Insertion and abstraction mechanisms in collisions of O^- with H_2^+ and CH^+

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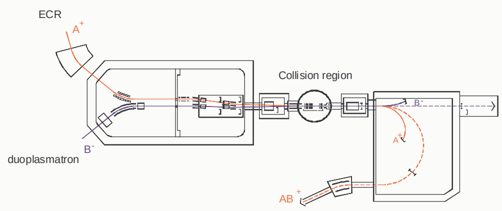
Experimental method: merged beams



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

$$F(z) = \frac{\int_L dz \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} j_1(x,y,z)\, j_2(x,y,z)\,dx\,dy}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} j_1(x,y)\,dx\,dy \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} j_2(x,y)\,dx\,dy}$$

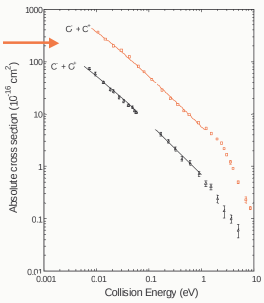
Difficulties to measure **true** cross sections at low energy

$$E_{coll} \approx \frac{\mu}{2} v_d^2$$

$$\sigma_{app} = \frac{\langle \sigma v \rangle}{v_d}$$

$$v_d = \left| \sqrt{\frac{2E_A}{M_A}} - \sqrt{\frac{2E_B}{M_B}} \right|$$

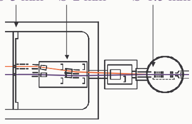
$$E_i = q_i (A_i - V_{obs}) \quad i = A,B$$



Numerical simulation of apparent cross sections at low collision energy

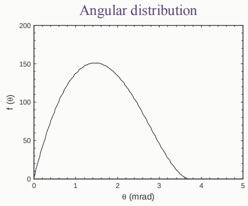
Reaction rate $\alpha = \int_0^\infty \sigma(v) f(v)\, v\, dv$ and $\sigma \propto E^{-1} \propto v^{-2}$

$$f(v) = \iiint g(v_1)\, g(v_2)\, f(\theta)\, \delta\left(v - \sqrt{v_1^2 + v_2^2 - 2 v_1 v_2 \cos\theta}\right) dv_1\, dv_2\, d\theta$$

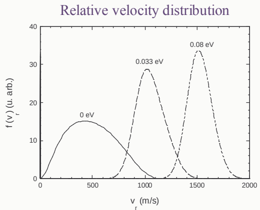


Beams = all possible trajectories delimited by the set of diaphragms

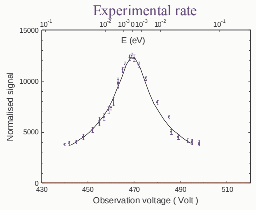
Angular distribution



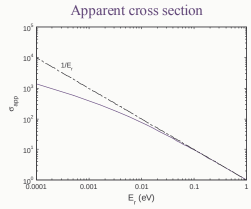
Relative velocity distribution



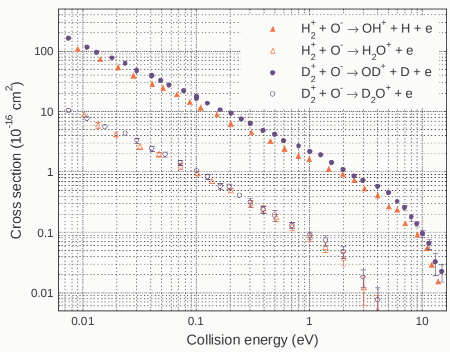
Experimental rate



Apparent cross section

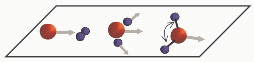


$H_2^+/D_2^+ + O^-$ collisions

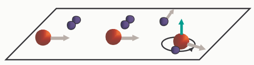


$$H_2^+(X\,^2\Sigma_g^+) + O^-(^2P) \rightarrow H_2O(\tilde{X}\,^1A_1) + 19.2\,eV$$
$$\rightarrow H_2(X\,^1\Sigma_g^+) + O(^3P) + 14.2\,eV$$
$$\rightarrow OH(X\,^2\Pi) + H(^2S) + 14.1\,eV$$
$$\rightarrow H(^2S) + H(^2S) + O(^3P) + 9.4\,eV$$
$$\rightarrow H_2O^+(\tilde{X}\,^2B_1) + e + 6.6\,eV$$
$$\rightarrow OH^-(X\,^1\Sigma^+) + H^+ + 2.3\,eV$$
$$\rightarrow OH^+(X\,^3\Sigma^-) + H^-(^1S) + 1.9\,eV$$
$$\rightarrow OH^+(X\,^3\Sigma^-) + H(^2S) + e + 1.1\,eV$$
$$\rightarrow OH(X\,^2\Pi) + H^+ + e + 0.5\,eV$$
$$\rightarrow H_2(X\,^1\Sigma_g^+) + O^+(^4S) + e + 0.3\,eV$$

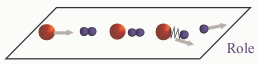
Associative ionisation : insertion mechanism



Proton transfer : insertion mechanism



Proton transfer : abstraction mechanism

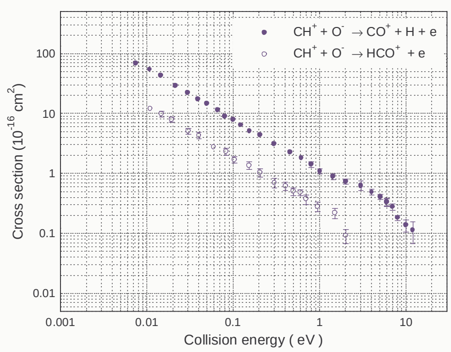


Role of autoionizing state?

- Propensity for OH^+ formation in agreement with H_2O^+ dissociative excitation experiments by Jensen *et al*
- Isotope effect : $\sigma_{OD^+}/\sigma_{OH^+} \cong \sqrt{2} = \sqrt{M_D/M_H}$

  characteristic time for autoionisation and/or rearrangement
- Next step : $HD^+(v\rightarrow 0) + O^- \rightarrow HDO^+ + e$ / $OD^+ + H + e$ / $OH^+ + D + e$

$CH^+ + O^-$ collisions



- Associative ionisation with same cross section as $H2^+ + O^-$ reaction
- CO^+ formation dominant but weaker due to stronger CH^+ bond

References

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