Merged beam study of the associative ionization (C^+, N^+ and O^+)+O^-, D^++O^- and O^++ D^-

AI and RIP : the possible connections

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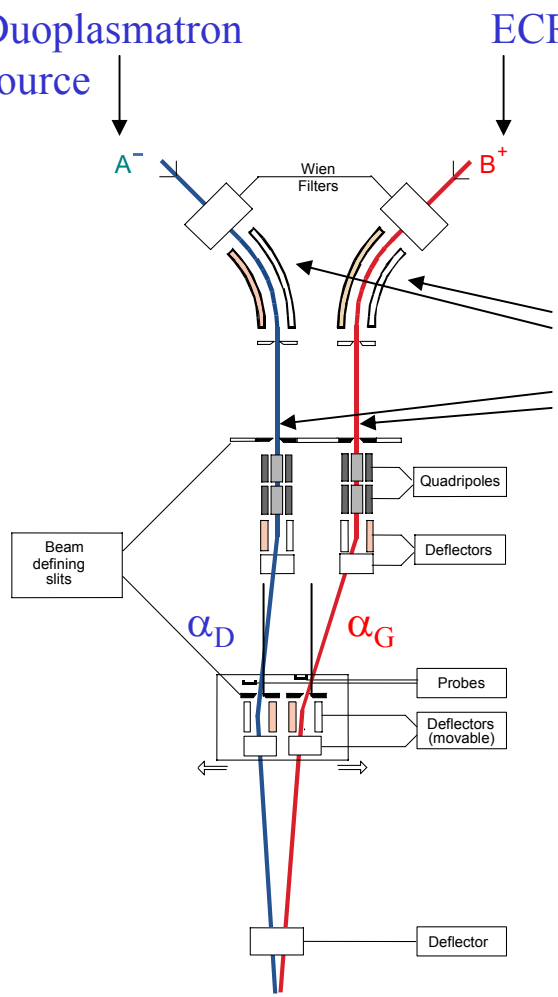
Outline

- Introduction
- Associative Ionization (Belgium)
  - Experimental setup : Merged Beam apparatus MB2
  - Results that concern the atmospheric gases (CO, NO and O_2)
  - Results that concern OD
  - Conclusions

MB2 machine
UCL Belgium



Wien filters :
Beam velocity selection

Cylindrical deflectors

Diaphragms 1mm

Horizontal and vertical deflectors

Movable plate

Merging conditions :

$\alpha_G/\alpha_D = A_D/A_G$

CINEMATICS OF THE EXPERIMENT

Center-of-mass energy in the interaction region (for beams merging at 0 angle) :

$$E_{CM} = \mu \left[\sqrt{\frac{q_2 (A_2 - V_0)}{m_2}} - \sqrt{\frac{q_1 (A_1 - V_0)}{m_1}} \right]^2$$

With :

$q_1 = q_G = 1$ $\quad m_1 = m_G$ $\quad A_1 = A_G$

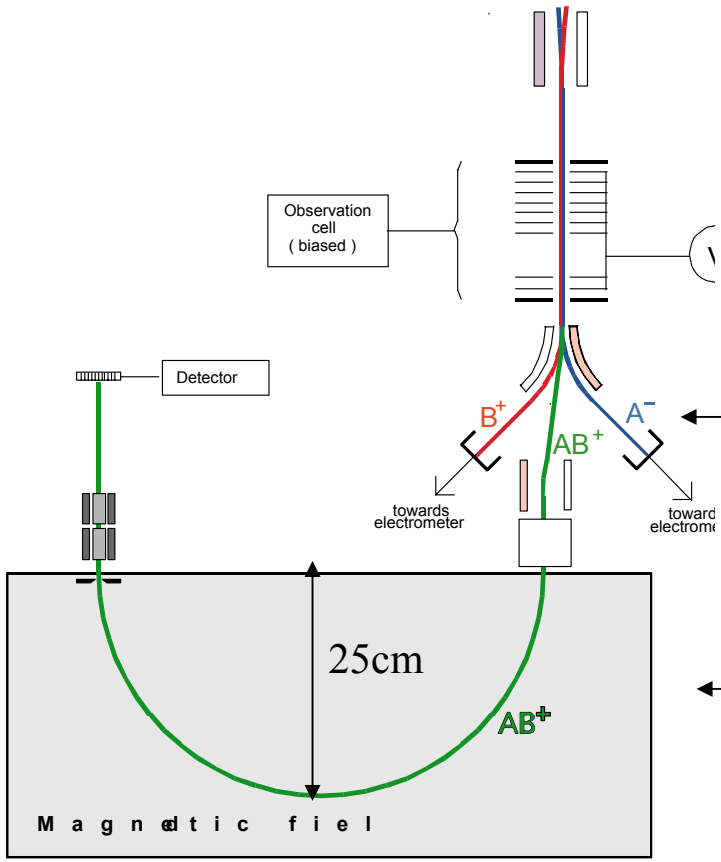
$q_2 = q_D = -1$ $\quad m_2 = m_D$ $\quad A_2 = A_D$

Beams assumed to be monoenergetic and with velocities close from each other in the lab frame !

and :

Observation potential V_0

ENERGY RESOLUTION : 2meVat Ecm = 10meV !!!!!!!!!!!!



Interaction region
(11 plates electrically isolated, 5mm apart)

Observation potential V_0

Charged species separation

Magnetic analyzer

CROSS SECTION DETERMINATION

$$\sigma = q_1.q_2 \frac{v_1.v_2}{v_r} \frac{1}{\int_0^T I_1(t).I_2(t).dt} \frac{N(T)}{F}$$

Total number of events

Current integral

With :

$q_1 = q_G = 1$ $\quad v_1 = v_G$ $\quad I_1 = I_G$

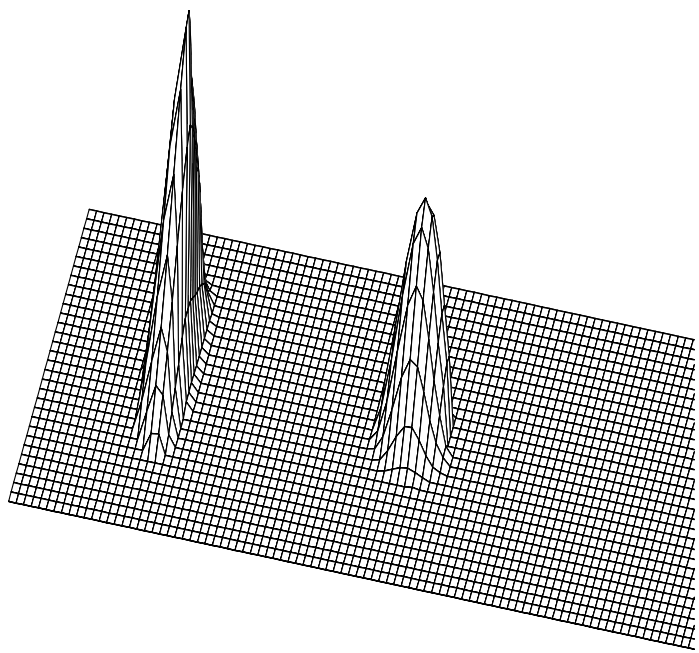
$q_2 = q_D = -1$ $\quad v_2 = v_D$ $\quad I_2 = I_D$

and :

Relative velocity v_r

Form factor F

$$F(z) = \frac{\int_{-\infty}^{+\infty}\int_{-\infty}^{+} j_1(x,y,z).j_2(x,y,z,t).dxdy}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} j_1(x,y).dxdy \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} j_2(x,y).dxdy}$$



ASSOCIATIVE IONIZATION

$$A_{(L_A, S_A, J_A)} + B_{(L_B, S_B, J_B)} \rightarrow AB^{+}_{(Elect, v, J)} + e + KER$$

$$A^{+}_{(L_A, S_A, J_A)} + B^{-}_{(L_B, S_B, J_B)} \rightarrow AB^{+}_{(Elect, v, J)} + e + KER$$

- Efficient process when the time spent by the nuclei in the binding part of the potential is in the same order than the vibrating period.
- When the dissociation energy of the molecular ion is overcome, the Penning ionization is competing.
- The product molecular ion is formed in different electronic and rovibrational states !
- To have more information concerning the v, N distributions, means to record the energy spectrum of the electrons ; NOT POSSIBLE with this setup!

Work on (C^+, N^+ and O^+) + O^-

FEW EXAMPLES…

•ASTROCHEMISTRY

CO detected in emission in the Supernovae 1987A

⇒processes that enter the production scheme of CO and CO^+ are important.

Radiative association $C+O \rightarrow CO + h\nu$

$C^+ + O \rightarrow CO^+ + h\nu$

$C+O \rightarrow CO^+ + e$ not considered (endothermic) but also $C^+ + O^- \rightarrow CO^+ + e$ (exothermic)

•COMBUSTION

In ammonia and hydrogen-oxygen-nitrogen flames, the primary source of nitrogen oxide cations is $N(^2D, ^2P) + O(^3P) \rightarrow CO^+ + e$

EXPERIMENTAL DIFFICULTIES

Electronic excitation of the target ions

- O^- and D^- produced with the duoplasmatron ion source.

