \sigma^{3+} + \ \ldots$$

$$\sigma_{\text{gross}} = \sigma^{+} + 2\sigma^{2+} + 3\sigma^{3+} \ + \ \ldots$$

Wannier exponent



Ion signal as a function of electron energy for the formation of He^{n+}.

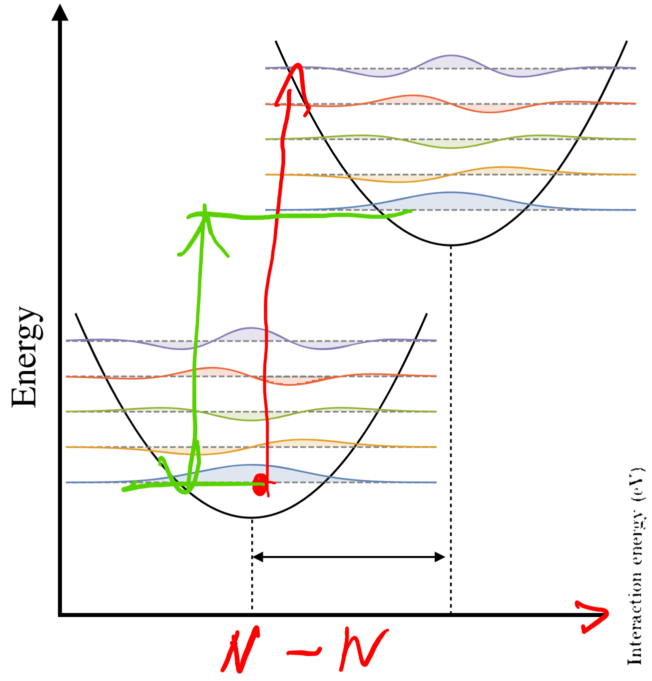


Ion signal as a function of electron energy for the formation of Kr^{n+} ions (n = 1–6) in the near-threshold region.

Denifl S. et al. *J. Phys. B: At. Mol. Opt. Phys.* 35 (2002) 4685. doi: 10.1088/0953-4075/35/22/310

Ionization details near threshold - molecules

$N_2 + e^- \rightarrow N_2(\Sigma) + e^- + e^-$



Comparison of observed and calculated energy separation of various vibrational levels of H_2^+

Energy separations (eV)						
Vibnl. levels	0–1	1–2	2–3	3–4	4–5	5–6
Calculated	0·269	0·254	0·238	0·223	0·208	0·192
Observed	0·272	0·263	0·233	0·237	0·21	0·20

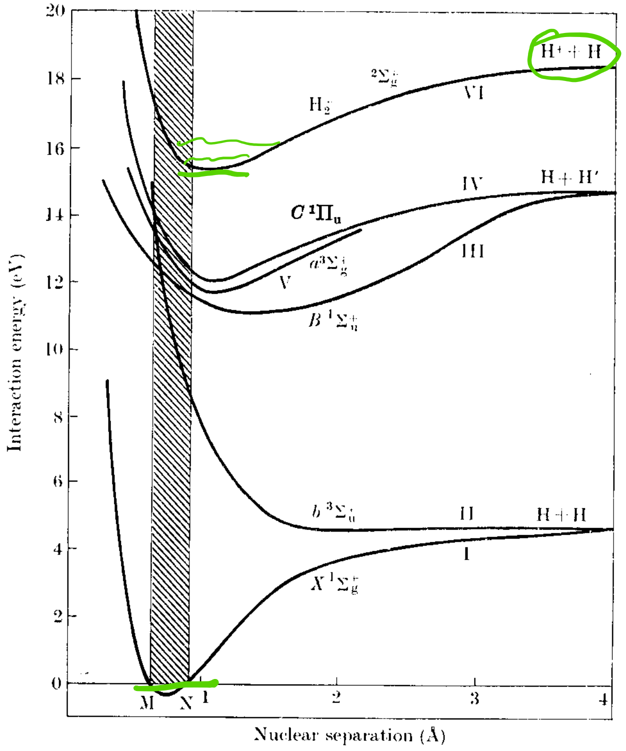


FIG. 13.1. Potential energy curves for electronic states of H_2 and H_2^+ lying within 20 eV of the ground state.

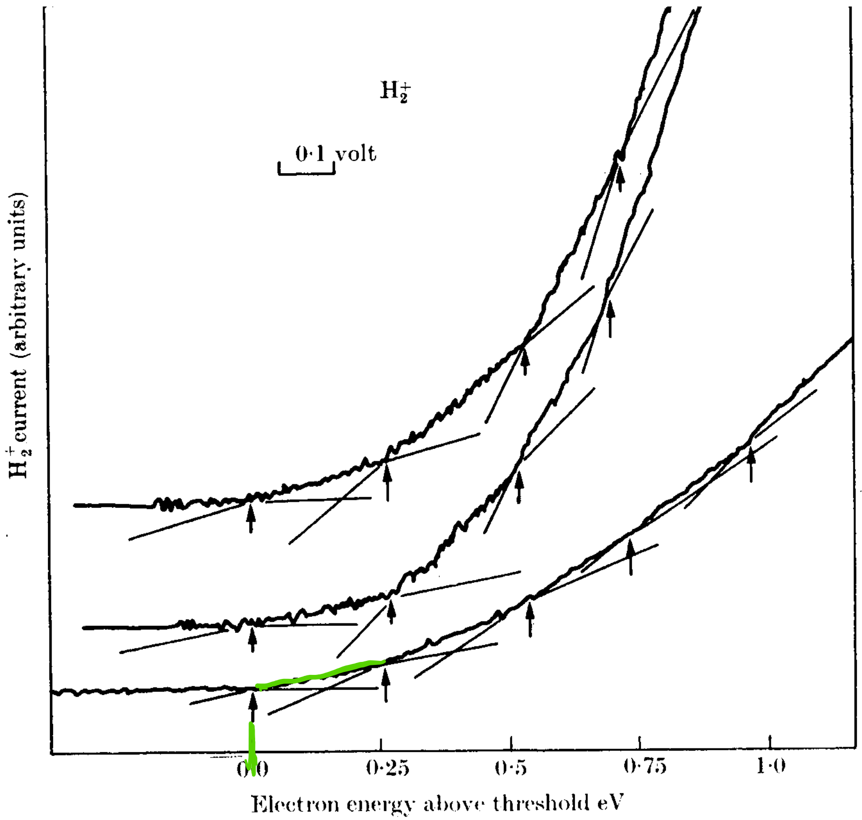


FIG. 13.19. Variation of the ionization cross-section of H_2 near the threshold as observed by Marmet and Kerwin.

