Orientation Effects in Ion–Molecule Collisions

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Collaborators

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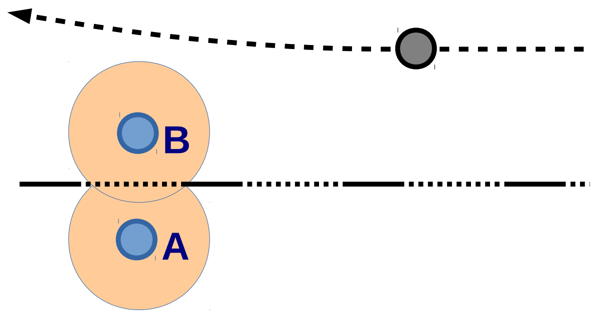
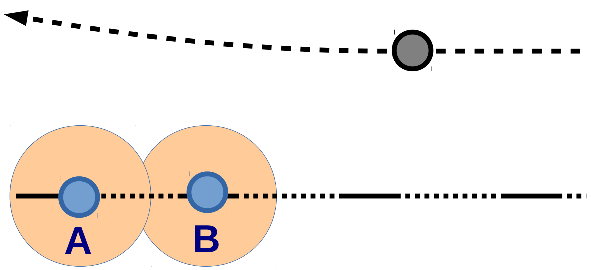
Introduction

- Molecules are not spherically symmetric, so the outcome of a collision between an ion and a molecule should depend on the relative angle between the molecular axes and the projectile direction

- Diatomic molecule aligned perpendicular to the incident projectile:
  - ⋆ projectile interacts mainly with the electron cloud of one atom
  - ⋆ low-charge molecular ions expected

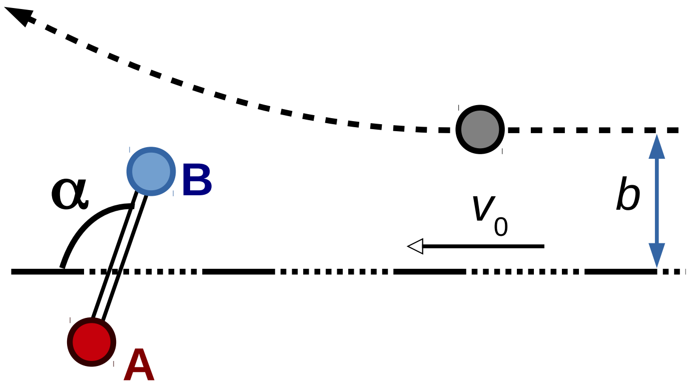


- Diatomic molecule aligned parallel to the incident projectile:
  - ⋆ projectile interacts equally with the electron cloud of both the atoms
  - ⋆ high-charge molecular ions expected

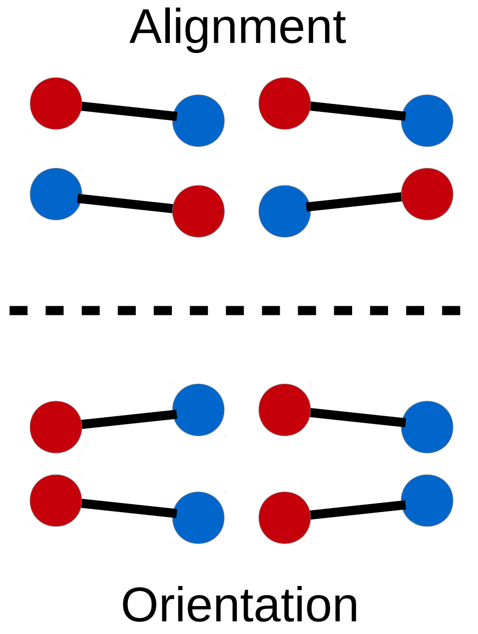


Introduction

- For a diatomic molecule there can be Alignment and Orientation
  - ⋆ Alignment implies axis parallel w.r.t the projectile
  - ⋆ Orientation implies alignment plus specific pointing



- Homonuclear diatomics:
  - ⋆ only alignment is meaningful
  - ⋆ Outcome of a collision: anisotropy possible, but forward-backward asymmetry not possible
- Heteronuclear diatomics:
  - ⋆ orientation is meaningful
  - ⋆ Outcome of a collision: there may be anisotropy as well as asymmetry



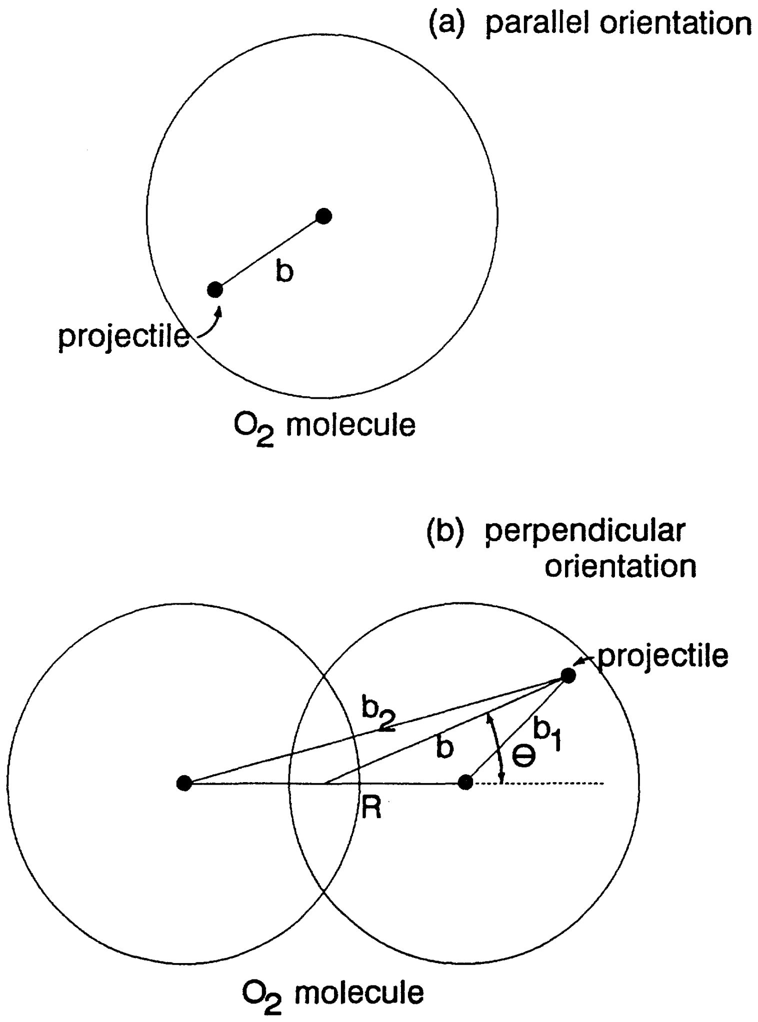
A simple theoretical model

Wohrer and Watson (1993 Phys Rev A)

- Assume independent atoms
- Add cross-sections for multiple ionisation of the two atoms in perpendicular and parallel orientations

Wang (1989 Phys Rev A)