No metastable states!

- C^+, N^+ and O^+ produced with the ECR ion source (carbon monoxide and nitrous oxide).

C^+: ^2P, ^4P (5.33eV - 6.7ms) and ^2D (9.29eV - 3.5ns) FIRST EXCITED POPULATED

N^+: ^3P, ^1D (1.90eV – 275s), ^1S (4.05eV – 855ms) and ^5S (5.85eV – 5.5ms) TWO FIRST EXCITED POPULATED (Harrison 1963)

O^+: ^4S, ^2D (3.32eV – 6290s) and ^2P(5.02eV – few ns) ALL POPULATED (Reid 1992)

The lifetimes have to be compared to the sum of the residence time within the ion source and of the time-of-flight source/interaction region (roughly 10μs!).

EXPERIMENTAL DIFFICULTIES

Energy resolution

The form factor and collision velocity distributions are obtained by numerical simulation of the particle distribution limited by the set of defining apertures (1.5 mm in diameter) present along both beam trajectories. The interaction volume is discretized, and all possible pairs of trajectories emerging from discrete surface elements of the first defining aperture are considered, provided they are transmitted by the second defining aperture located at the entrance of the biased interaction region. The angle formed by the velocity vectors is computed, and the corresponding histogram built. Finally, the collision energy distribution $F(E_{cm})$ is obtained by folding this angular distribution $f(\theta)$ with the gaussian energy spread of both beams, $g(E_i)$ (our model assumes 5 eV of energy dispersion for both ionic beams), using the equation relating the

$$F(E_{cm})=\iiint g(E_1)g(E_2)f(\theta)\delta\left(E_{cm}-\mu\left[\frac{E_1}{m_1}+\frac{E_2}{m_2}-2\sqrt{\frac{E_1E_2}{m_1m_2}}\cos\theta\right]\right)dE_1dE_2d\theta$$

The apparent cross section is obtained by dividing the reaction rate by the velocity detuning v_d (defined for rigorously parallel and monoenergetic beams):

$$\sigma_{app}=\int\sigma(E_{cm})\frac{v_{cm}}{v_d}F(E_{cm})dE_{cm}$$

In the case of pure Coulomb interaction, the cross section behaves like E_{cm}^{-1} in the low energy limit, and the apparent cross section is then:

$$\sigma_{app}\propto\int\frac{F(E_{cm})}{\sqrt{E_{cm}E_d}}dE_{cm}$$

$C^+ + O^-$

ENERGETICS…

$$\rightarrow CO(X^1\Sigma^+) + 20.89eV$$

Locht 1975 : INEFFICIENT PROCESS

$$\rightarrow C(^3P) + O(^3P) + 9.80eV$$

$$\rightarrow CO^+(X^2\Sigma^+) + e + 6.88eV$$

$$C^+(^2P) + O^-(^2P) \rightarrow C^+(^2P) + O(^3P) + e - 1.46eV$$

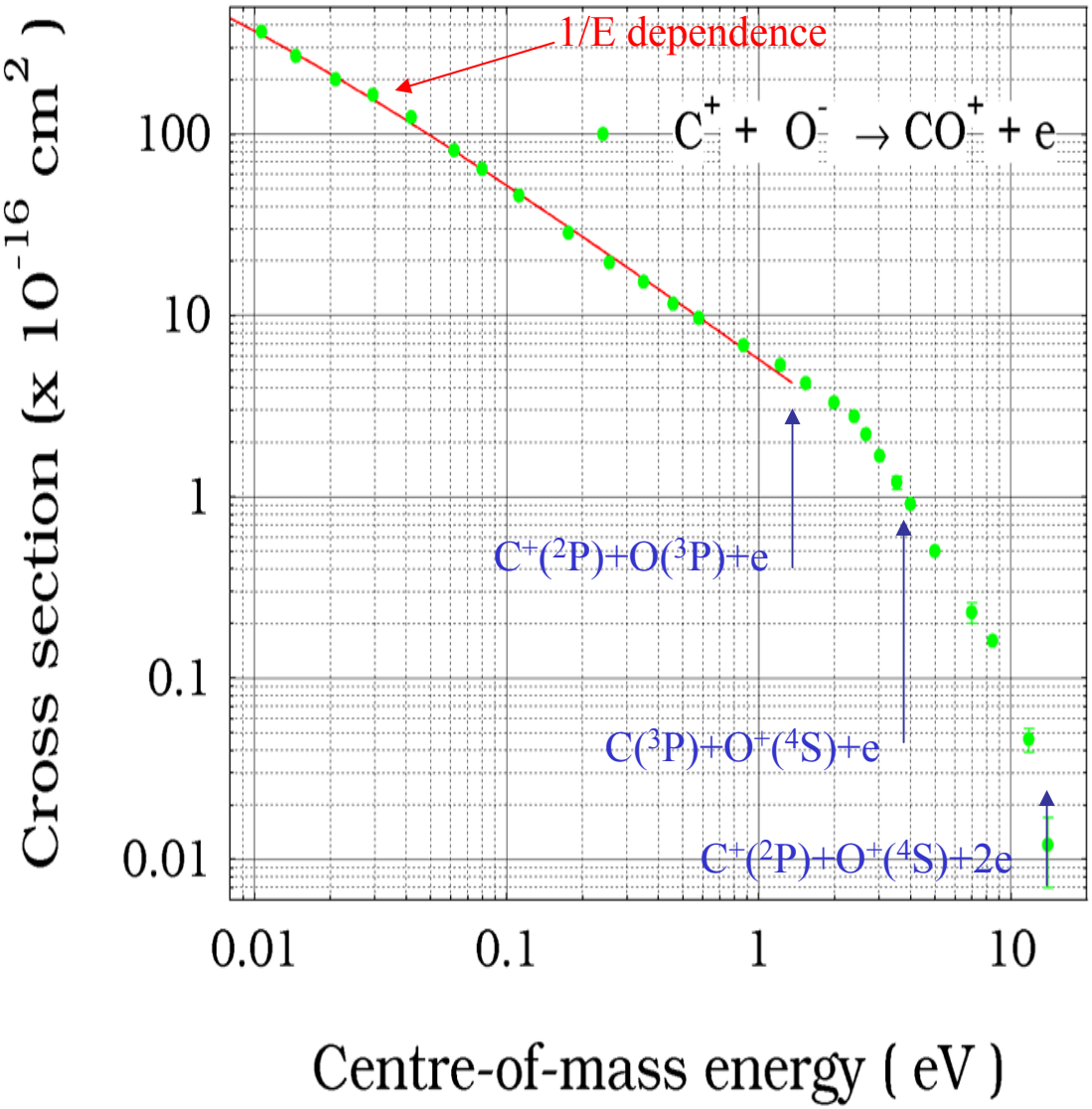
$$\rightarrow C(^3P) + O^+(^4S) + e - 3.82eV$$

$$\rightarrow C^+(^2P) + O^+(^4S) + 2e - 15.08eV$$

$$\rightarrow CO^{2+}(X^3\Pi) + 2e - 20.38eV$$

INTERPLAY

TOTAL AI CROSS SECTIONS



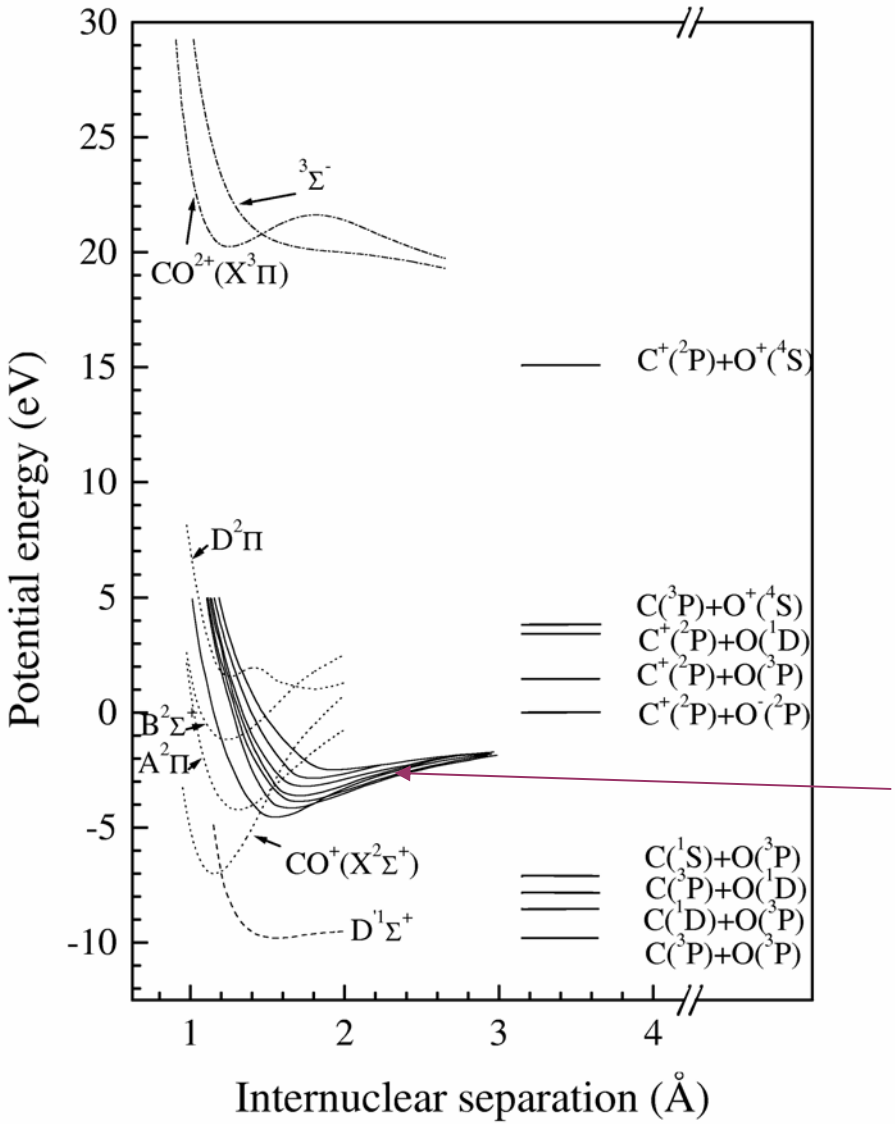
Theoretical upper limit to the cross sections:

$$\sigma_{AI}(E_{cm}) = \frac{\pi(N_{max}+1)^2\hbar^2}{2\mu E_{cm}}$$

one electronic state populated!

One gets: $\sigma = 6 \times 10^{-13}$ cm^2 at 10 meV (for the grnd state)

LOWER EXPERIMENTAL VALUE
⇒EXCITED STATES POPULATED



Molecular ionic states likely to be populated at low energies…

$X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$

and further up in energy…

$C^2\Delta_r$, $D^2\Pi$...

Correlation rules Wigner and Wittmer:
-12 states for the limit $C^+(^2P)+O^-(^2P)$

$^{1,3}\Sigma^+(2)$, $^{1,3}\Sigma^-(1)$, $^{1,3}\Pi(2)$ and **$^{1,3}\Delta(1)$,**
-7 of them are displayed here!

$N^+ + O^-$

$$\rightarrow NO(X^2\Pi_r) + 19.55eV$$

$$\rightarrow N(^4S) + O(^3P) + 13.07eV$$

Hayton and Peart 1993

$$\rightarrow NO^+(X^1\Sigma^+) + e + 10.29eV$$

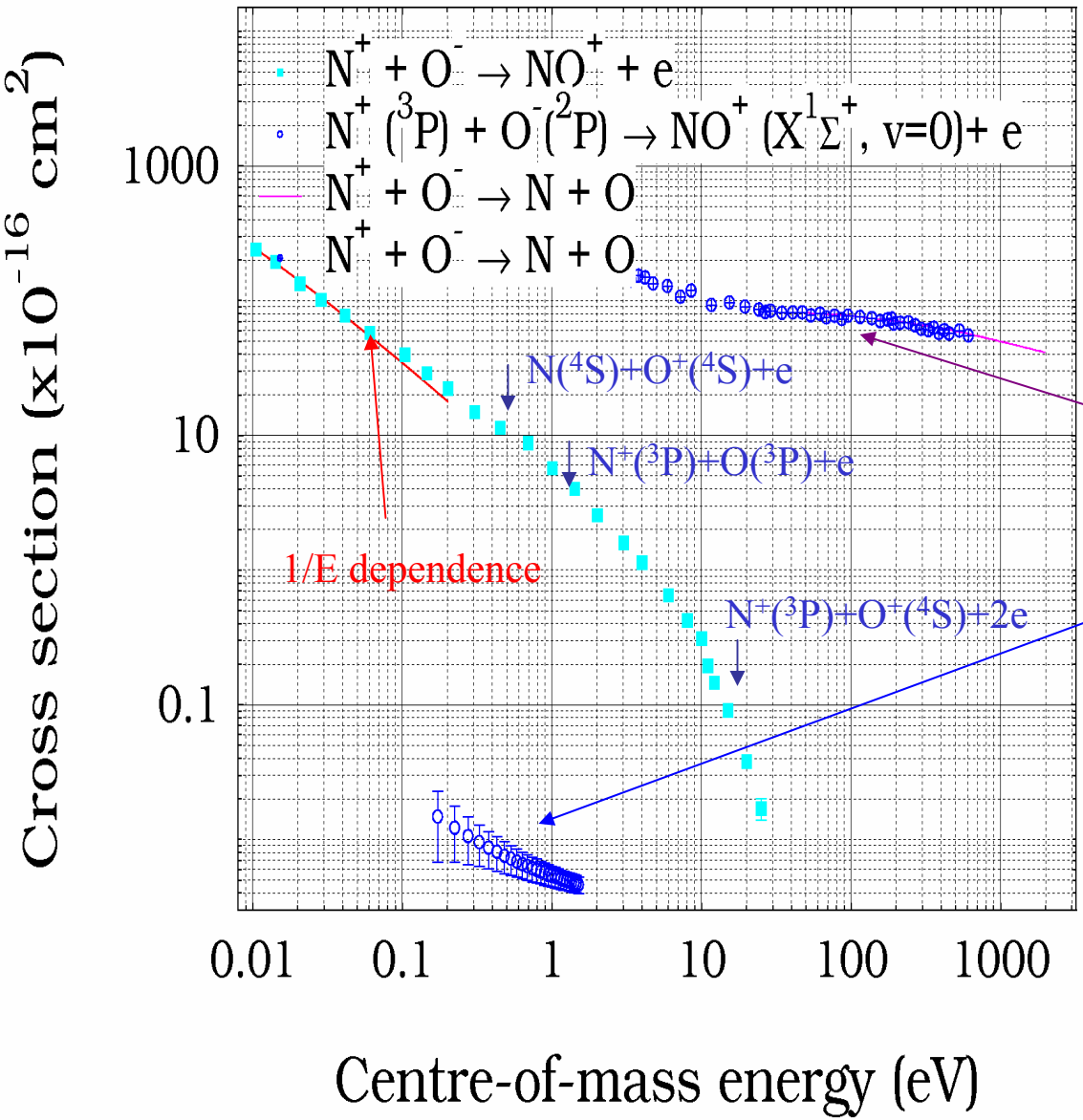
$$N^+(^3P) + O^-(^2P) \rightarrow N(^4S) + O^+(^4S) + e - 0.54eV$$

$$\rightarrow N^+(^3P) + O(^3P) + e - 1.46eV$$

$$\rightarrow N^+(^3P) + O^+(^4S) + 2e - 15.07eV$$

$$\rightarrow NO^{2+}(X^2\Sigma^+) + 2e - 18.85eV$$

INTERPLAY

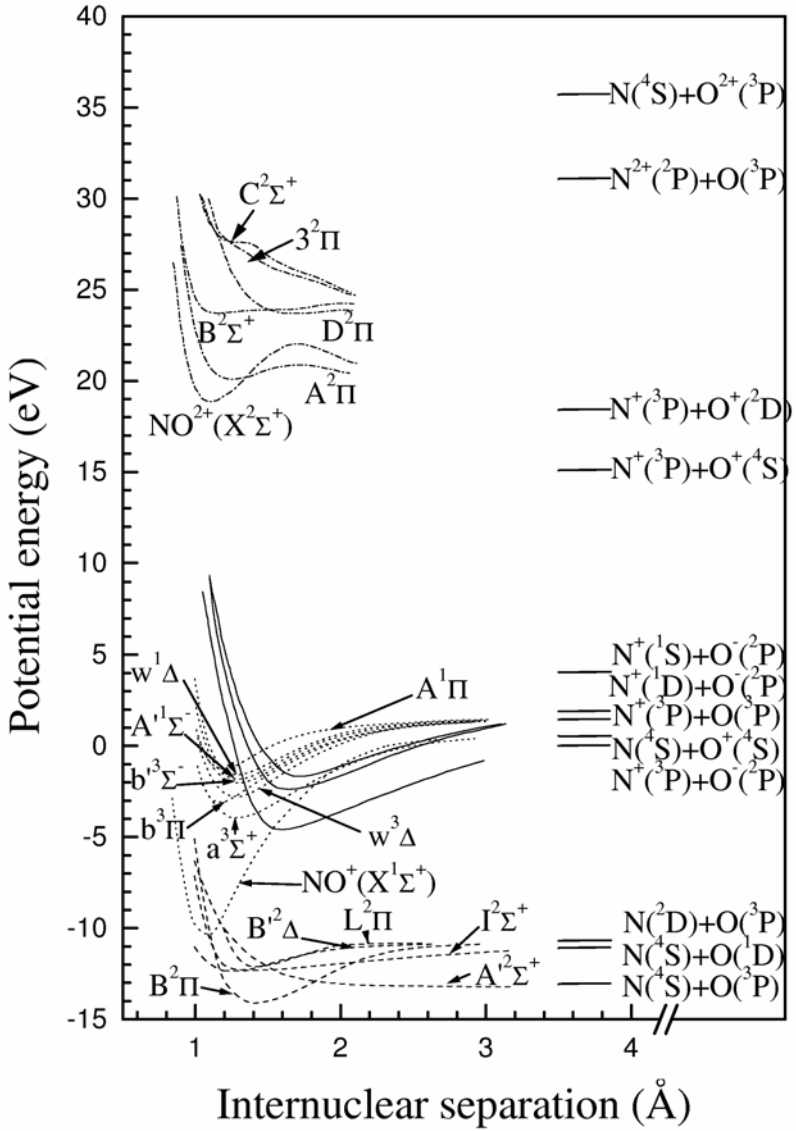


One gets: $\sigma=5.5x10^{-13}$ cm^2 at 10 meV (for the grnd state)