Maguire H. et al. *Phys. Rev. Lett.* 123 (2019) 093601.
doi: 10.1103/PhysRevLett.123.093601

N_2 molecule – ionization

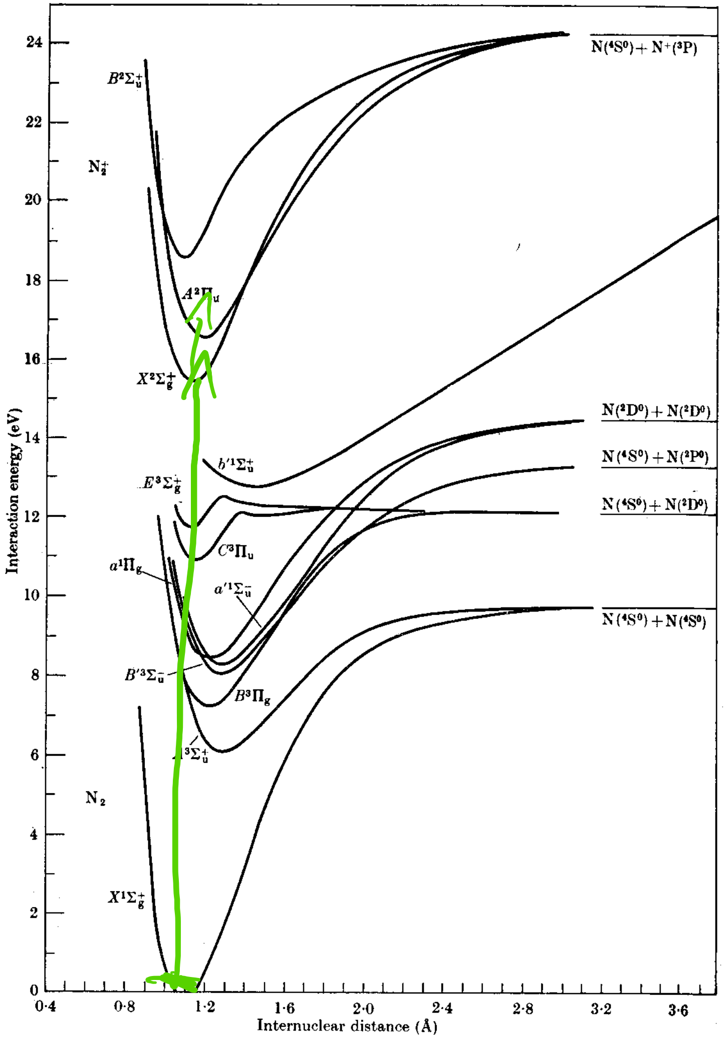


FIG. 13.46. Potential energy curves for some electronic states of N_2 and N_2^+.

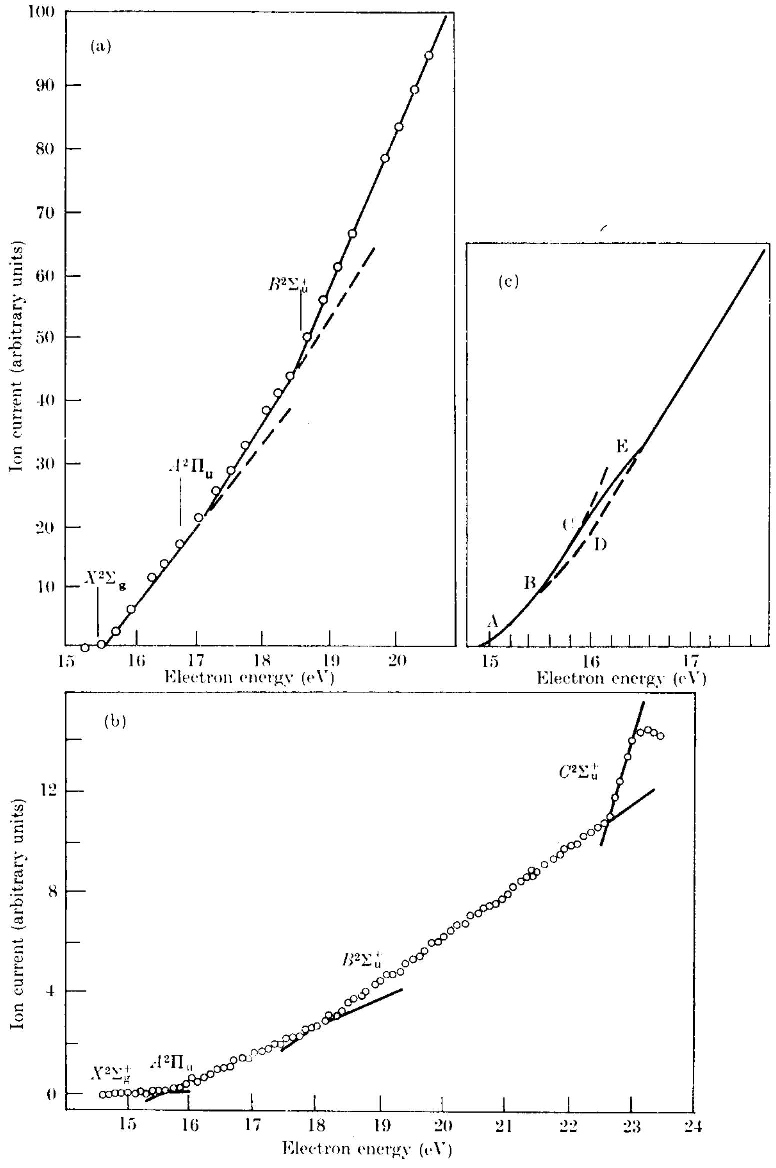


FIG. 13.58. Variation of the ionization cross-section of N_2 near the threshold as observed (a) by Fox and Hickam, (b) by Frost and McDowell, (c) by Clarke.

Ionization BEB theory

The Binary-Encounter-Bethe (BEB) model

electron – atom (molecule, ions)

$$\sigma_{\mathrm{BEB}} = \frac{S}{t+u+1}\left[\frac{\ln(t)}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln(t)}{t+1}\right]$$