- Added scattering amplitudes instead of cross-sections

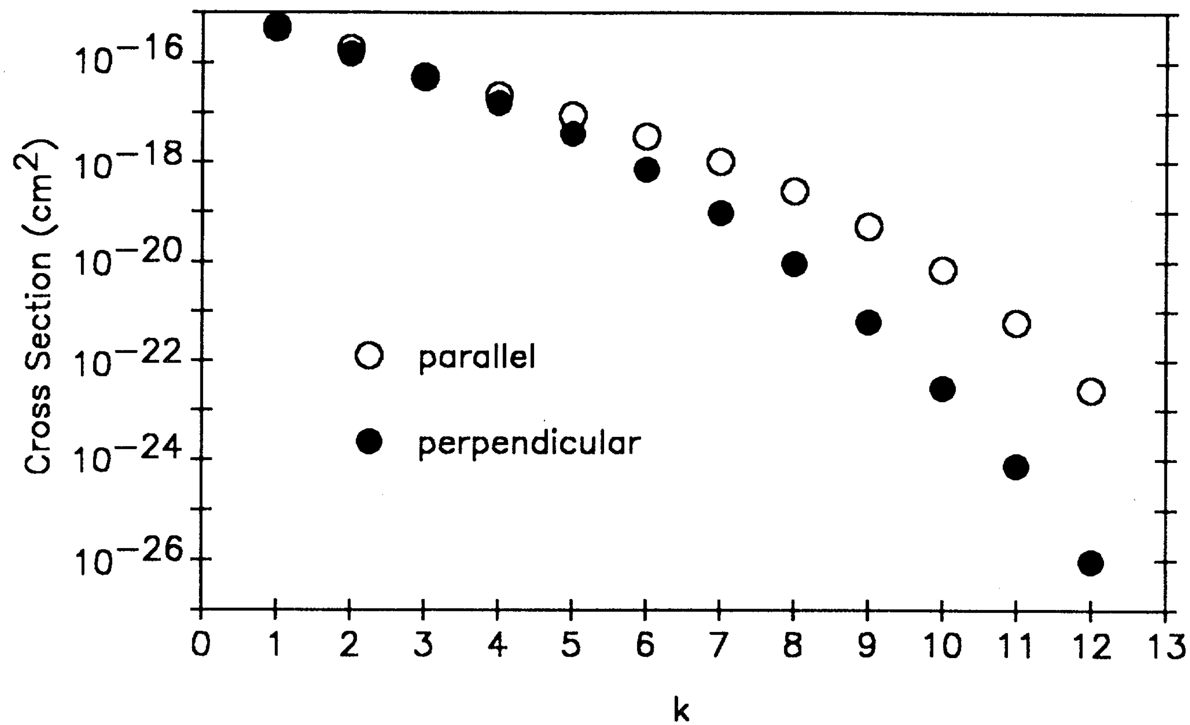


(end-view, along the projectile)

A simple theoretical model

Wohrer and Watson (1993 Phys Rev A)

- Ionization cross sections are calculated in the independent electron approximation
- Predicted different cross-sections for O_2^{k+} $(k = 1 \dots 12)$



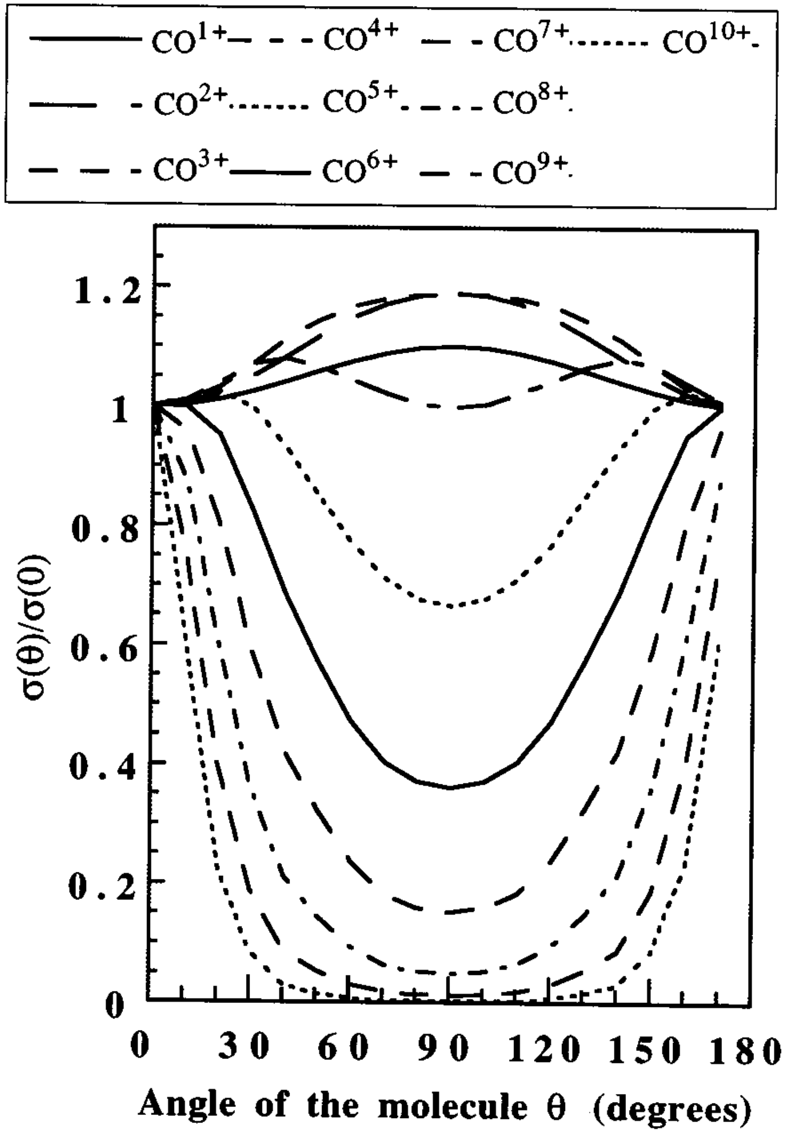
A simple theoretical model

Caraby et al. (1997 Phys Rev A)

- Applied the Wohrer–Watson model to CO^{q+} fragmentation and
- Predicted a symmetric distribution around 90° w.r.t. projectile

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}[1 + \beta P_2(\cos\theta)]$$

- β is a measure of enhancement or depletion of yield along the perpendicular direction relative to an anisotropic distribution



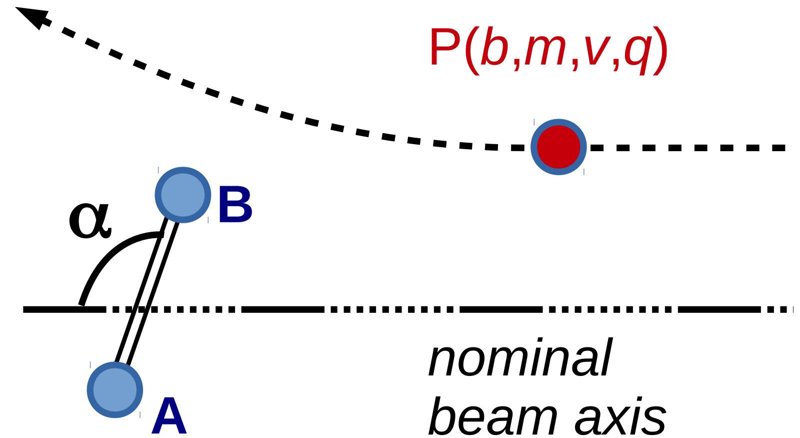
Experimental Strategy

Difficulty:
Molecules in an ensemble (e.g. in a cell or a jet) are randomly oriented. How do we determine orientation effects in the interaction?

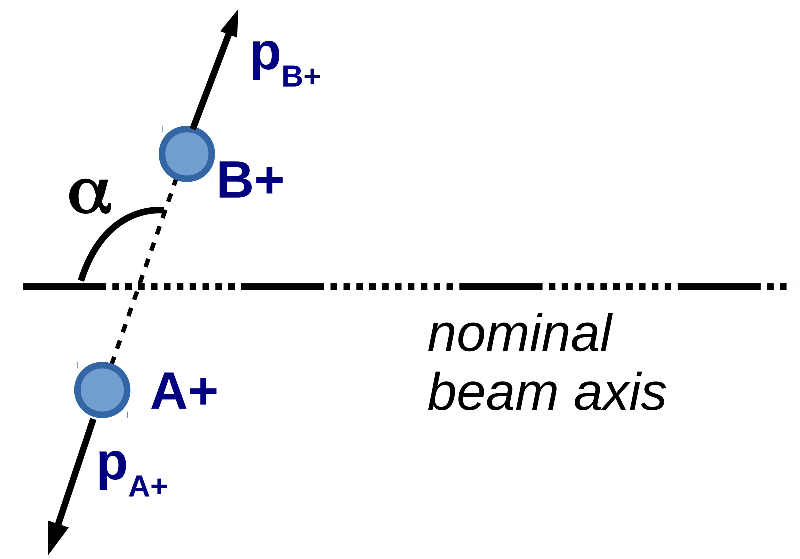
Way out:
Difficulty can be overcome in some processes
– viz. multiple ionisation leading to dissociation