LOWER EXPERIMENTAL VALUE
⇒EXCITED STATES POPULATED

Mutual neutralisation (Hayton and Peart) :
A LONG RANGE PROCESS (12Å)

Detailed balance model applied to the RIP NO^+ data (by Le Padellec *et al* PRA accepted)



Molecular ionic states likely to be populated at low energies…

$X^1\Sigma^+$, $a^3\Sigma^+$, $b^3\Pi_p$, $w^3\Delta$, $b'^3\Sigma^-$, $A'^1\Sigma^1$, $w^1\Delta$ and $a^1\Pi$

Correlation rules Wigner and Wittmer:

-12 states for the limit $N^+(^3P)+O^-(^2P)$

$^{2,4}\Sigma^+(1)$, $^{2,4}\Sigma^-(2)$, $^{2,4}\Pi(2)$ and $^{2,4}\Delta(1)$

-9 states for the limit $N^+(^1D)+O^-(^2P)$

$^2\Sigma^+(2)$, $^2\Sigma^-(1)$, $^2\Pi(3)$ and $^2\Delta(2)$ and $^2\Phi(1)$

HOW TO EXTRACT AI DATA FROM RIP DATA (obtained from CRYRING)?

The model is based on the detailed balance (DB) principle. For a given chemical reaction:

$$A + B \xleftarrow{\sigma,\sigma_{Rev}} C + D,$$

if one includes the total degeneracies associated with the angular momenta g_i (i=A, B, C and D), one gets the relation: $p^2 g_A g_B \sigma(p) = p'^2 g_C g_D \sigma_{Rev}(p')$ with $p^2 = 2\mu E_{cm}$, $p'^2 = 2\mu' E'_{cm}$, (μ, μ', E_{cm}, E'_{cm}, reduced masses of the entrance/exit channels and corresponding center-of-mass energies).

For the RIP/AI processes $AB^+ + e \leftrightarrow A^+ + B^-$, one has also to account for the rotation of the molecular ion AB^- (quantum number N). The theoretical treatment of the RIP and AI cross sections is fairly similar and can be expressed by a development in partial waves of the S matrix elements (k_{cm} and k'_{cm} are the modules of the wavevectors):

$$\sigma_{RIP}(k_{cm}) = \frac{\pi}{k_{cm}^2}|S|^2 \text{ and } \sigma_{AI}(k'_{cm}) = \frac{\pi}{k_{cm}'^2}\sum_N \sum_v |S^{N,v}|^2 (2N+1).$$

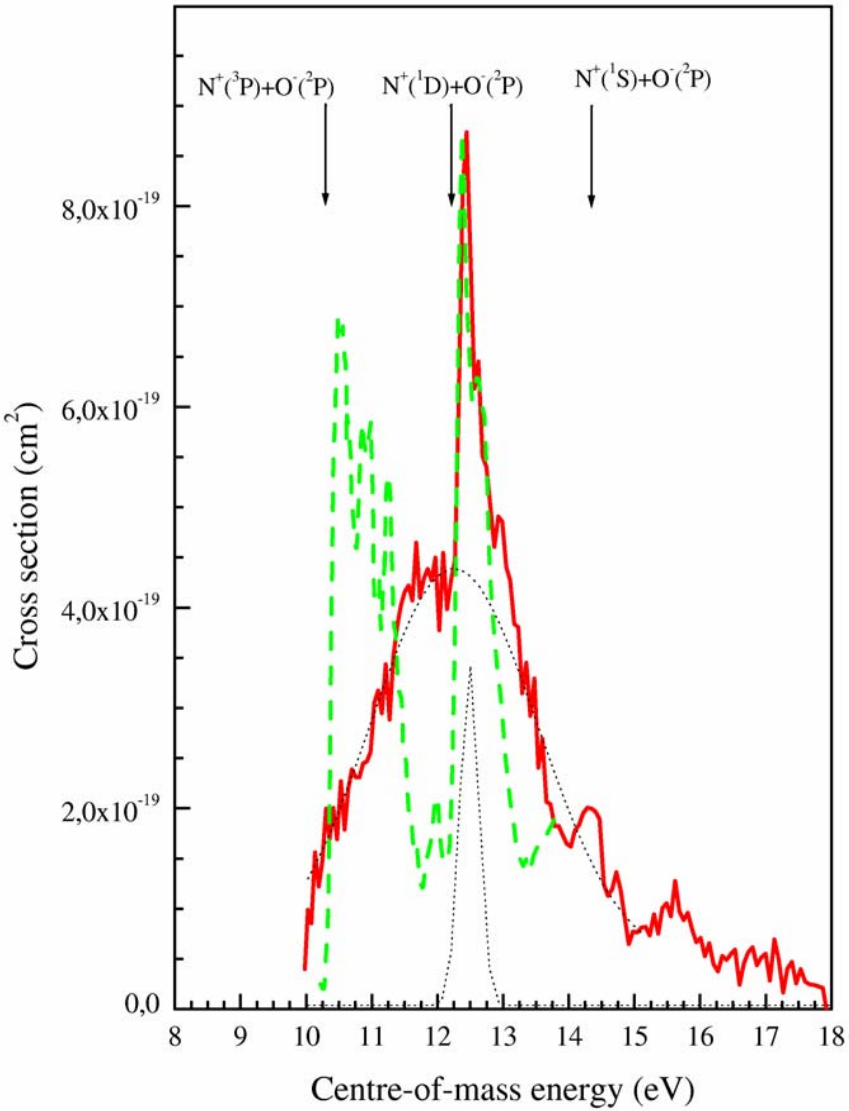
If, for simplification, one makes the assumption that the partial wave elements do not depend much on the rotational degree of freedom, it follows that:

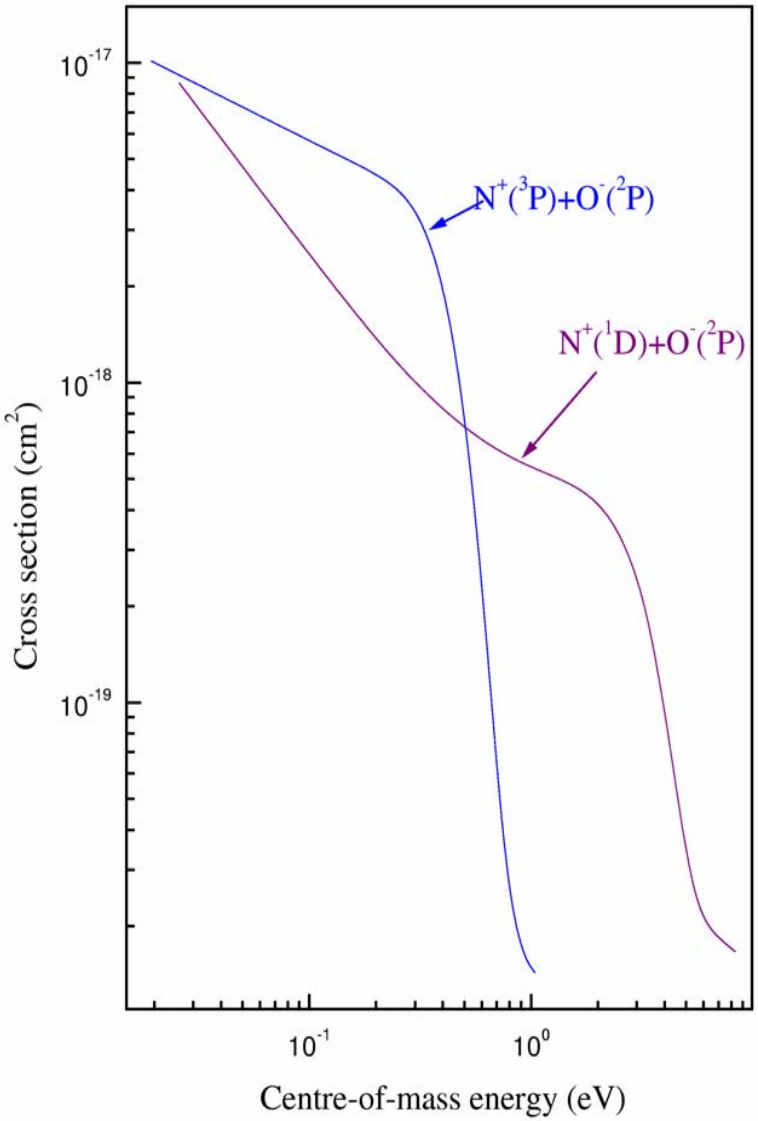
$$\sum_N \sum_v |S^{N,v}|^2 (2N+1) \approx \sum_N (2N+1) \sum_v |S^{N,v}|^2.$$

Since $|S|^2 = \sum_v |S^{N,v}|^2$, there is a simple link between the RIP and AI cross sections, if one takes into account the degeneracies g_i=2J_i+1 mentioned above (g_e=2 for the electron): $\sigma_{AI}(E'_{cm}) = \frac{\mu}{\mu'}\frac{E_{cm}}{E'_{cm}}\frac{g_{AB^-} g_e}{g_{A^+} g_{B^-}} \sum_0^{N_{max}} (2N+1) \quad \sigma_{RIP}(E_{cm})$.