$t = T/B$
$u = U/B$
$S = 4\pi a_0^2 N R^2/B^2$

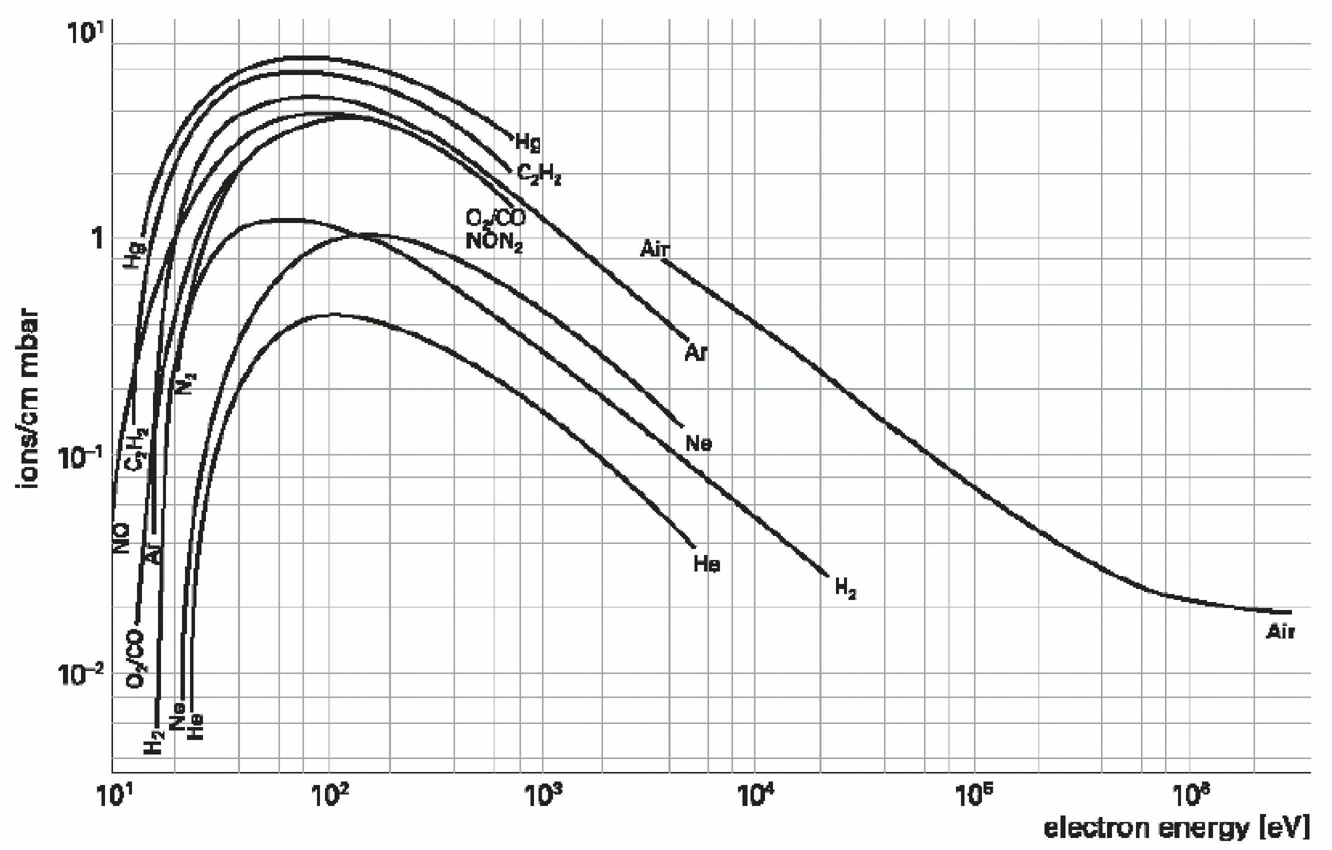
a_0 Bohr radius (= 0.5292 Å)
R Rydberg energy (= 13.6057 eV)

T incident electron energy
N electron occupation number
B binding energy
U average kinetic energy of the orbital

physics.nist.gov/ionxsec

Kim Y.-K., Rudd M. E. *Phys. Rev. A* 50 (1994) 3954. doi: 10.1103/PhysRevA.50.3954
Kim Y.-K et al. *J Res Natl Inst Stand Technol* 105 (2000) 285. doi: 10.6028/jres.105.032
http://physics.nist.gov/ionxsec

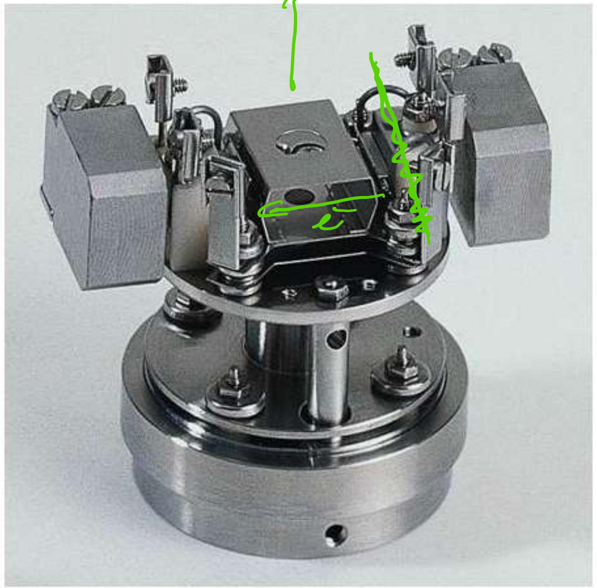
Ionization – Residual Gas Analysis (RGA)



Ionization by electron impact

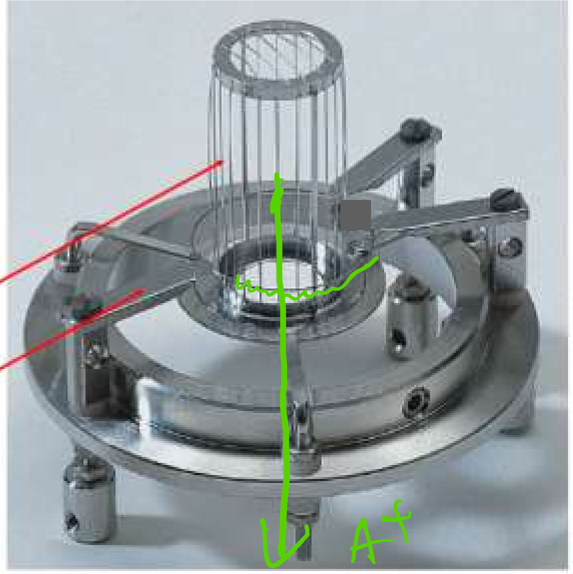
Cross Beam ion source
with magnets

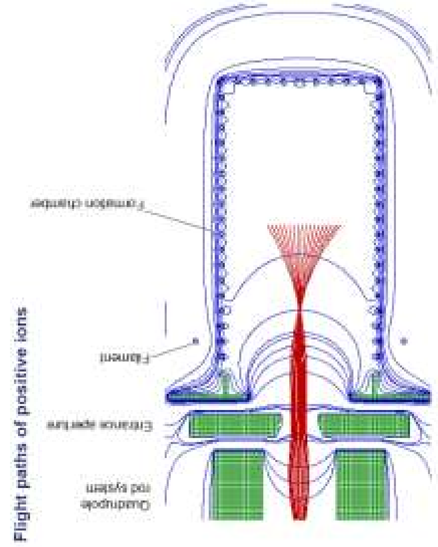
- Two filaments
- Easy to degas
- Good ion focussing
- Bakeable to 300°C