Experimental Strategy

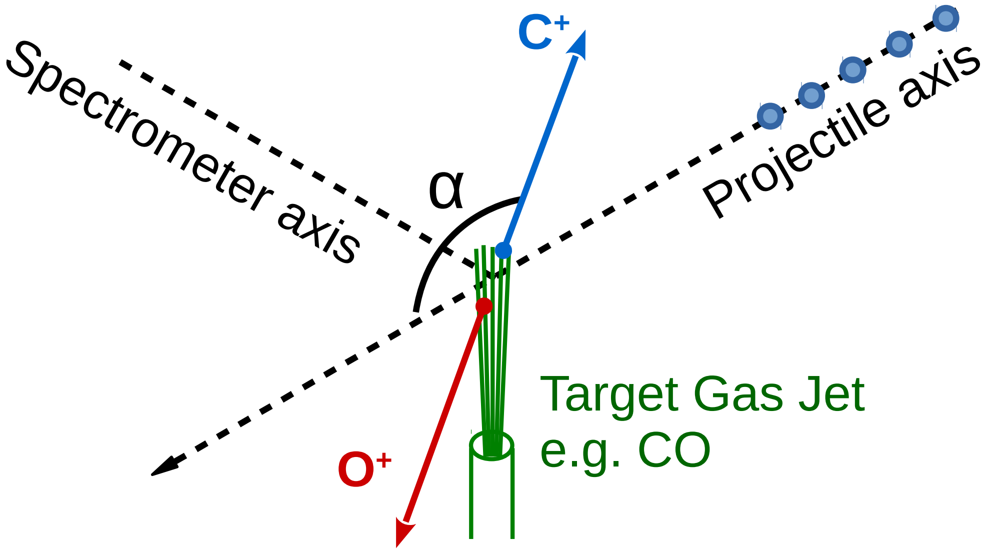
- Under single collision condition
  - ⋆ direction of fragments can be related to the molecule's orientation
  - ⋆ need mass and velocity vector of each fragment for every collision



- Assumptions
  - ⋆ collision times are shorter than rotational times
  - ⋆ initial momentum of the parent molecule is much smaller than the fragment momentum
  - ⋆ For ionic fragmentation
    lab-frame ≡ molecular frame



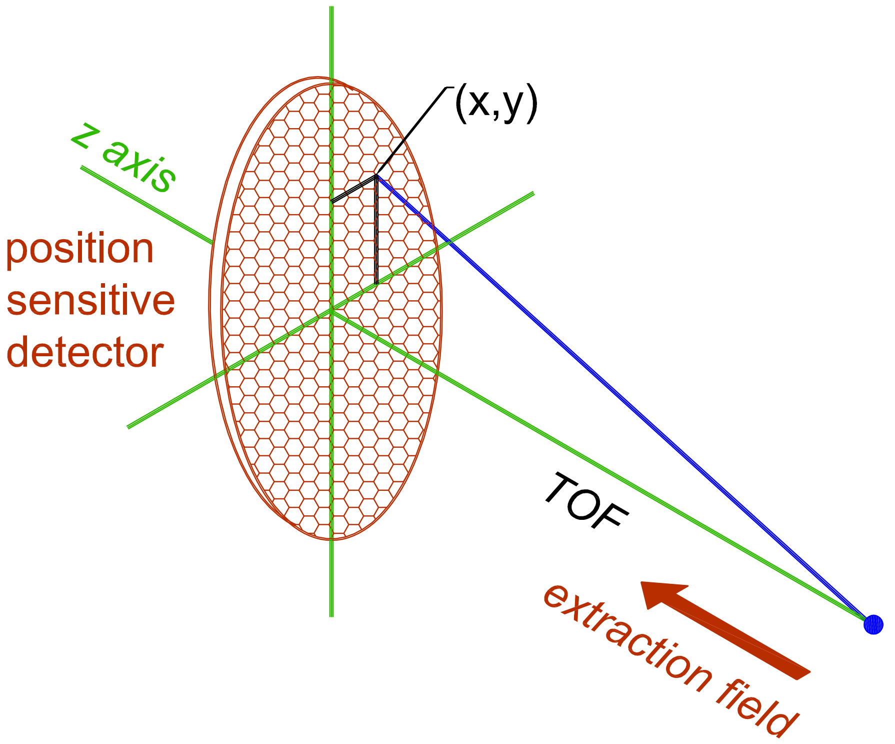
Experimental Strategy



- measure three momentum components of each ion for each event
- obtain ejection angle w.r.t. projectile axis event-by-event
- extract dissociation probability as a function of angle from the list mode data
- in the present case the angle is referred to $\vec{P}_C$

Measurement of ion momentum

- spatial and temporal dispersion of charged particles in a uniform electric field
- simultaneous measurement of flight-time and spatial spread
- requires an internally cold, well-localised source of particles



- For $p_z = 0$

$$t_0 = [8s/E]^{1/2}\,(m/q)^{1/2}$$

- For $\vec{p} \neq \vec{0}$

$$\begin{aligned} p_z &\approx (t - t_0)qE \\ p_x &= m(x - x_0)/t \\ p_y &= m(y - y_0)/t \end{aligned}$$