The last term to be quantified is N_{max}, which appears in the summation $\sum_0^{N_{max}} (2N+1) = (N_{max}+1)^2$ and is energy dependent. It is related to the rotational temperature and gives the cutoff beyond which the molecular ion is unbound. This is obtained from the centrifugal distortion of the potential curves: $U_J(R) = V_0(R) - J(J+1)\frac{\hbar}{2\mu R^2}$. For energies with $N_{max} > N_{max,unbound\ state}$, the effective N_{max} is taken to be $N_{max,unbound\ state}$. The J quantum number in can be connected to the rotational quantum number N by simple vector construction.

CRYRING


N+(3P)+O-(2P)
N+(1D)+O-(2P)
N+(1S)+O-(2P)
8,0x10-19
6,0x10-19
4,0x10-19
2,0x10-19
0,0
Cross section (cm2)
8 9 10 11 12 13 14 15 16 17 18
Centre-of-mass energy (eV)


10-17
10-18
10-19
Cross section (cm2)
N+(3P)+O-(2P)
N+(1D)+O-(2P)
10-1
100
Centre-of-mass energy (eV)

$O^+ + O^-$

$$O^+(^4S) + O^-(^2P) \rightarrow O_2(X^3\Sigma_g^-) + 17.27eV$$ **Lacome 1994**

$$\rightarrow O(^3P) + O(^3P) + 12.15eV$$ **Hayton and Peart 1993**

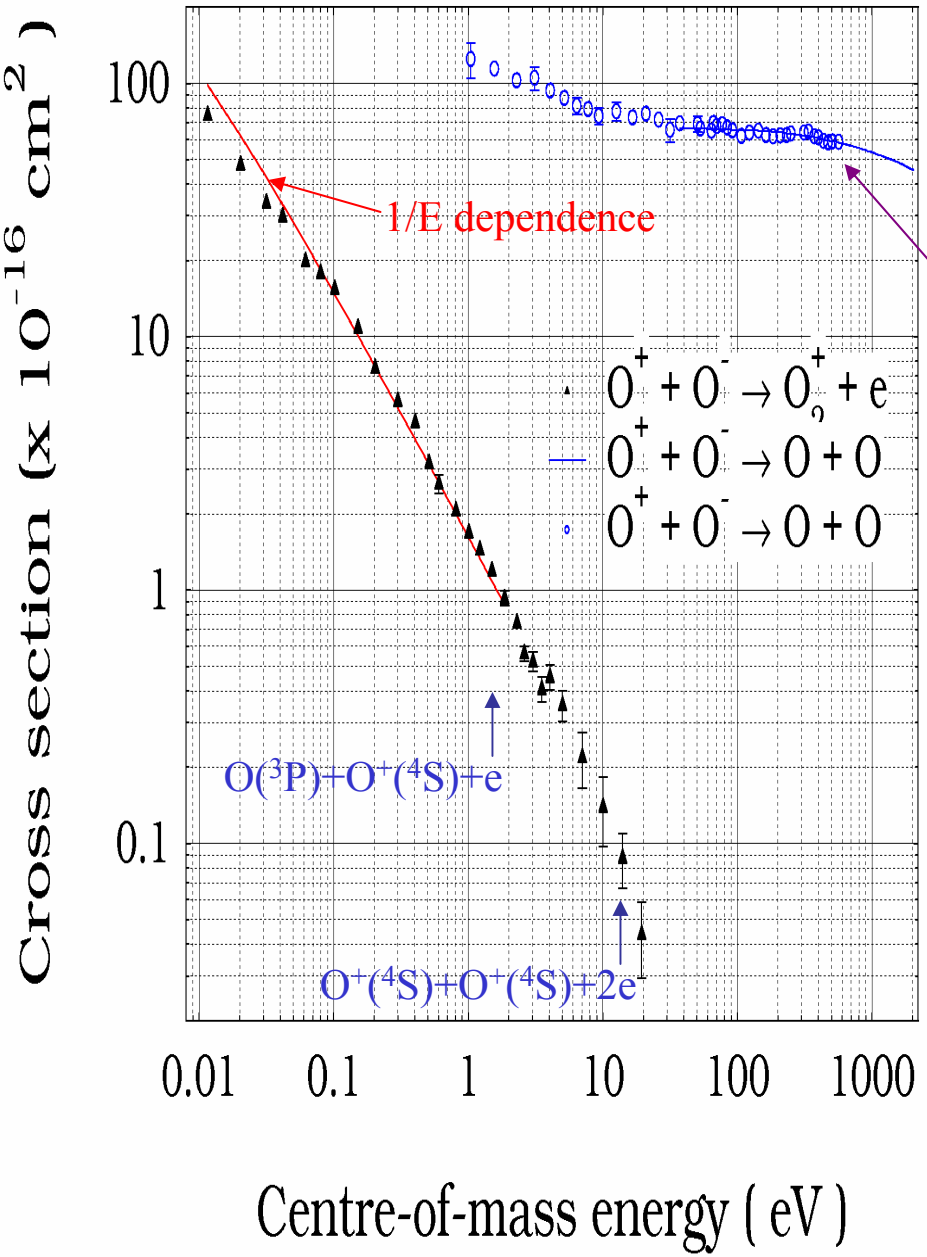
$$\rightarrow O_2^+(X^2\Pi_g) + e + 5.20eV$$

$$\rightarrow O(^3P) + O^+(^4S) + e - 1.46eV$$

$$\rightarrow O^+(^4S) + O^+(^4S) + 2e - 15.07eV$$

$$\rightarrow O_2^{2+}(X^1\Sigma_g^+) + 2e - 18.65eV$$

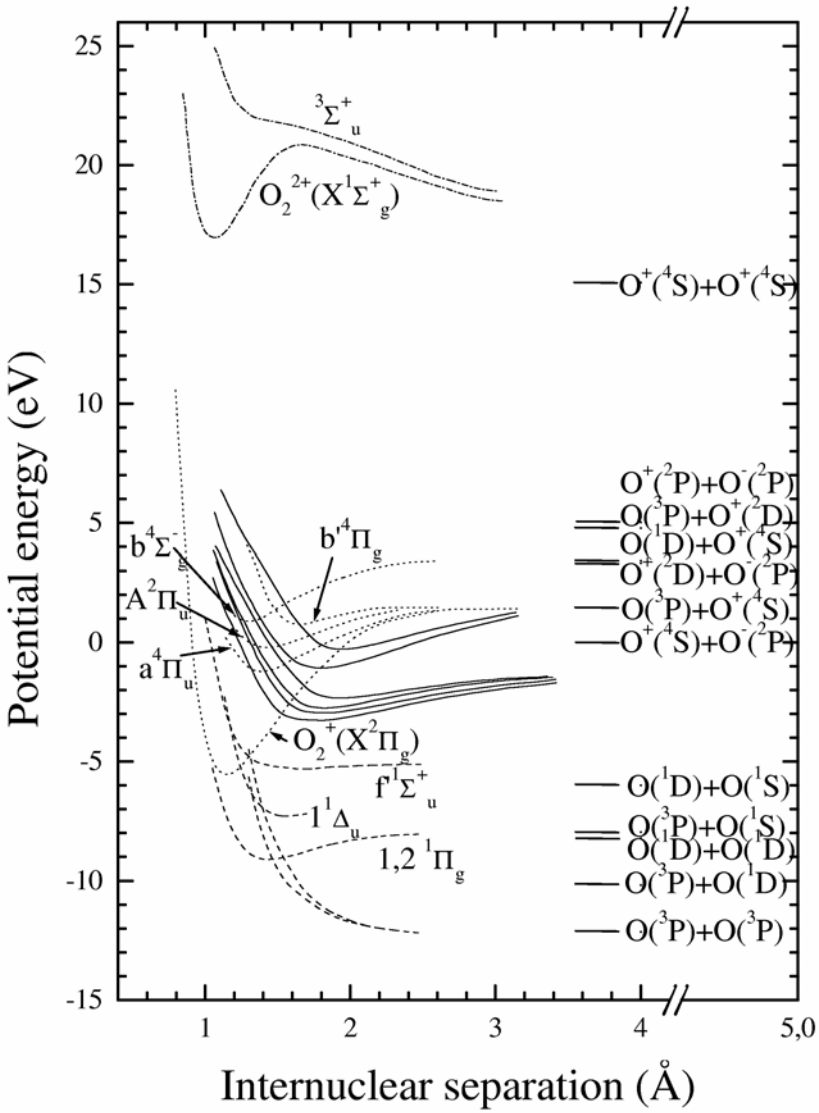
INTERPLAY



One gets: $\sigma=5.2\times10^{-13}$ cm^2 at 10 meV (for the grnd state)