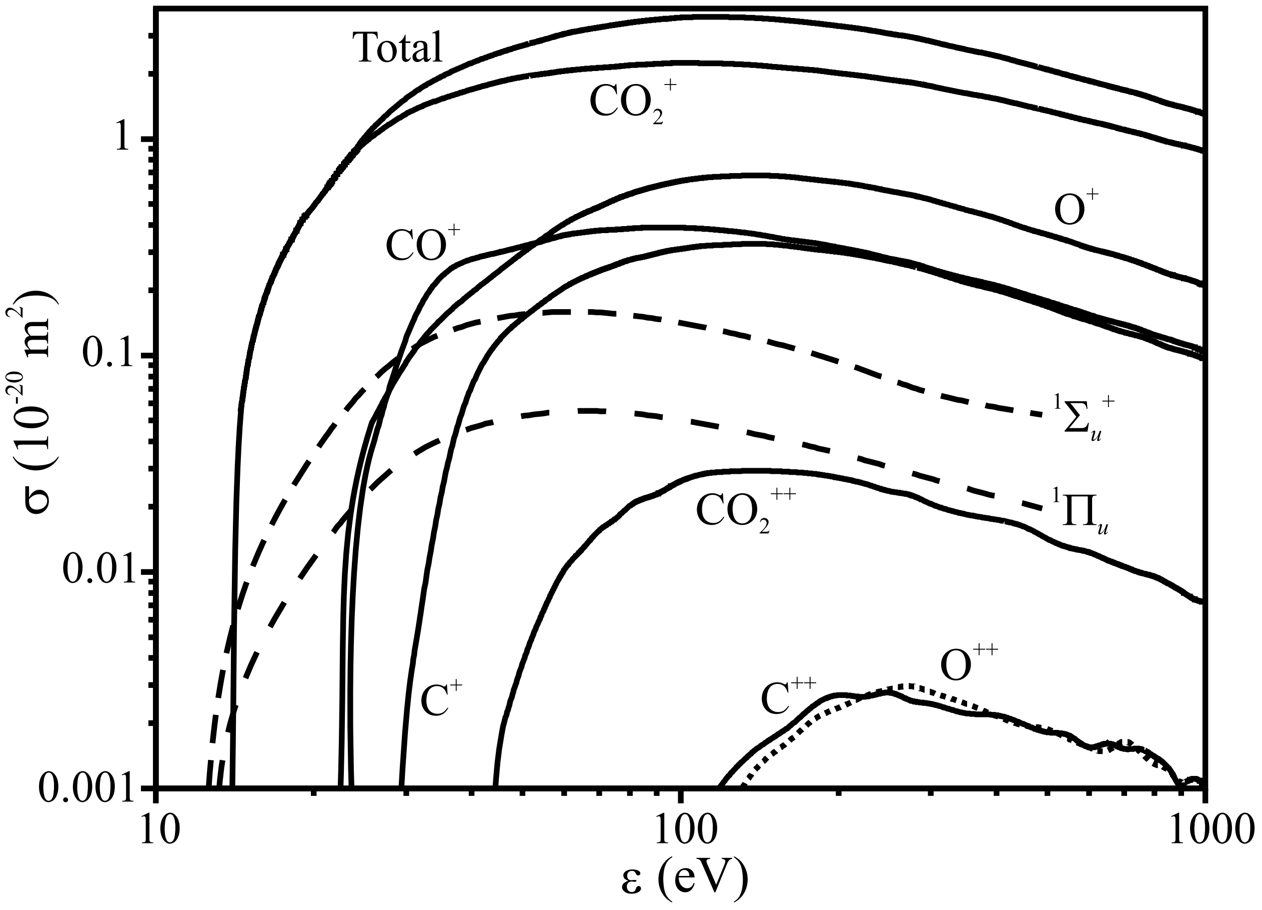
Grid ion source

- Open design
- Two filaments (W)
- Low degassing rate
  - mimimum amount of material
  - Pt-Ir wires for formation chamber
  - Molybdenum filament holders
- Easy to degas via electron bombardment
- Filaments on positive potential





Electron – Molecule collisions Fragmentation

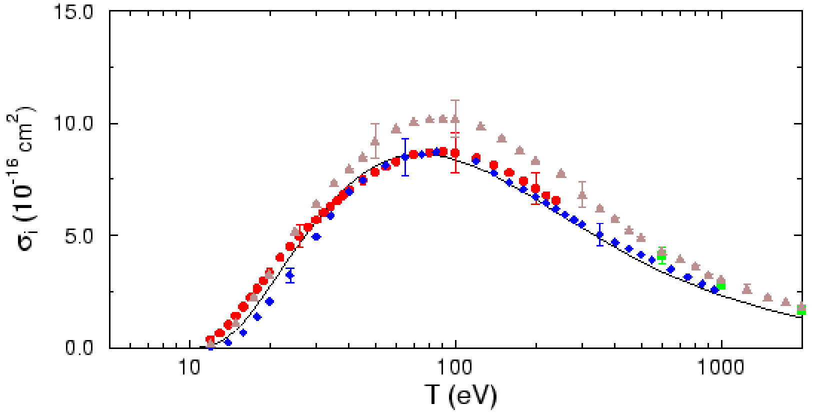


Integral cross sections for electron impact ionization and for the $^1\Sigma_u^+$ and $^1\Pi_u$ state excitation of CO_2

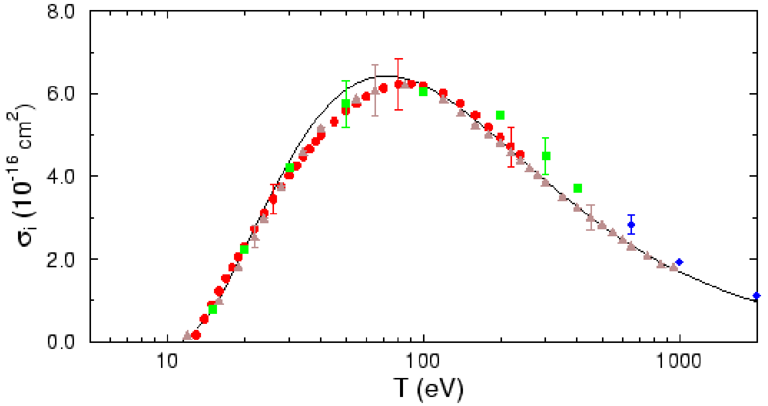
Stanković V. V. et al. *Plasma Chem. Plasma P.* 40 (2020) 1621.
doi: 10.1007/s11090-020-10106-x