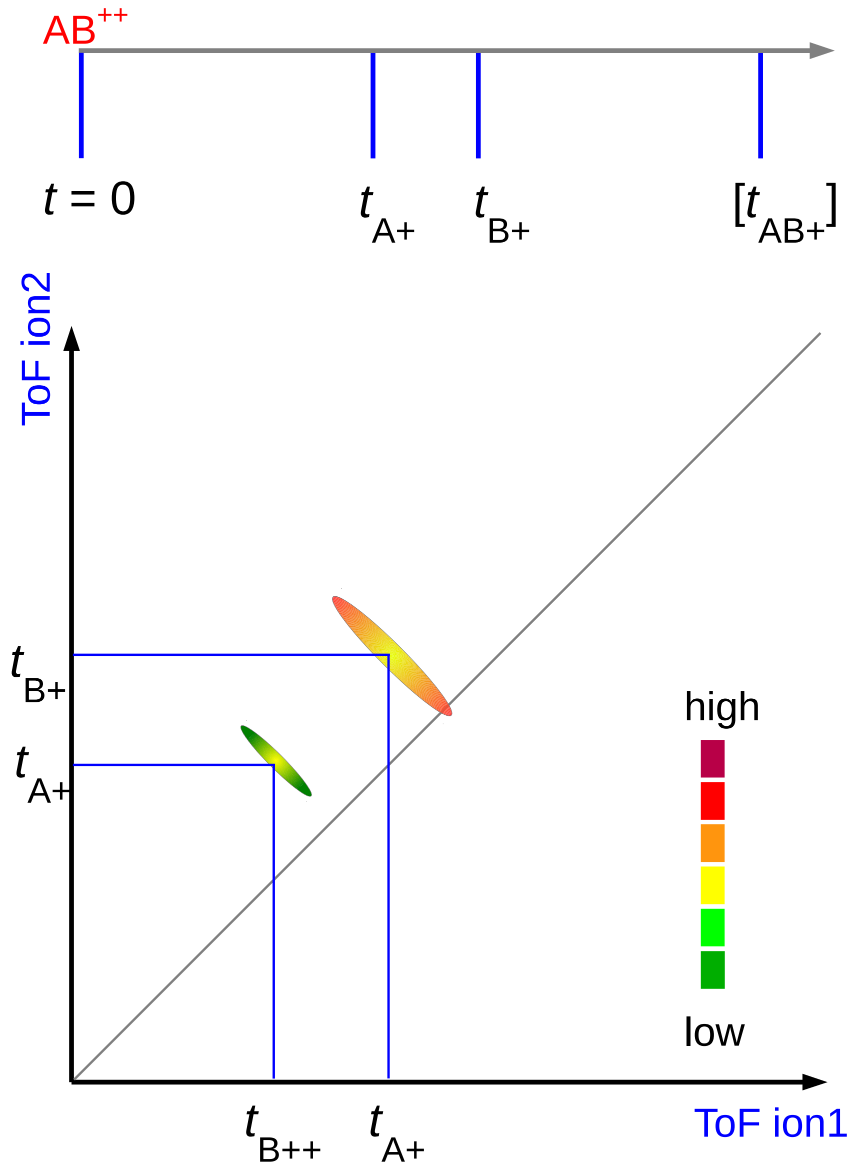
Detecting multiple ions in coincidence

- Aim: measurement of momenta of fragments in reactions of type

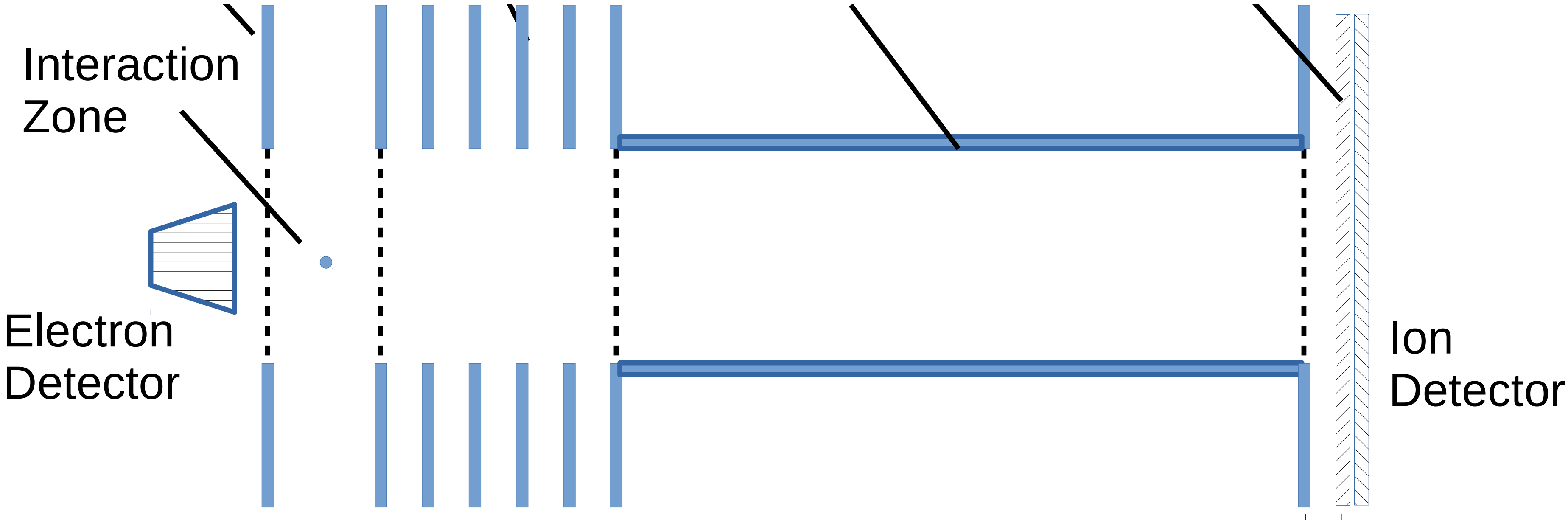
$$AB \rightarrow AB^{n+} \rightarrow A^{m+} + B^{(n-m)+}$$

- Strategy: Record both ions arising from one event, build a correlation map

- list mode record of all events



Collisions with CO



Projectiles used:

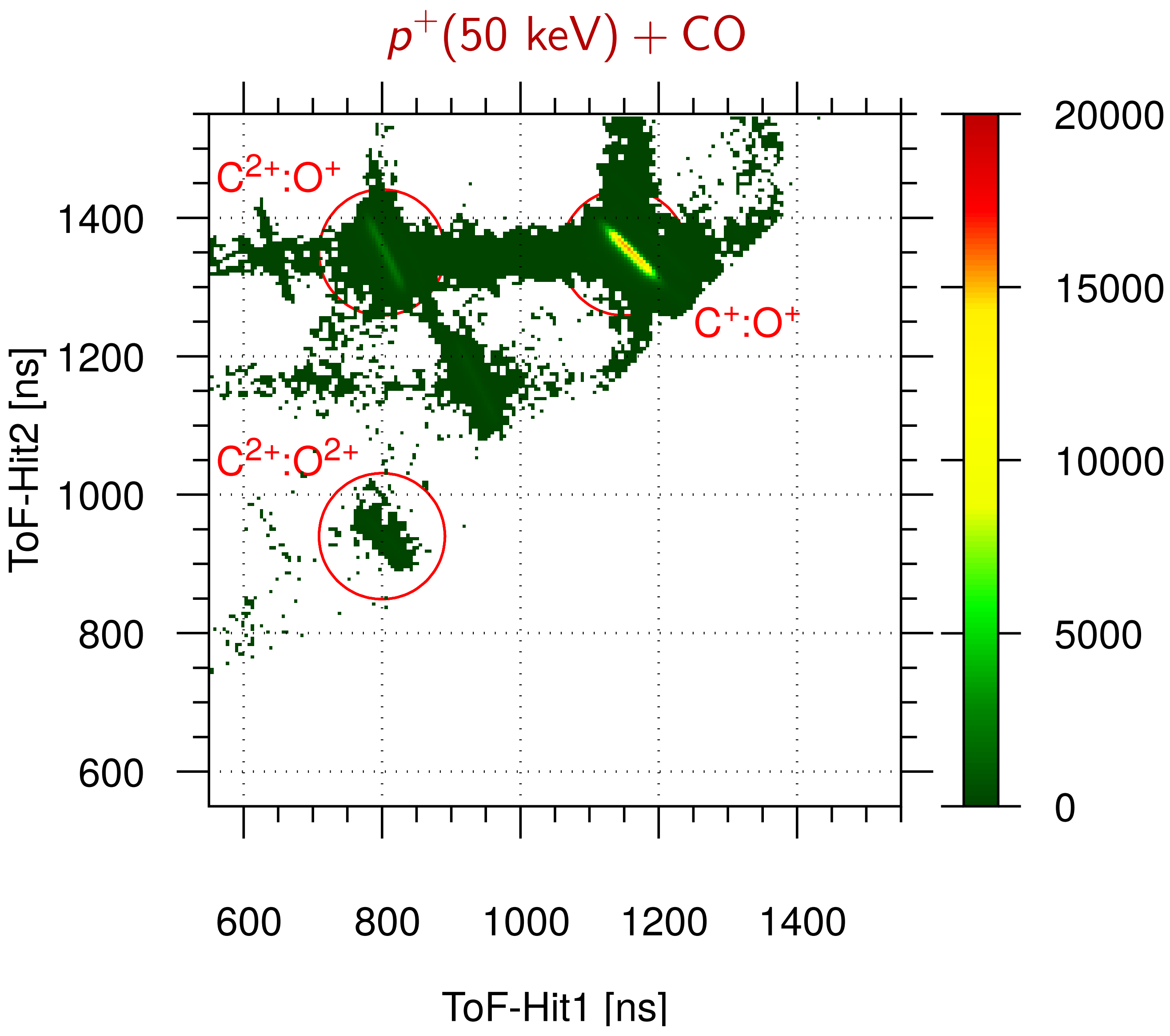
p^+	25–200 keV	q/v=1. . . 0.35
Xe^{9+}	450 keV	$q/v = 24$

Collisions with CO

Results for two distinct perturbations:

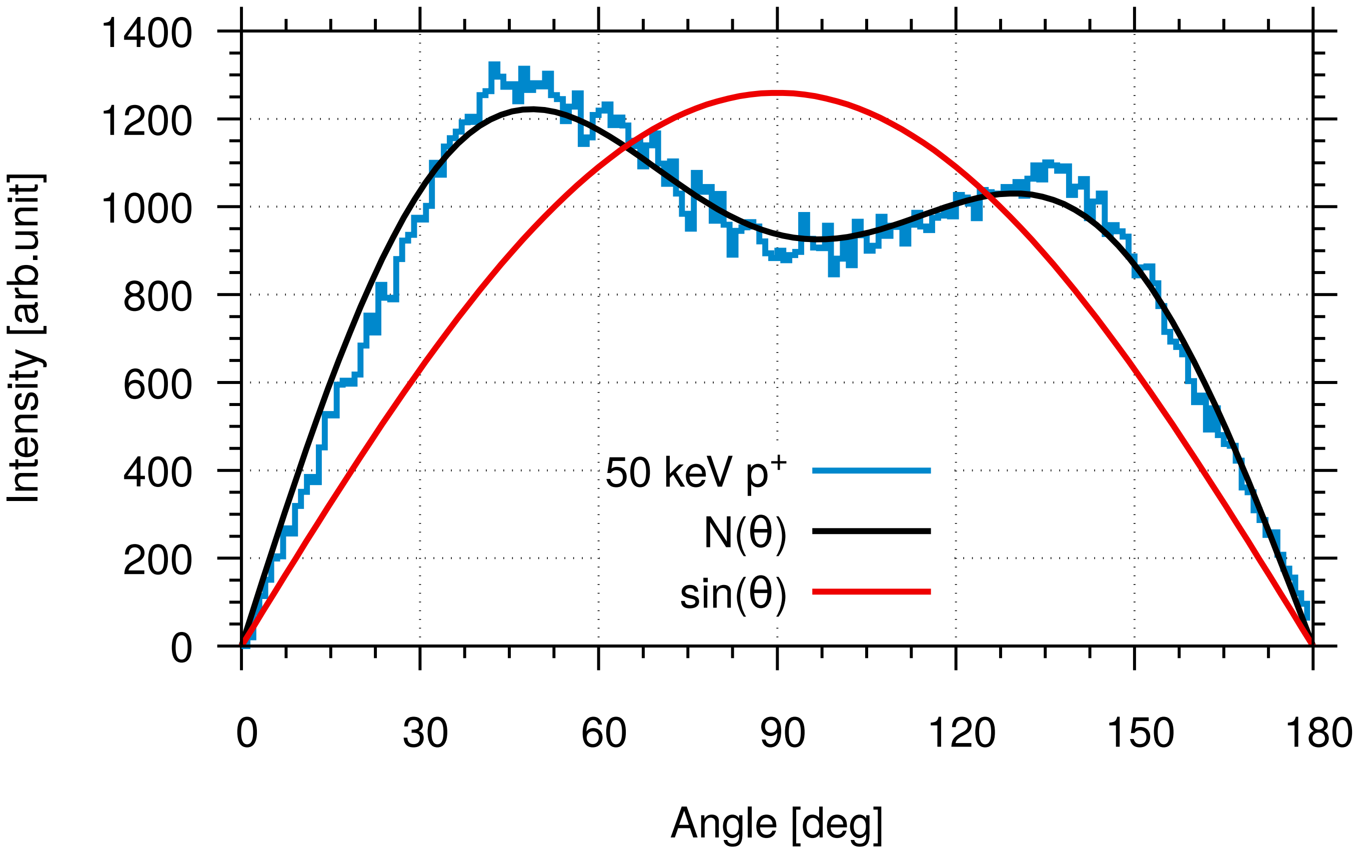
p^+	50 keV	$q/v \approx 0.7$
Xe^{9+}	450 keV	$q/v = 24$

Collisions with CO



Collisions with CO

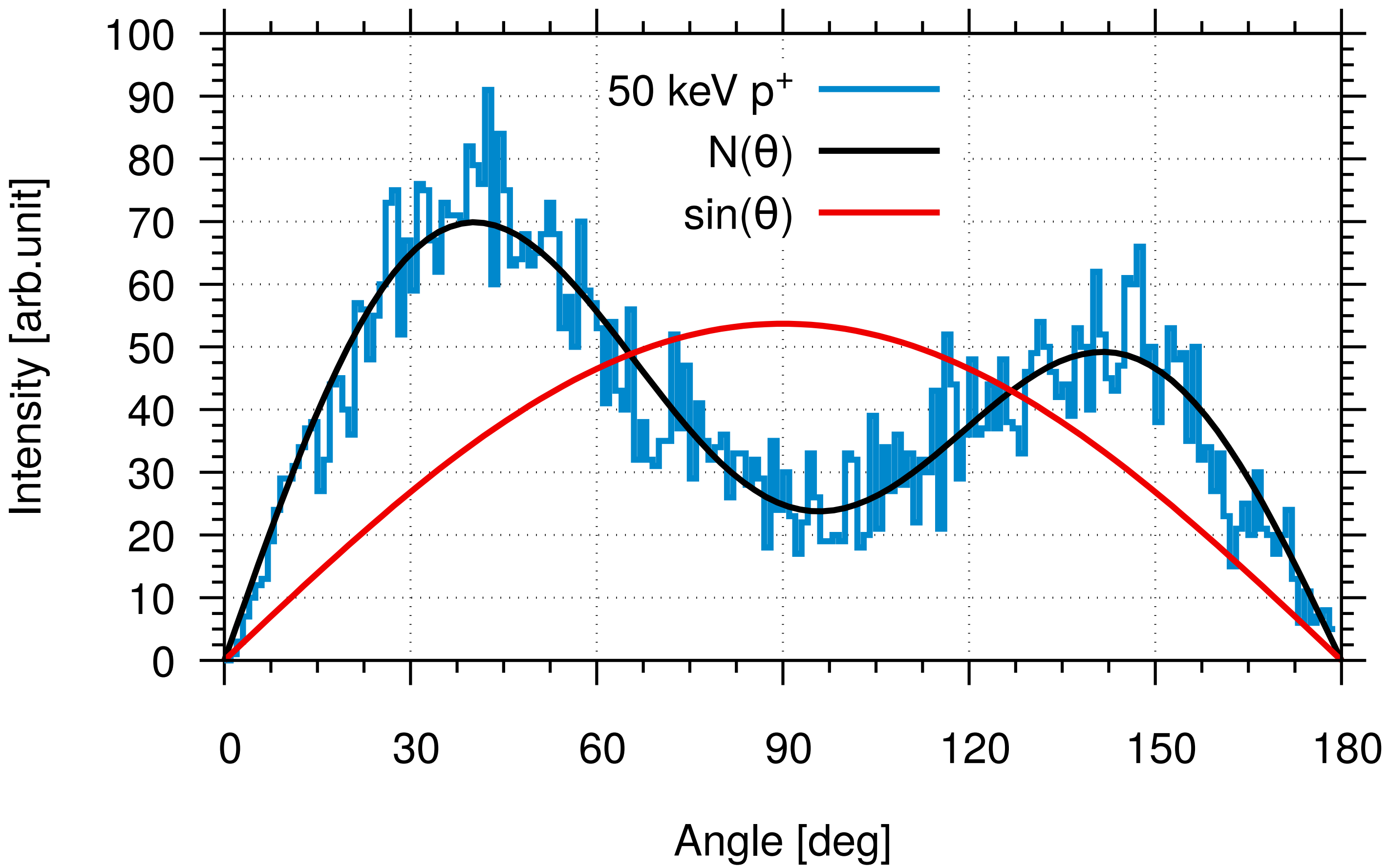
$p^+(50\text{ keV}) + \text{CO} \rightarrow \text{CO}^{3+}$



$$N(\theta) = N_0[1 + \beta_1 P_1(\cos\theta) + \beta_2 P_2(\cos\theta)] \sin\theta$$