LOWER EXPERIMENTAL VALUE
⇒EXCITED STATES POPULATED

Mutual neutralisation (Hayton and Peart) :
A LONG RANGE PROCESS (8.4 Å)



Molecular ionic states likely to be populated at low energies…

$X^2\Pi$, $a^4\Pi_{ui}$ and $A^2\Pi_u$

and further up in energy…
$b'^4\Pi_g$, $b^4\Sigma^-_g$, $C^2\Phi_u$…

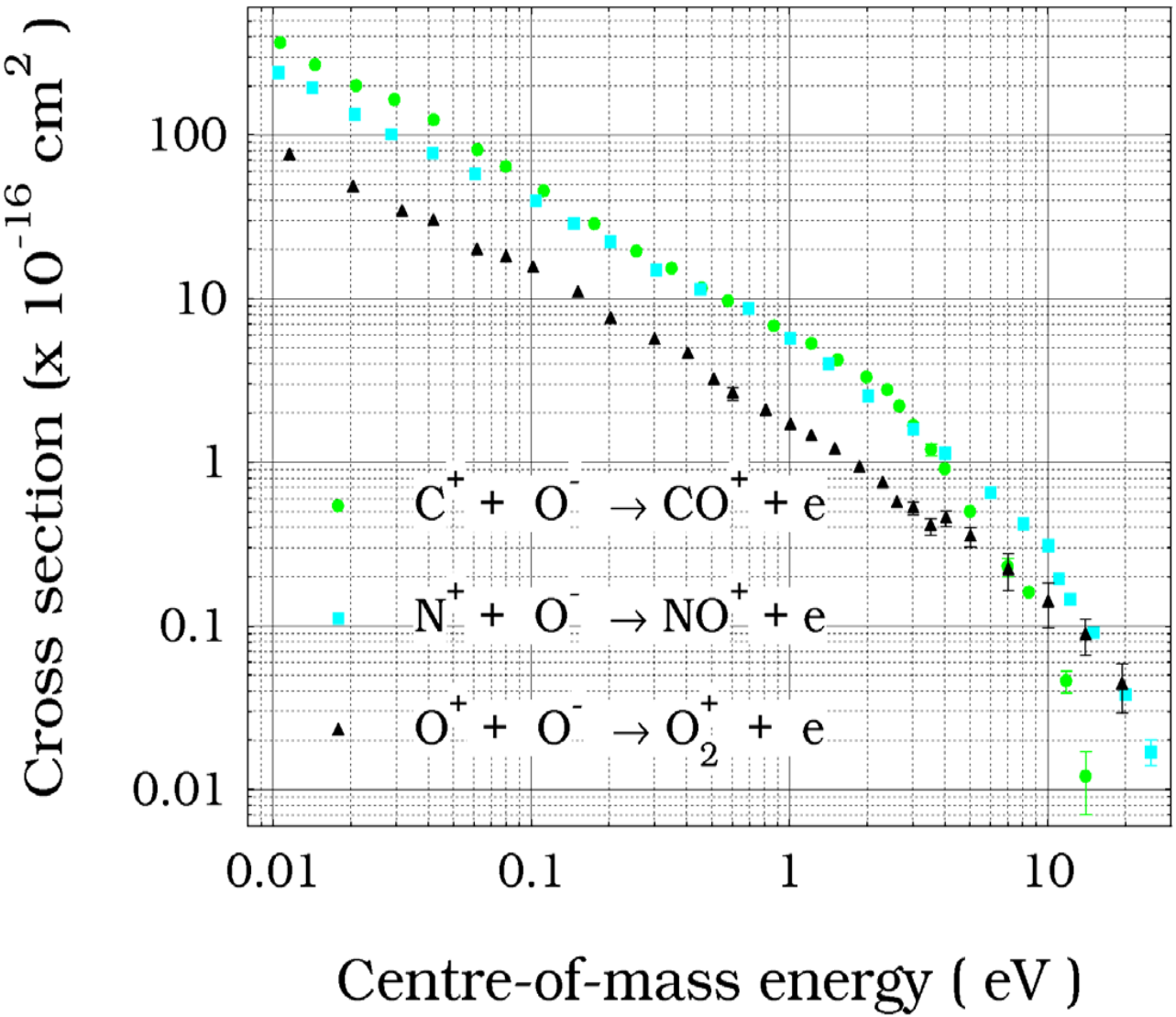
Correlation rules Wigner and Wittmer:

-8 states for the limit $O^+(^4S)+O^-(^2P)$

$^{3,5}\Sigma^+_{u,g}(1)$ and $^{3,5}\Pi_{u,g}(1)$

-36 states for the limit $O^+(^2D)+O^-(^2P)$

$^{3,5}\Sigma^+_{u,g}(2)$, $^{3,5}\Sigma^-_{u,g}(1)$, $^{3,5}\Pi_{u,g}(3)$, $^{3,5}\Delta_{u,g}(2)$ and $^{3,5}\Phi_{u,g}(1)$



$$\sigma_{AI}(E_{cm}) = \frac{\pi(N_{max}+1)^2\hbar^2}{2\mu E_{cm}}$$

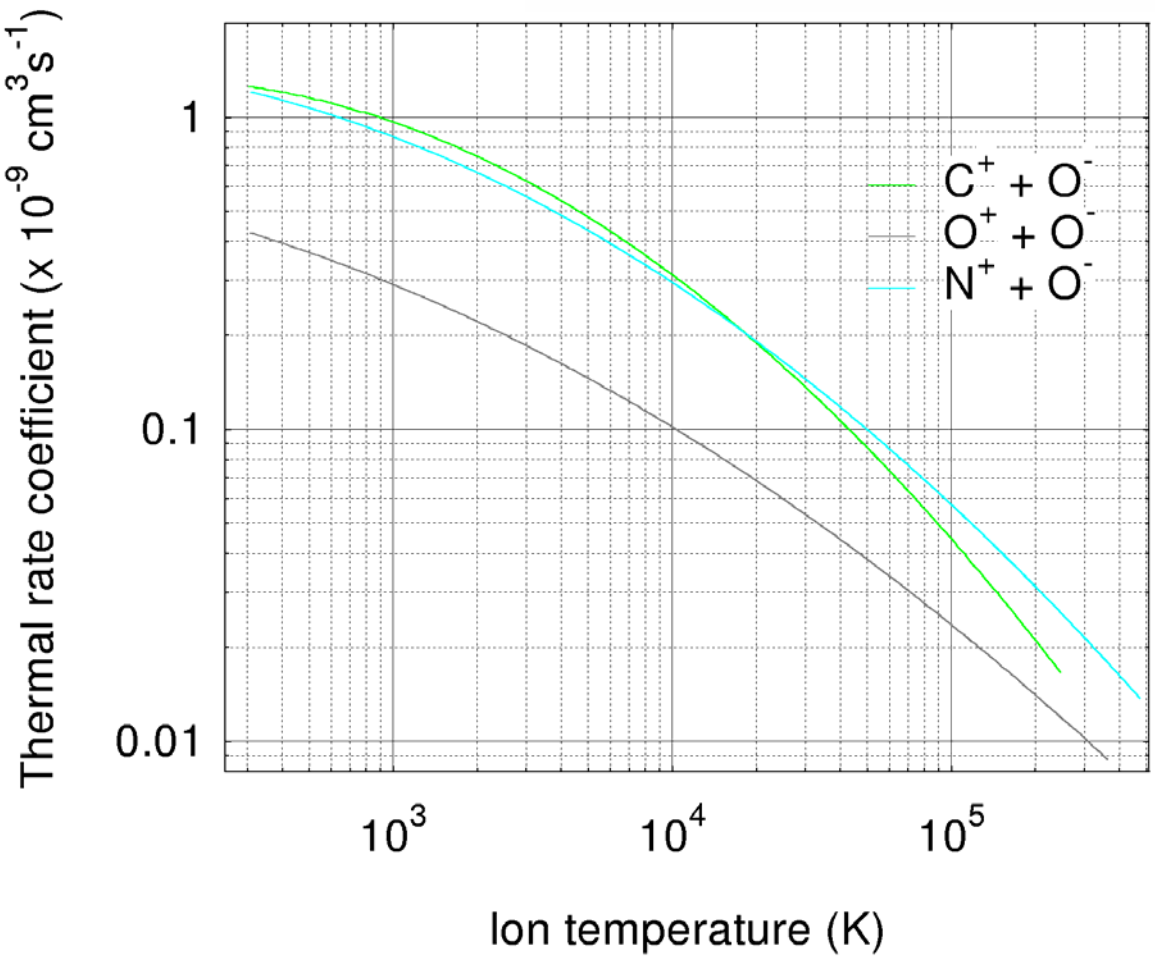
At a given E_{cm}

$\sigma\downarrow$ while $\mu\uparrow$

THIS WHAT IS OBSERVED!