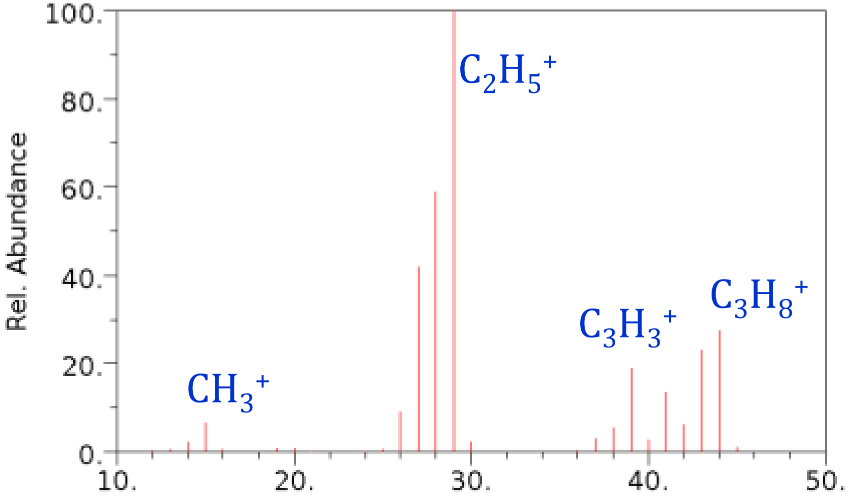
Ionization – fragmentation patterns

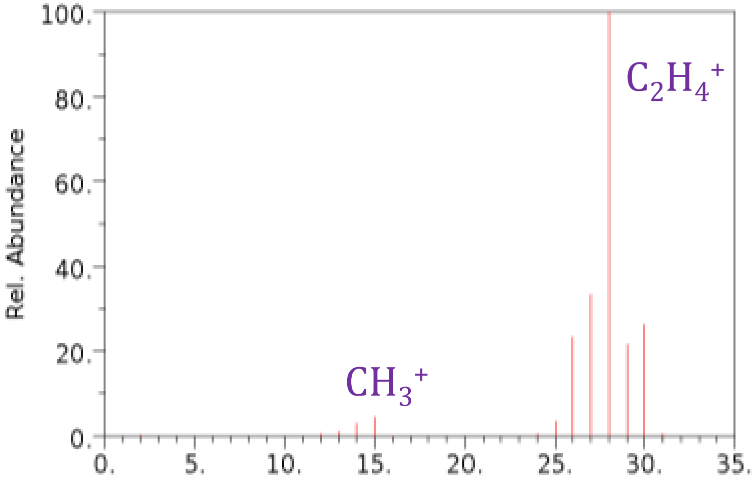
e^- on C_3H_8



e^- on C_2H_6

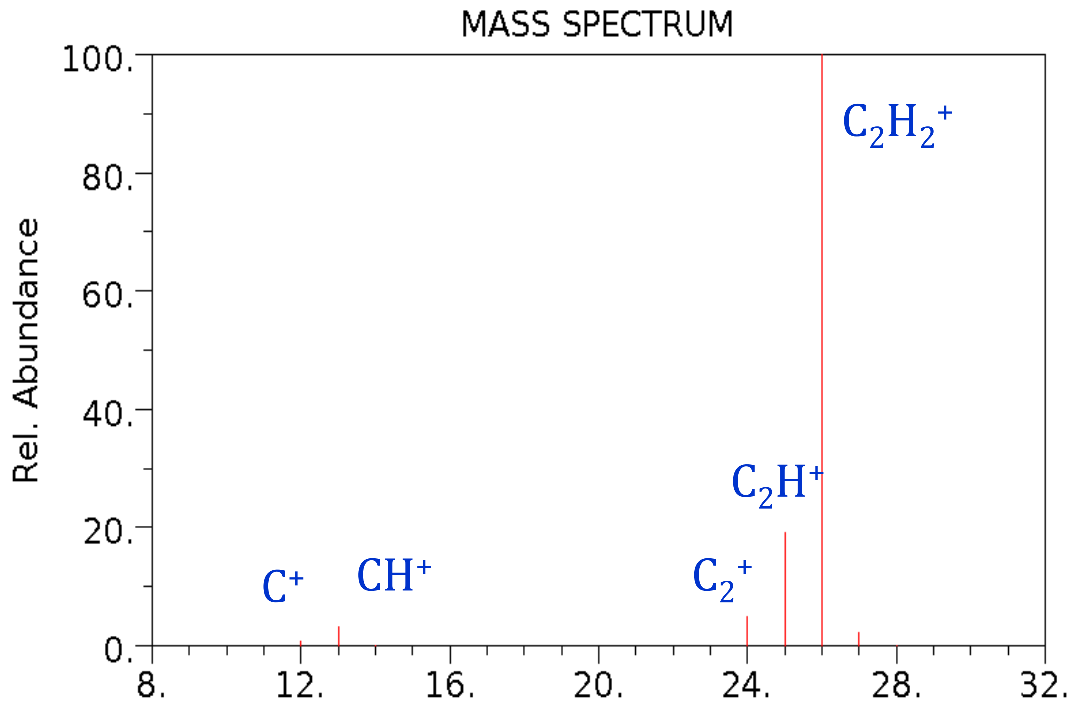






NIST Mass Spectrometry Data Center

Ionization – fragmentation patterns



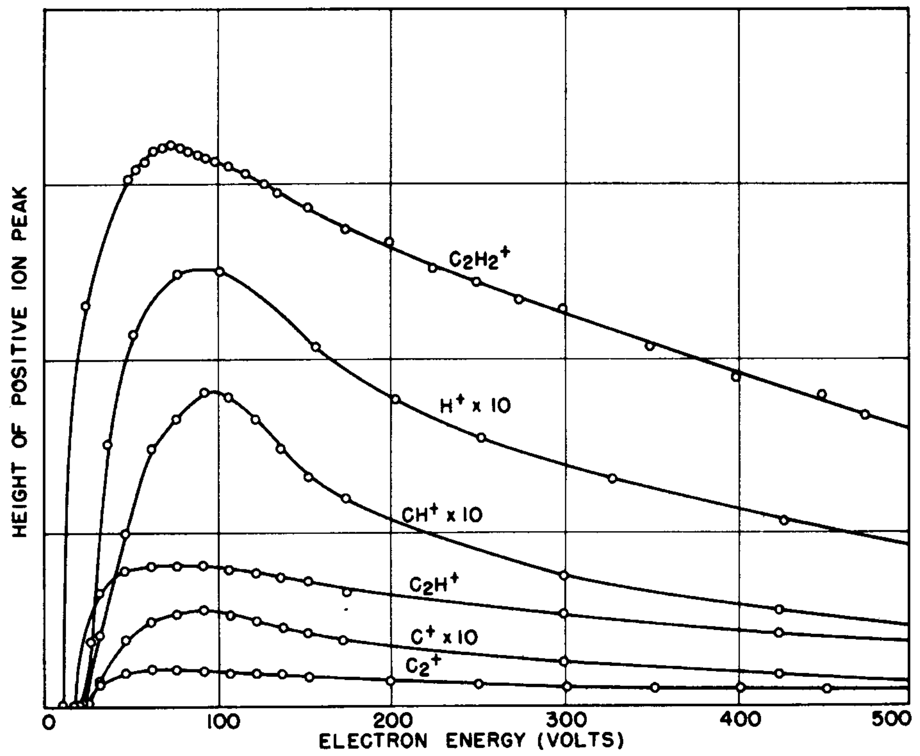


FIG. 6. Ionization efficiency curves for several ions from acetylene (493).

NIST Mass Spectrometry Data Center

Penning ionization

$$X^* + A \rightarrow X + A^+ + e^-$$
$$X^* + AB \rightarrow X + AB^+ + e^-$$

Penning Ionization (PI)

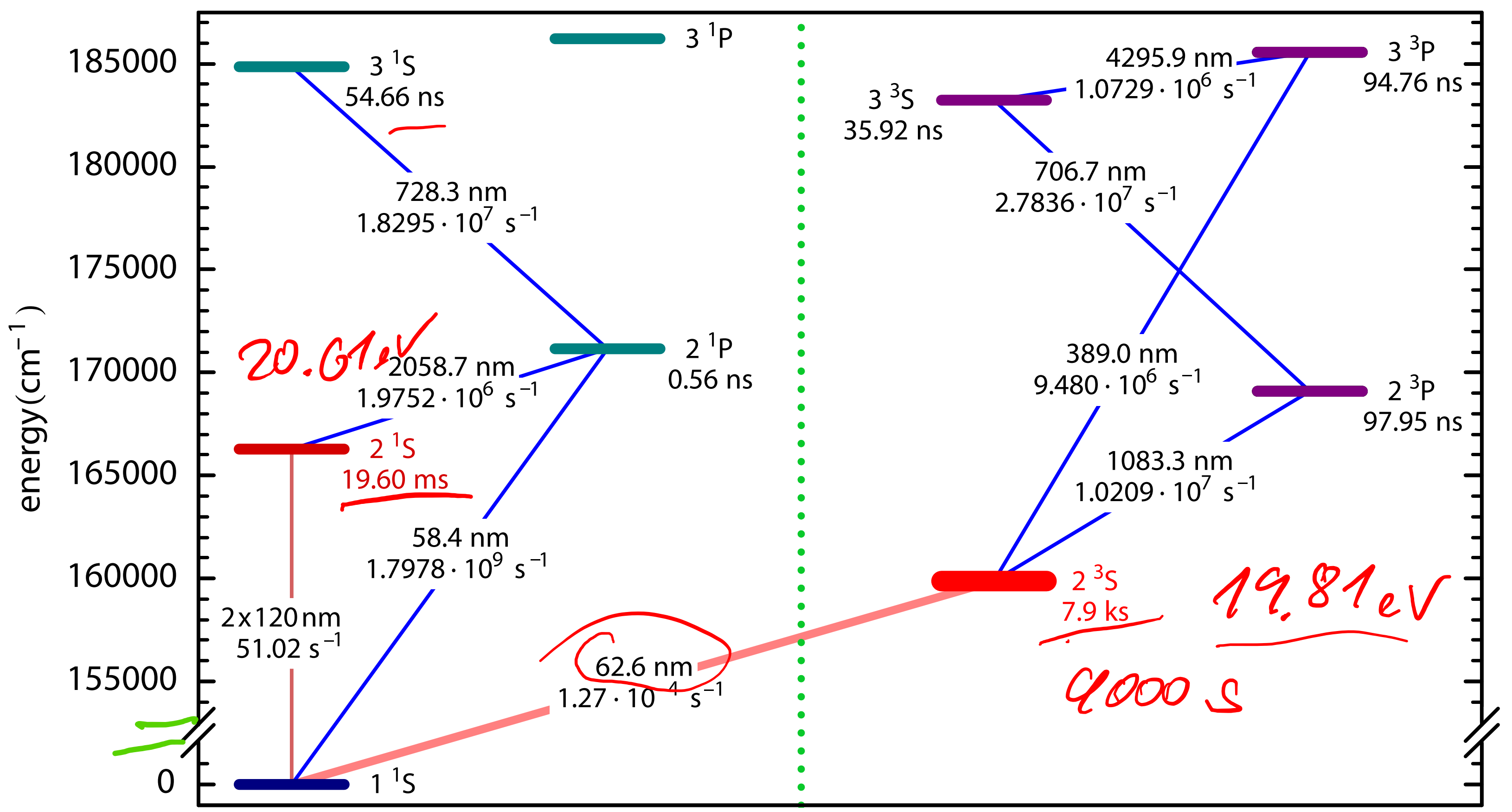
$$X^* + A \rightarrow XA^+ + e^-$$
$$X^* + AB \rightarrow XAB^+ + e^-$$