Collisions with CO

$p^+(50\text{ keV}) + CO \to CO^{4+}$



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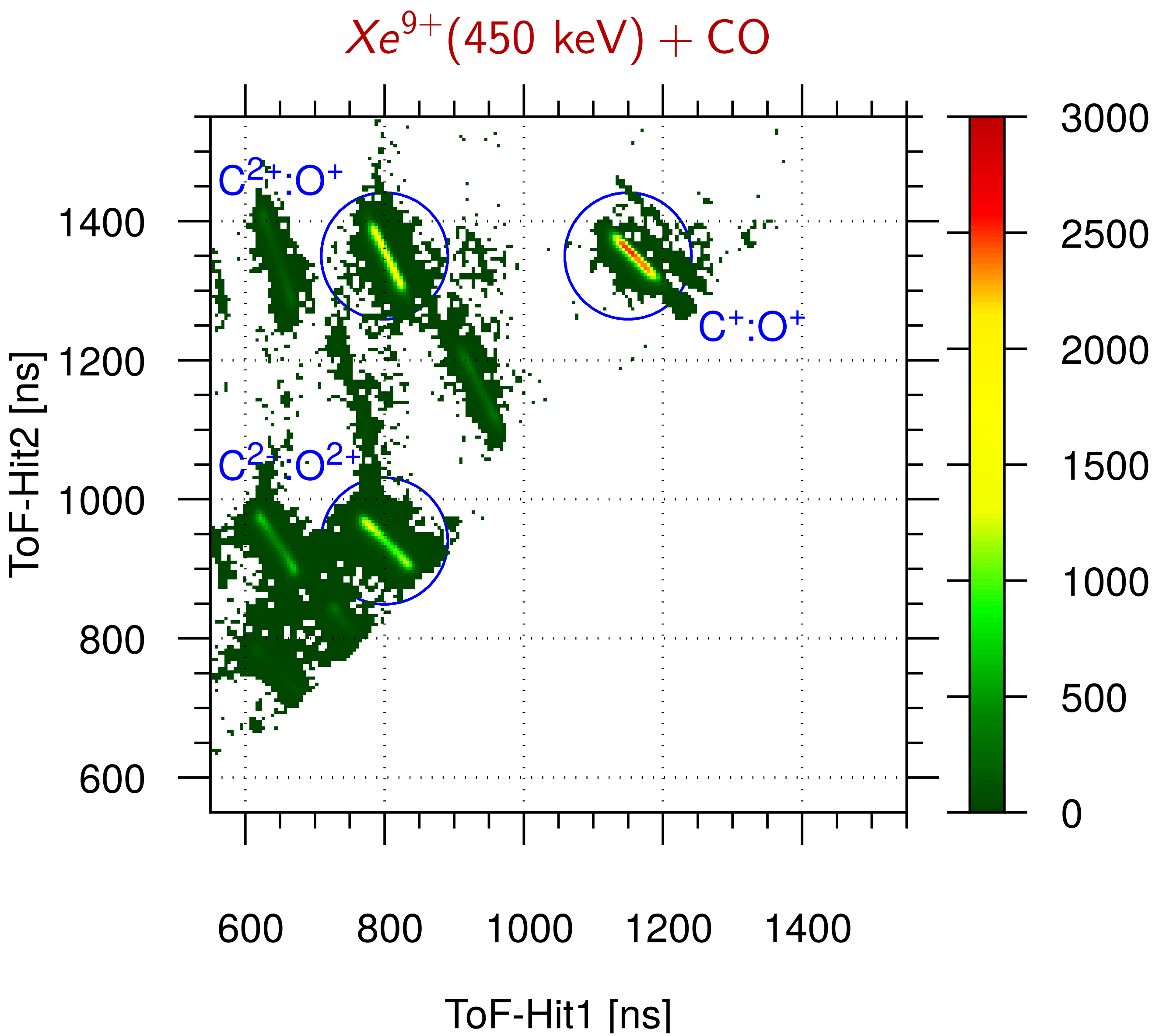
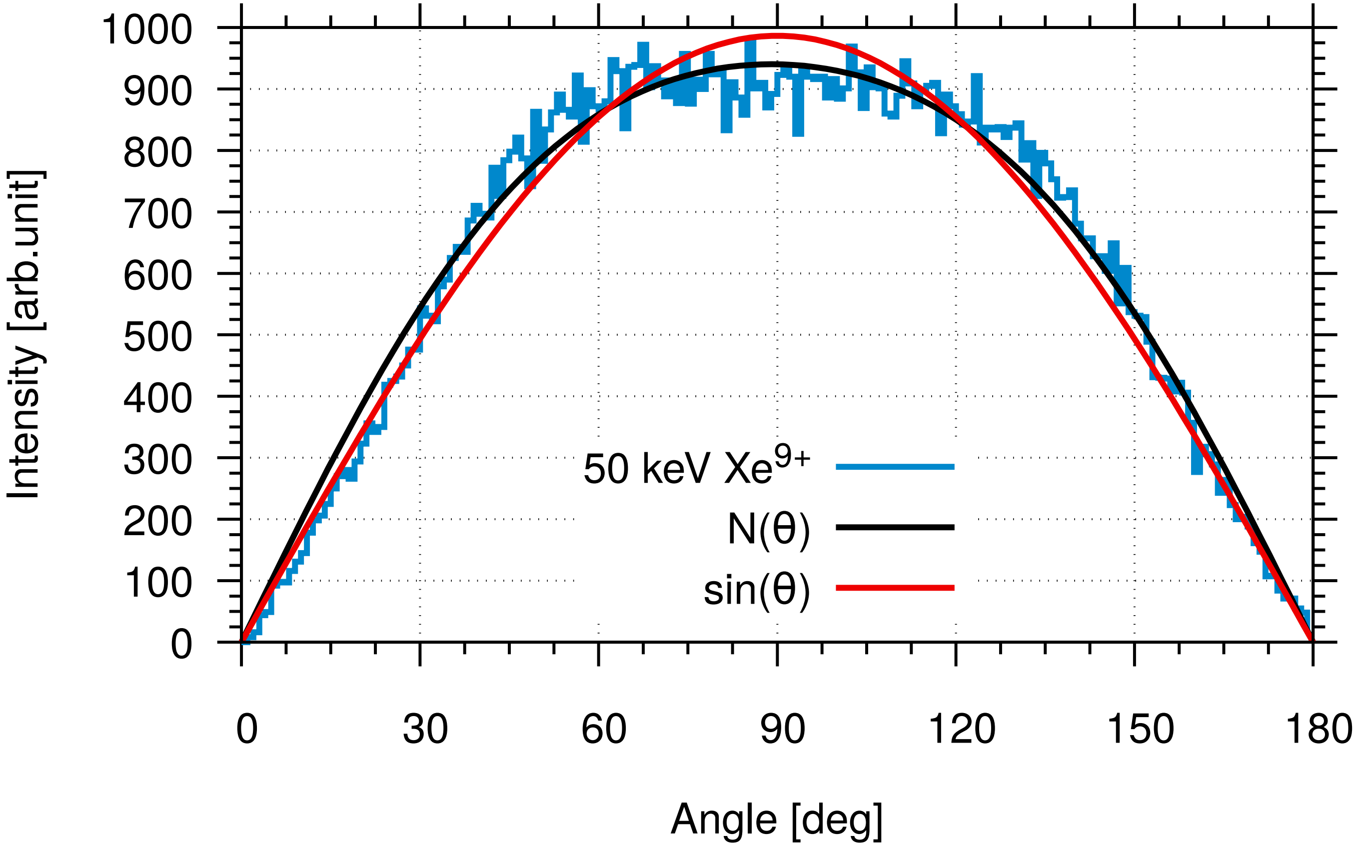
Collisions with CO



Collisions with CO

$Xe^{9+}(450\ \text{keV}) + CO \rightarrow CO^{3+}$



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Collisions with CO

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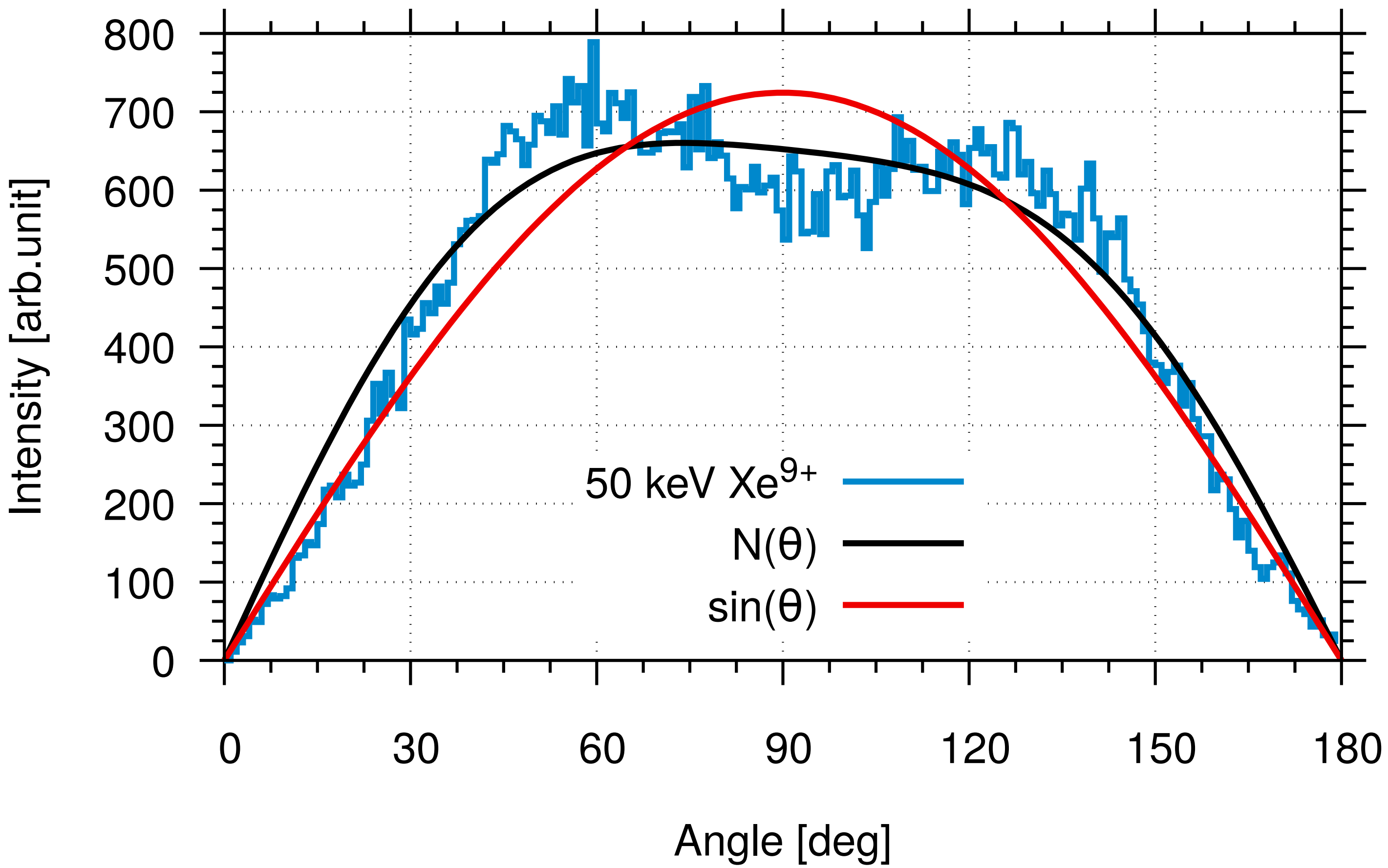