THERMAL RATE COEFFICIENT

$$\alpha(T)=\frac{8\pi\mu}{(2\pi\mu k_B T)^{3/2}}\int_0^{\infty}\sigma(E_{cm})E_{cm}\exp(-E_{cm}/k_B T)dE_{cm}$$



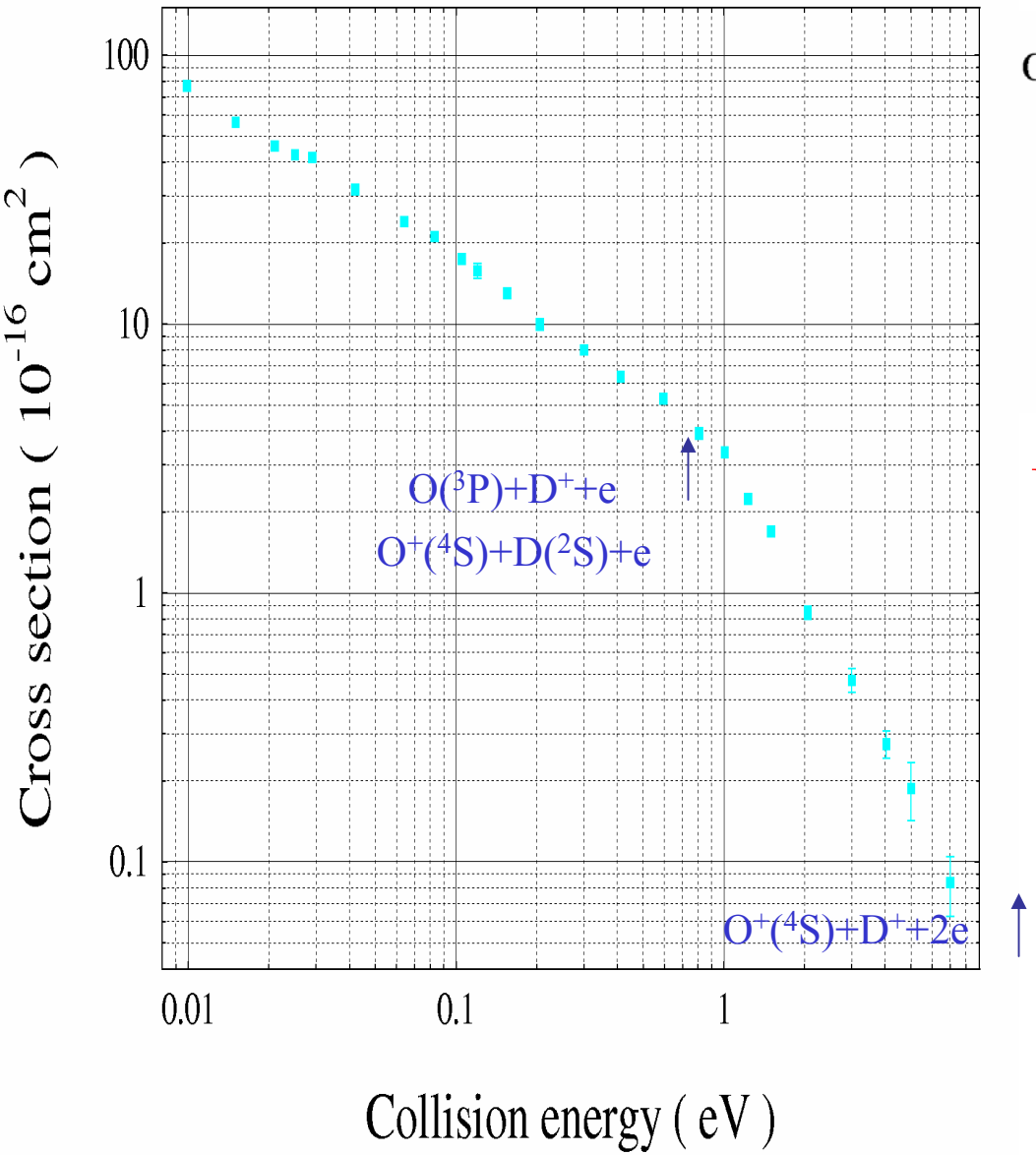
Work on $D^+ + O^-$ and $O^+ + D^-$

OH^+ detected in various environments:

- Interstellar clouds (its destruction leads to H_3O^+) (importance of the Dissociative Recombination)
- Comets
- Planetary atmospheres

HOW IS IT FORMED?

$$O^+ + D^- \rightarrow OD^+ + e$$

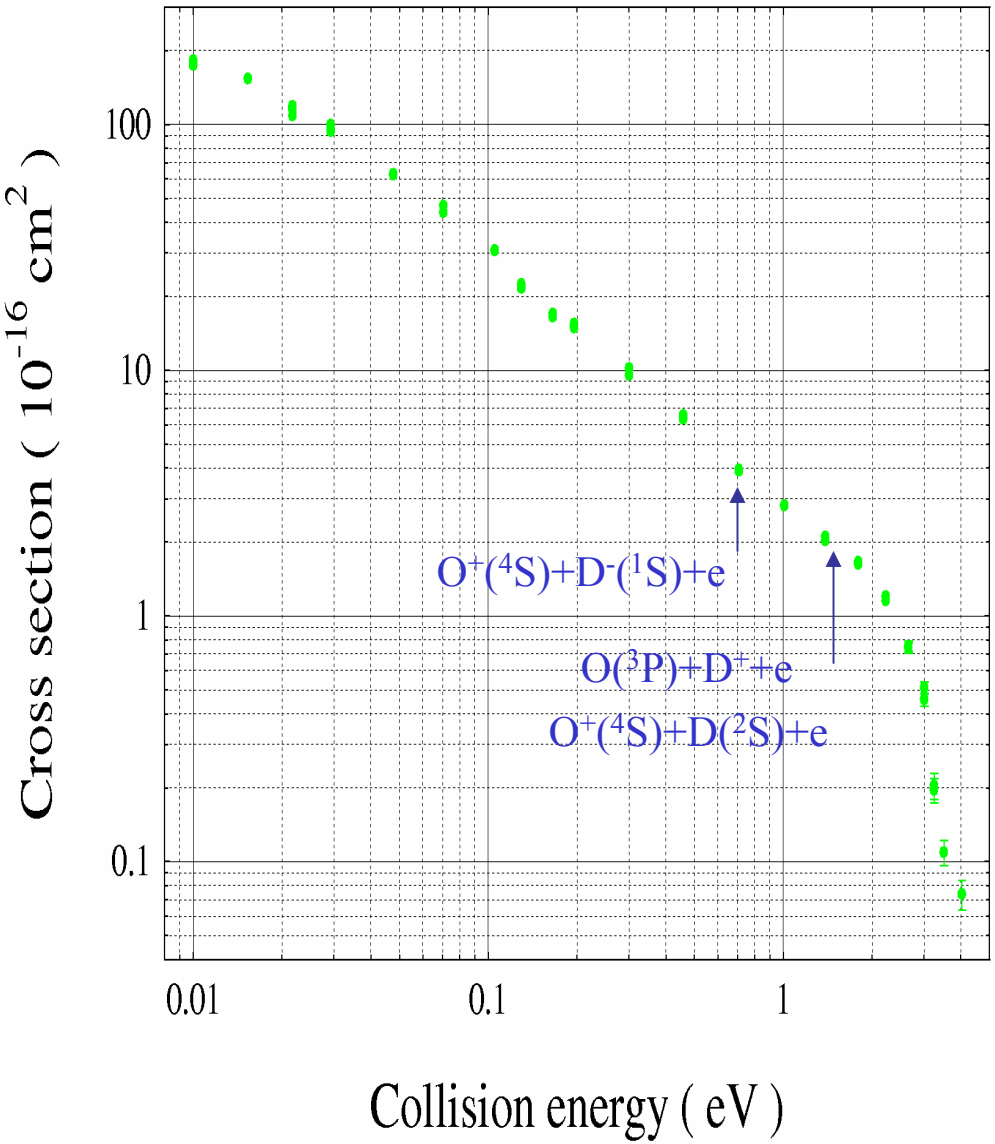


$O^+(^4S) + D^-(^1S)$

- $\rightarrow OD(X^2\Pi) + 17.25$ eV
- $\rightarrow O(^3P) + D(^2S) + 12.86$ eV
- $\rightarrow OD^+(X^3\Sigma^-) + 4.23$ eV
- $\rightarrow O^-(^2P) + D^+ + 0.72$ eV
- $\rightarrow O(^3P) + D^+ - 0.74$ eV
- $\rightarrow O^+(^4S) + D(^2S) - 0.76$ eV
- $\rightarrow O^+(^4S) + D^+ - 14.36$ eV

UNUSUAL LOW ENRGY DEPENDENCE !

$$O^- + D^+ \rightarrow OD^+ + e$$



$O^-(^2P) + D^+$

$\rightarrow OD(X^2\Pi) + 16.53$ eV

$\rightarrow O(^3P) + D(^2S) + 12.14$ eV

$\rightarrow OD^+(X^3\Sigma^-) + 3.51$ eV

$\rightarrow O^+(^4S) + D^-(^1S) - 0.72$ eV

$\rightarrow O(^3P) + D^+ - 1.46$ eV

$\rightarrow O^+(^4S) + D(^2S) - 1.48$ eV

$\rightarrow O^+(^4S) + D^+ - 15.08$ eV

$O^+(^4S)+D^+ +2e$

$$\sigma_{AI}(E_{cm}) = \frac{\pi(N_{max}+1)^2\hbar^2}{2\mu E_{cm}}$$

$\Rightarrow \sigma = 3.2 \times 10^{-13}$ cm^2 at 10 meV (for the grnd state)

LOWER THAN FOR THE ATMOSPHERIC GASES !!