Associative Ionization (AI)

$$He^* + He \rightarrow He_2{}^+ + e^-$$

Hornbeck-Molnar process

Helium metastable



Grotrian diagram of the lowest energy levels in helium.

Tol P. J. J. *Trapping and Evaporative Cooling of Metastable Helium,* thesis, Vrije Universiteit (2005)

Metastable species

Excited Species	Excitation Energy (eV)	Lifetime (s)
$H^*(2s^2S_{1/2})$	10.1988	0.14
$He^*(2^1S_0)$	20.6158	0.0196
$He^*(2^3S_1)$	19.8196	9000
$Ne^*(^3P_0)$	16.7154	430
$Ne^*(^3P_2)$	16.6191	24.4
$Ar^*(^3P_0)$	11.7232	44.9
$Ar^*(^3P_2)$	11.5484	55.9
$Kr^*(^3P_0)$	10.5624	0.49
$Kr^*(^3P_2)$	9.9152	85.1
$Xe^*(^3P_0)$	9.4472	0.078
$Xe^*(^3P_2)$	8.3153	150
$O^*(2p^33s^5S_2)$	9.146	1.85×10^{-4}
$H_2^*(c^3\Pi_u^-)$	11.764	1.02×10^{-3}
$N_2^*(A^3\Sigma_u^+)$	6.169	1.9
$N_2^*(A^1\Pi_g)$	8.549	1.20×10^{-4}
$N_2^*(E^3\Sigma_g^+)$	11.875	1.90×10^{-4}
$CO^*(a^3\Pi)$	6.010	$\geq 3 \times 10^{-3}$

Hotop H. *Detection of metastable atoms and molecules*. In *Atomic, Molecular, and Optical Physics: Atoms and Molecules*; Dunning, F.B., Hulet, R.G., Eds.; Academic Press, Inc.: San Diego, CA, USA, 1996; pp. 191–216.

N_2 molecule – metastable

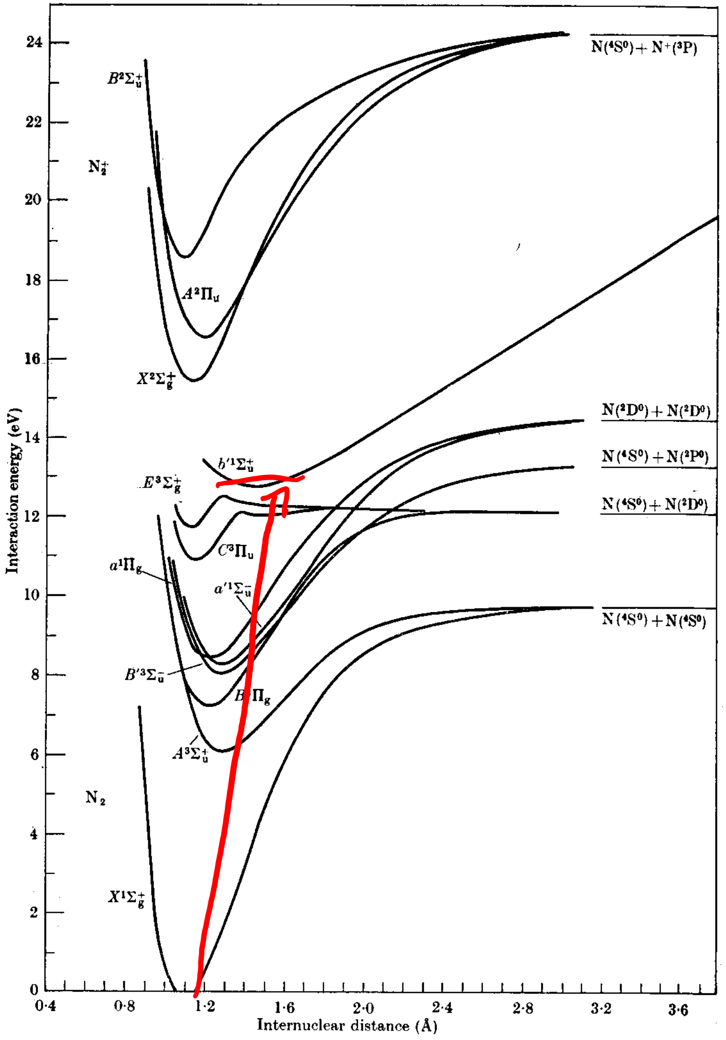


FIG. 13.46. Potential energy curves for some electronic states of N_2 and N_2^+.

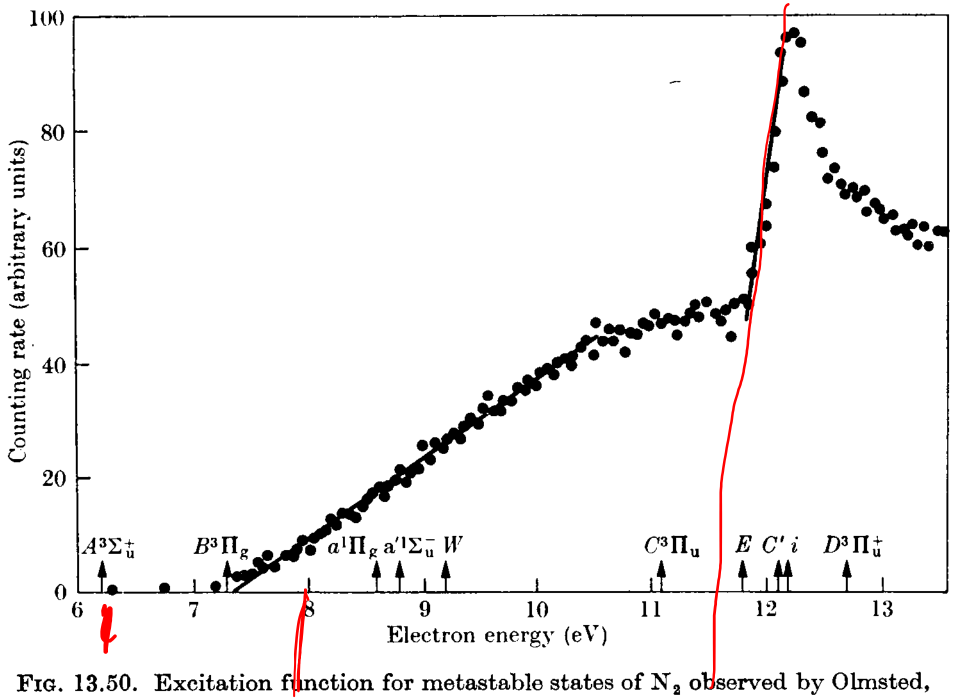
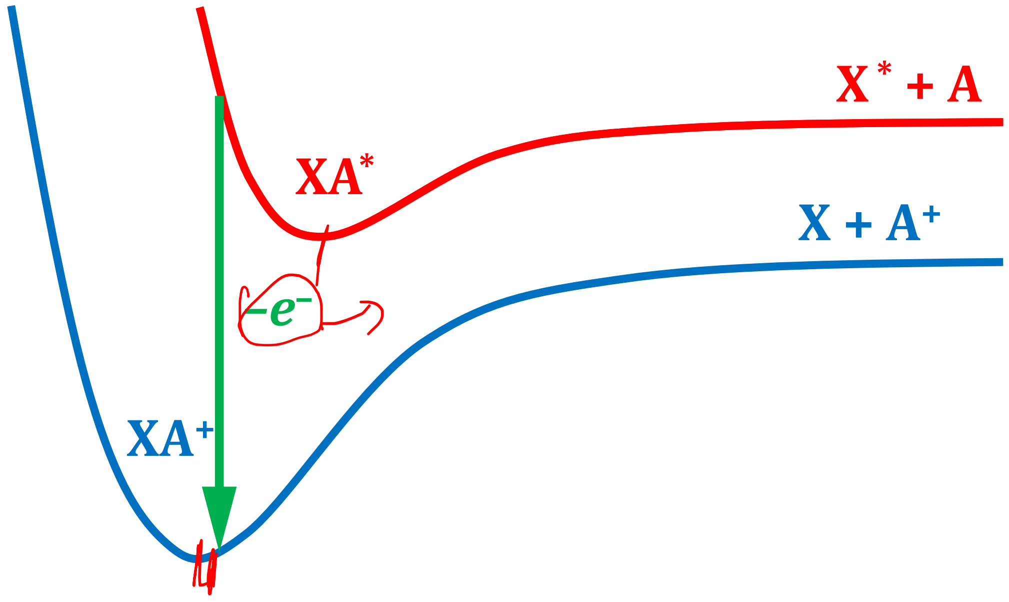


FIG. 13.50. Excitation function for metastable states of N_2 observed by Olmsted, Newton, and Street.

Penning ionization – model

$$X^* + A \rightarrow [XA]^* \rightarrow XA^+ + e^- \rightarrow X + A^+ + e^-$$



Penning ionization studies

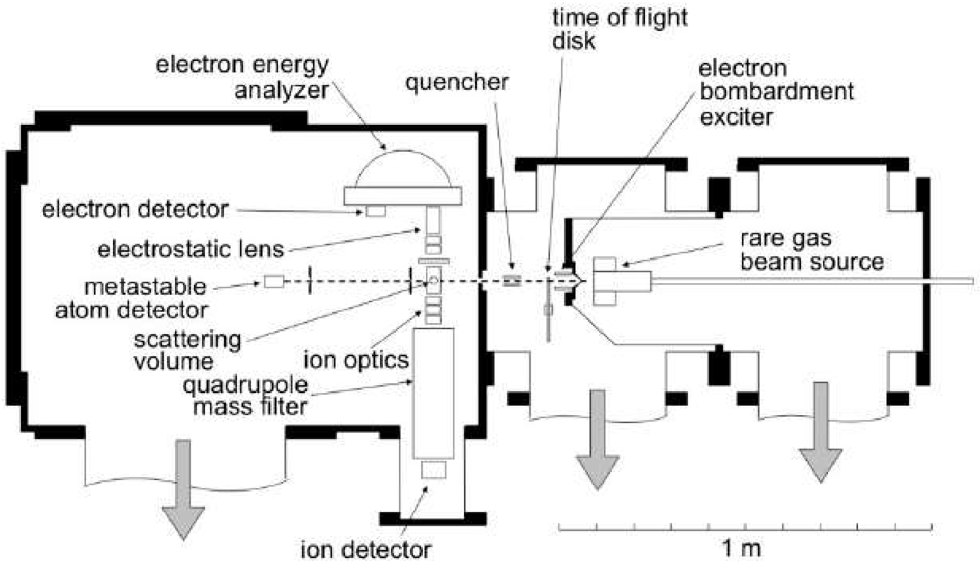
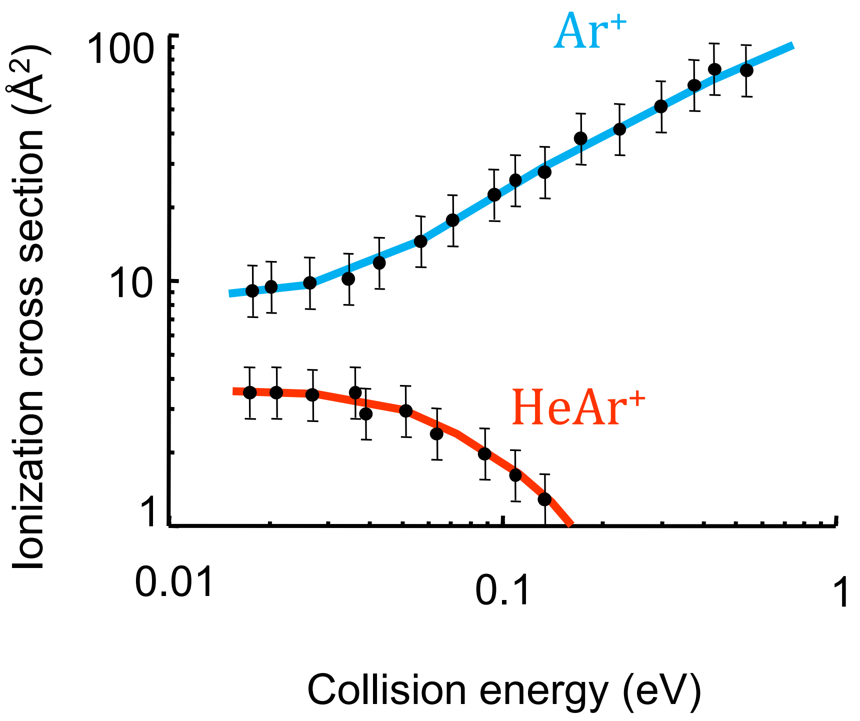


Figure 1. The crossed molecular beam apparatus used in Penning ionization studies.