Molecular ionic states likely to be populated at low energies…

$X^3\Sigma^-$, $a^1\Delta$, $b^1\Sigma^+$, and $A^3\Pi$

Correlation rules Wigner and Wittmer:

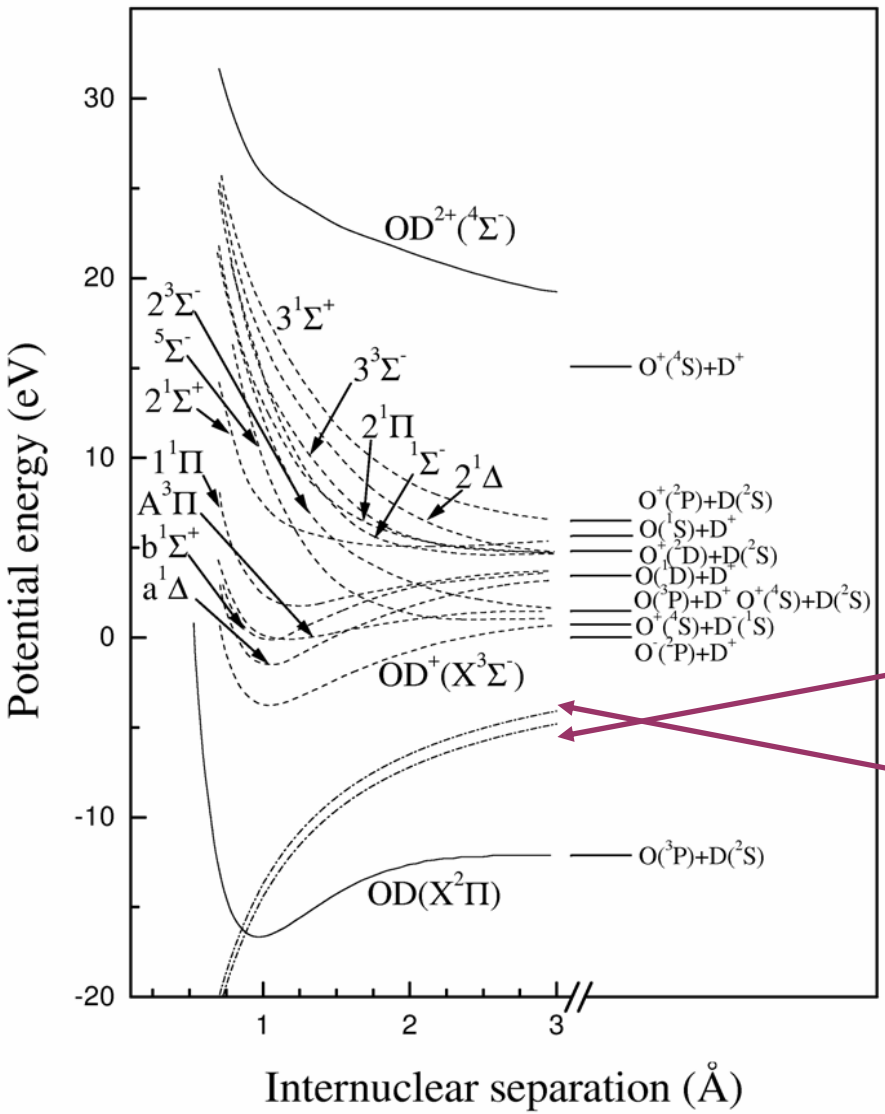
-2 states for the limit $D^+ + O^-(^2P)$

$^2\Sigma^+(1)$ and $^2\Pi(1)$

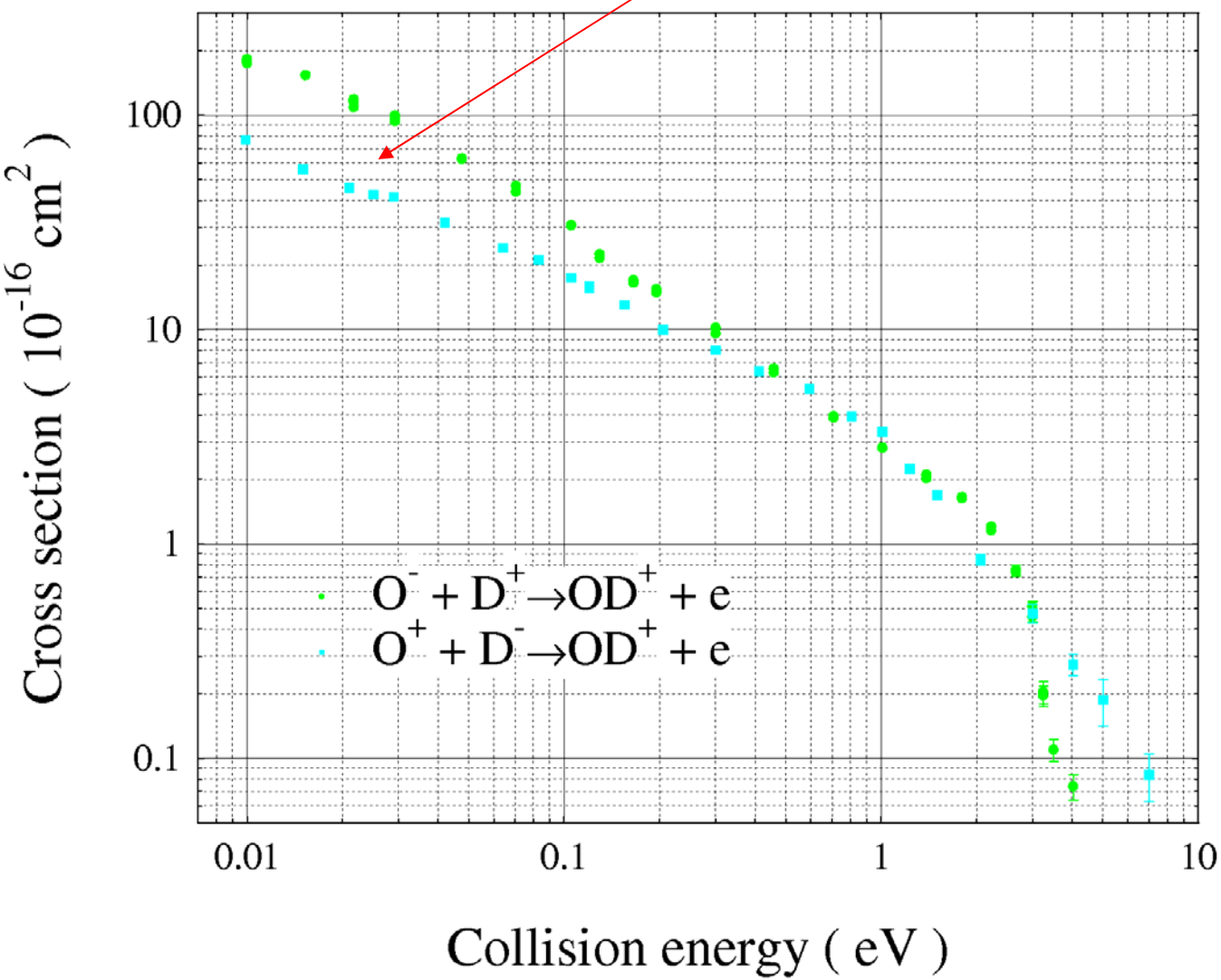
-6 states for the limit $O^+(^4S, ^2D, ^2P) + D^-(^1S)$

$^4\Sigma^-(1)$, $^2\Sigma^-(1)$, $^2\Pi(1)$, $^2\Delta(1)$, $^2\Sigma^+(1)$ and $^2\Pi(1)$

None of these states are known !!



The difference in magnitude is not understood at the present time!



Conclusion

- The associative ionization processes leading to CO^+, NO^+, O_2^+ and OD^+ are exothermic and quite efficient!
- There is a drastic lack of molecular data.
- The RIP and AI processes are very much connected and from that point of view, MB2 and CRYRING are complementary experimental techniques!

Acknowledgments

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W Zong

GH Dunn

N Djuric

The other members of the Molecular Physics Group