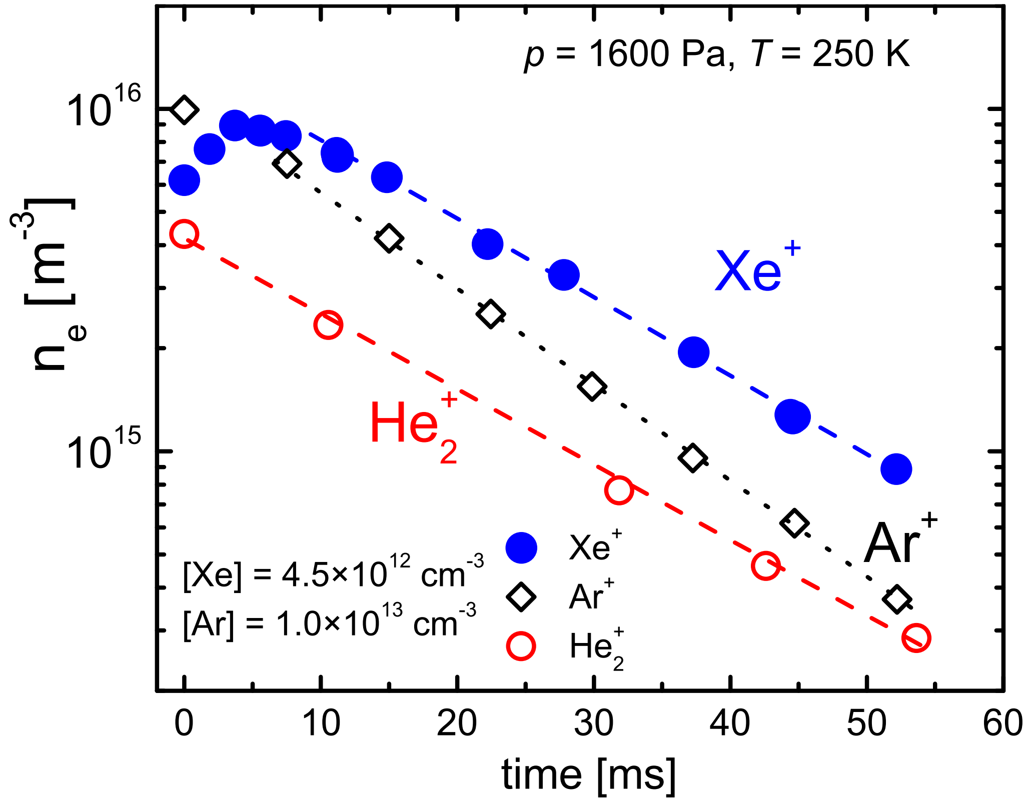
Penning ionization examples



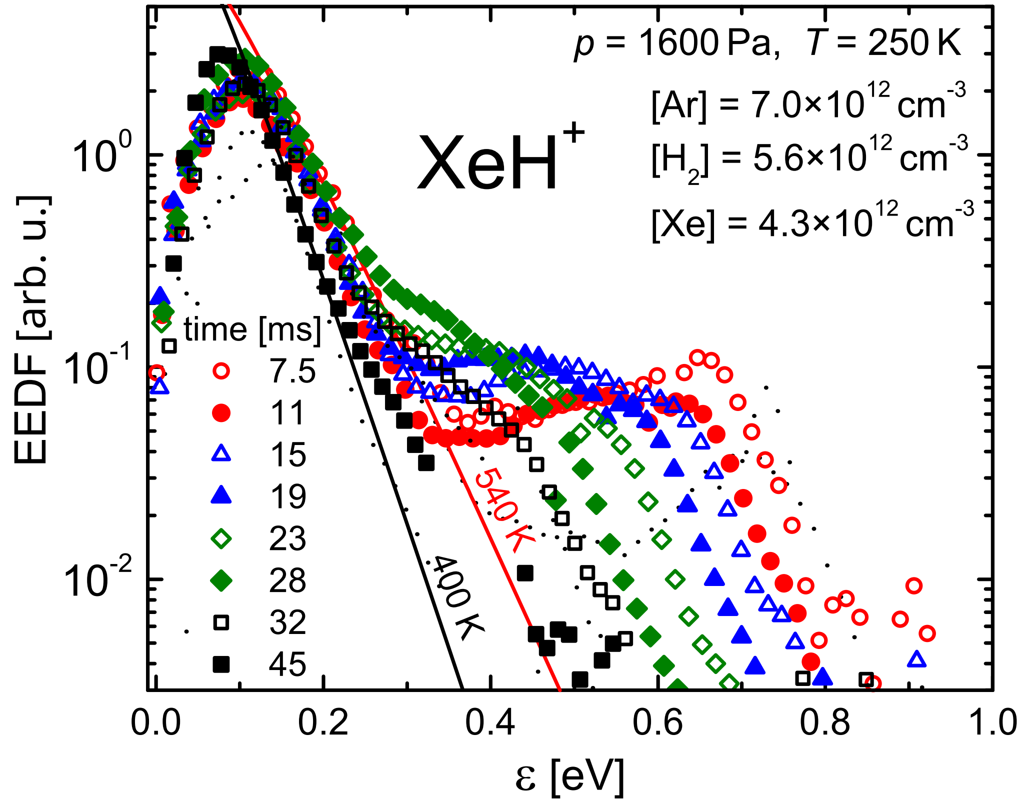
$$He^*(2^1S, 2^3S) + Ar$$
$$\rightarrow He + Ar^+ + e^-$$
$$\rightarrow HeAr^+ + e^-$$

$$He^*(2^3S) + Ar \rightarrow He + Ar^+(^2P_{3/2}) + e^-$$
$$He^*(2^3S) + Ar \rightarrow He + Ar^+(^2P_{1/2}) + e^-$$

Penning ionization, superelastic collisions



The measured decay of electron density in He_2^+ dominated afterglow plasma in pure He and the increase of n_e after injection of Xe.



Evolution of EEDF in He/Ar/Xe/H_2 plasma obtained from measured characteristics of Langmuir probe. The EEDFs are normalized to 1.

Plašil R. et al. *EPJD* 54 (2009) 391. doi: 10.1140/epjd/e2009-00144-3

Excimers

Excited molecules that are not stable at ground state

Typically, at least one atom has a valence shell completely filled with electrons.

$$Rg^* + Rg + M \rightarrow Rg_2^* + M$$

$$Rg^* + AB \rightarrow RgA^* + B$$

$$Rg^+ + A^- + M \rightarrow RgA^* + M$$

Excimer UV lamps

Excimer molecule	Wavelength (nm)	Photon energy (eV)
NeF^*	108	11.48
Ar_2^*	126	9.84
Kr_2^*	146	8.49
F_2^*	158	7.85
$ArBr^*$	165	7.52
Xe_2^*	172	7.21
$ArCl^*$	175	7.08
KrI^*	190	6.49
ArF^*	193	6.42
$KrBr^*$	207	5.99
$KrCl^*$	222	5.58
KrF^*	248	5.01
XeI^*	253	4.91
Cl_2^*	259	4.79
$XeBr^*$	282	4.41
Br_2^*	289	4.29
$XeCl^*$	308	4.03
I_2^*	342	3.63
XeF^*	351	3.53