$$N(\theta) = N_0[1 + \beta_1 P_1(\cos\theta) + \beta_2 P_2(\cos\theta)]\sin\theta$$

Collisions with CO

- Xe^{9+} on CO $(q/v = 24)$
  - ⋆ Nearly isotropic fragmentation for CO^{2+}, CO^{3+} and CO^{4+} channels
  - ⋆ $\beta_1 \approx 0, \beta_2 \approx 0$

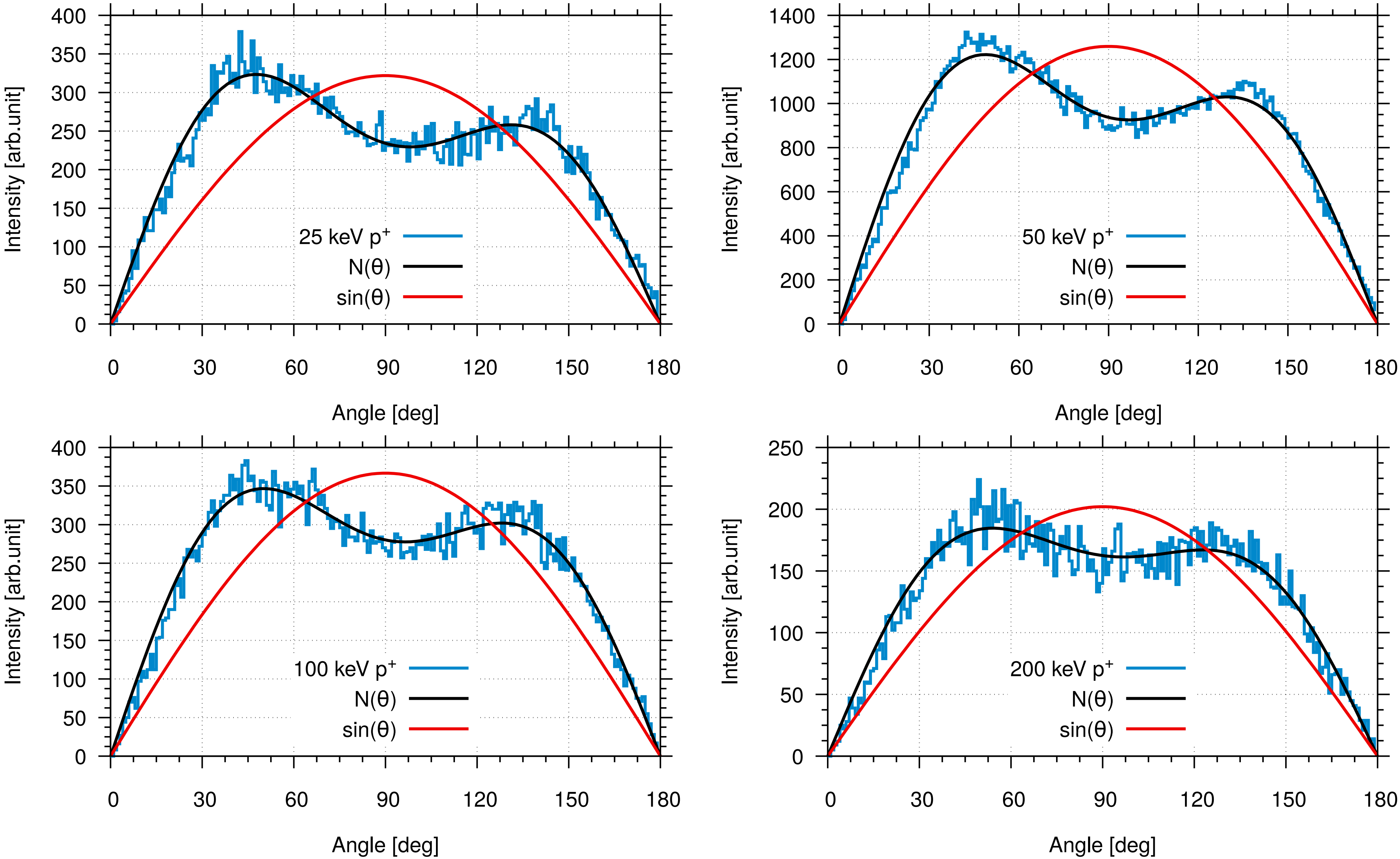
- p^+ on CO $(q/v = 0.7)$
  - ⋆ CO^{2+} fragmentation : isotropic fragmentation
    $\beta_1 \approx 0, \beta_2 \approx 0$
  - ⋆ CO^{3+} fragmentation: strong orientation dependence
    $\beta_2 = 0.63 \pm 0.01,\ \beta_1 = 0.14 \pm 0.001$
  - ⋆ CO^{4+} fragmentation: stronger orientation dependence
    $\beta_2 = 1.22 \pm 0.03,\ \beta_1 = 0.33 \pm 0.02$

Projectile Velocity Dependence

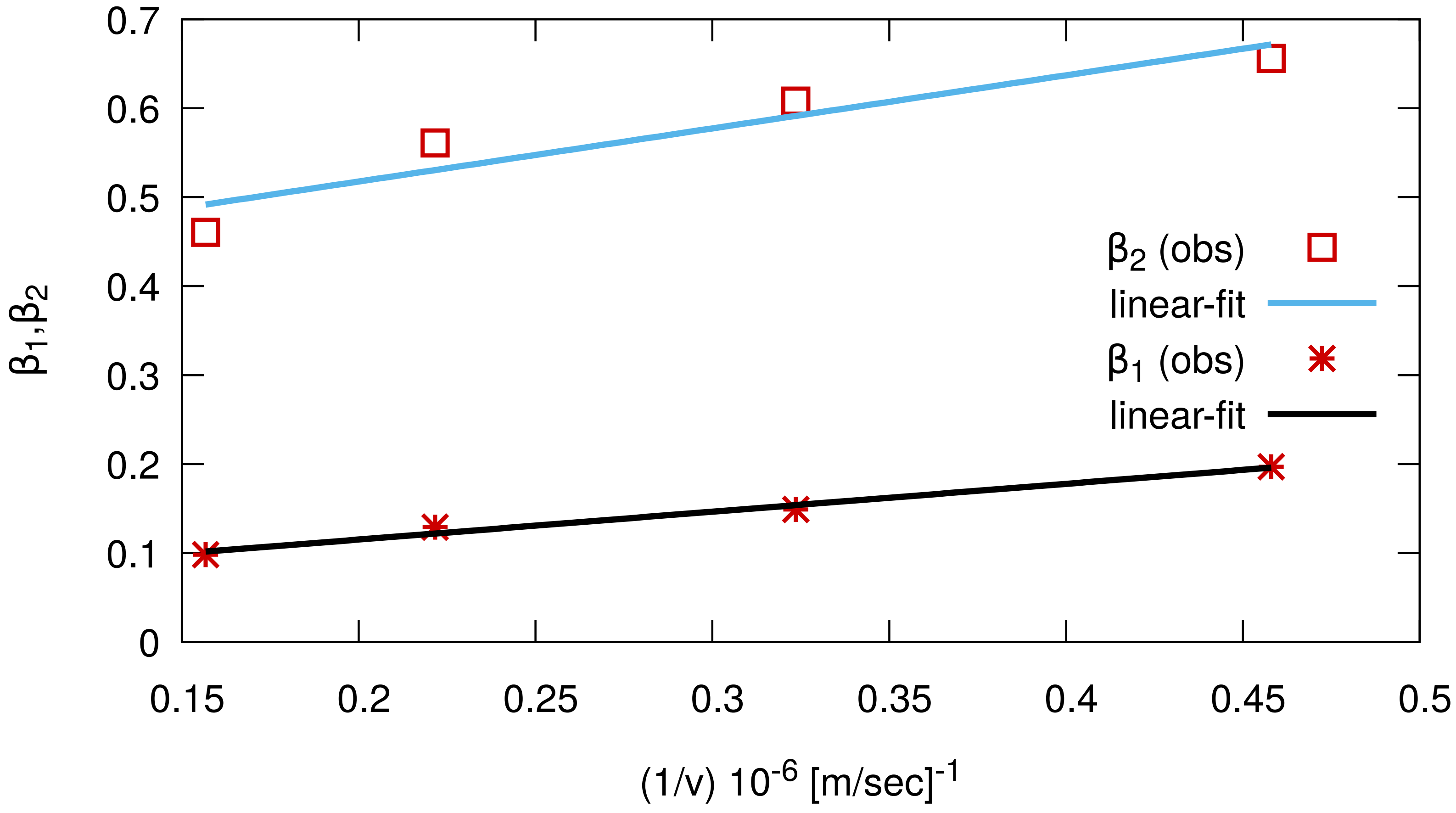
Results for same projectile at different velocities:

p^+ 25 keV–200 keV ($q/v = 1 \ldots 0.35$ au)

Projectile Velocity Dependence – CO^{3+}



Projectile Velocity Dependence – p+ on CO

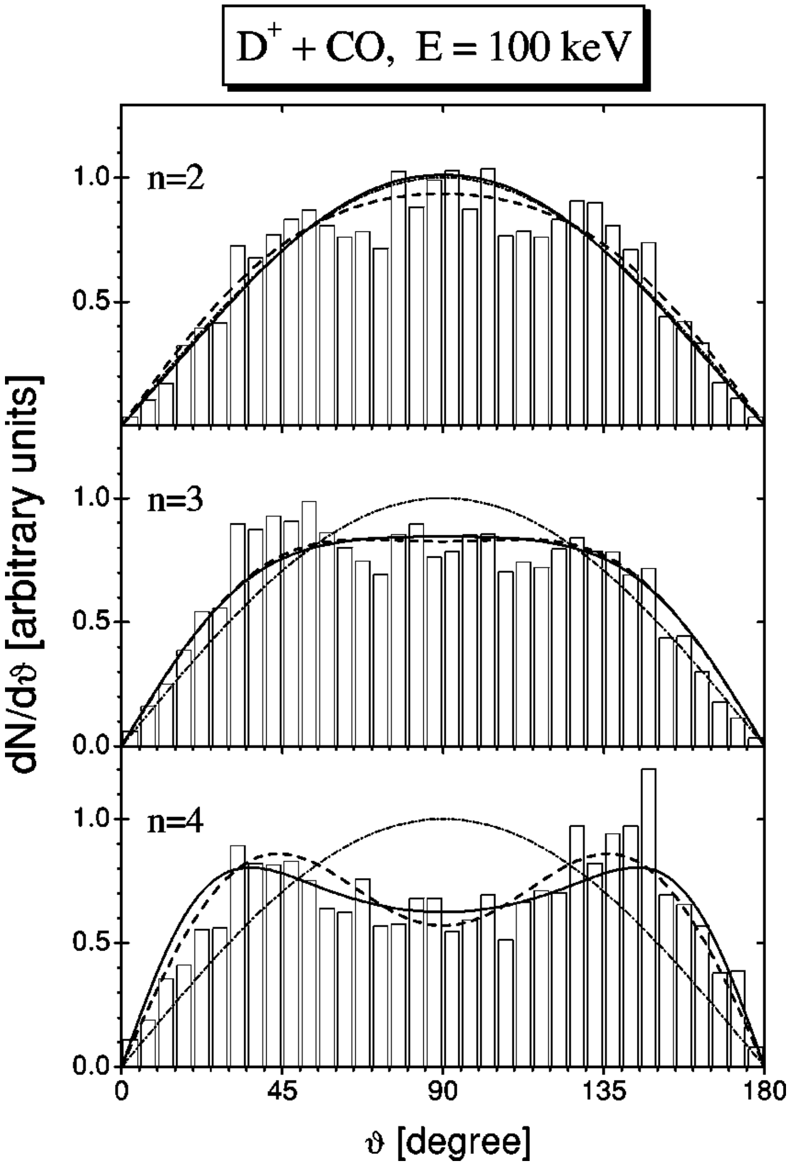


Anisotropy, as well as forward–backward asymmetry, increase with deceasing velocity.

Previous Experimental Result : CO

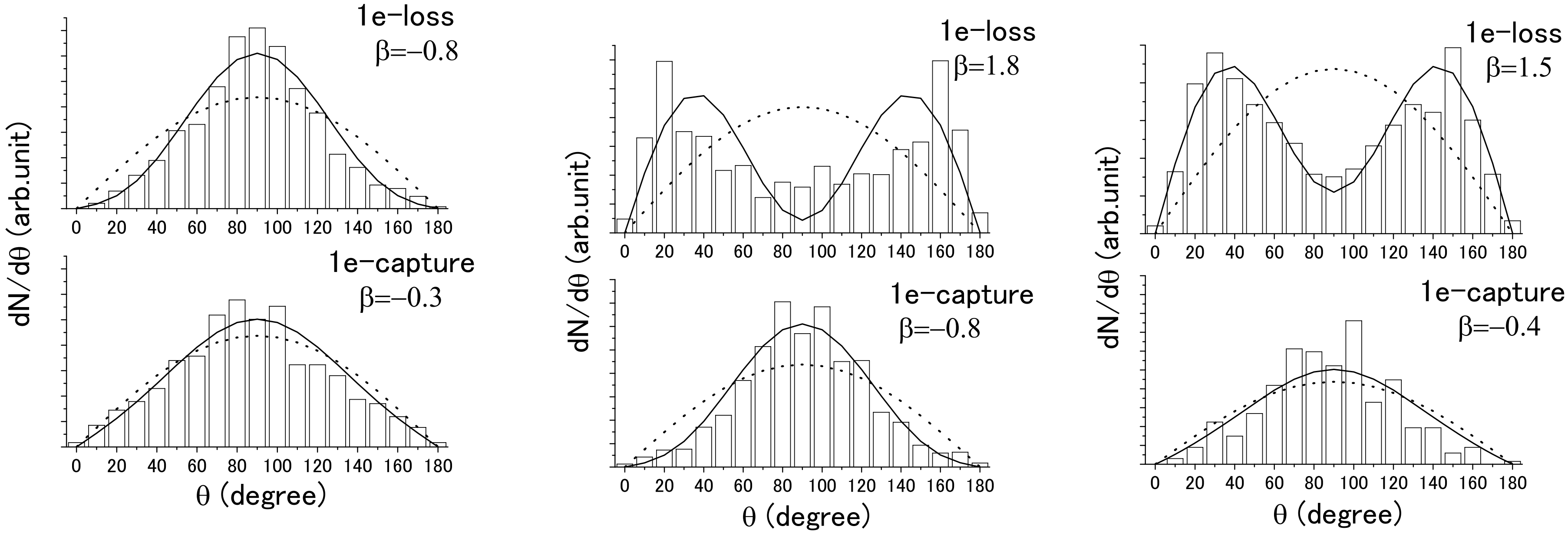
Siegmann et al. 2002 Phys Rev A

- Dissociation of CO^{n+} (D^+ at 100 keV on CO)
- Near-isotropic distribution for $n = 2$
- Anisotropic distribution for $n > 3$
- Slight asymmetry for $n > 4$
- Observations fitted to the Statistical Energy Deposition model



Another Result

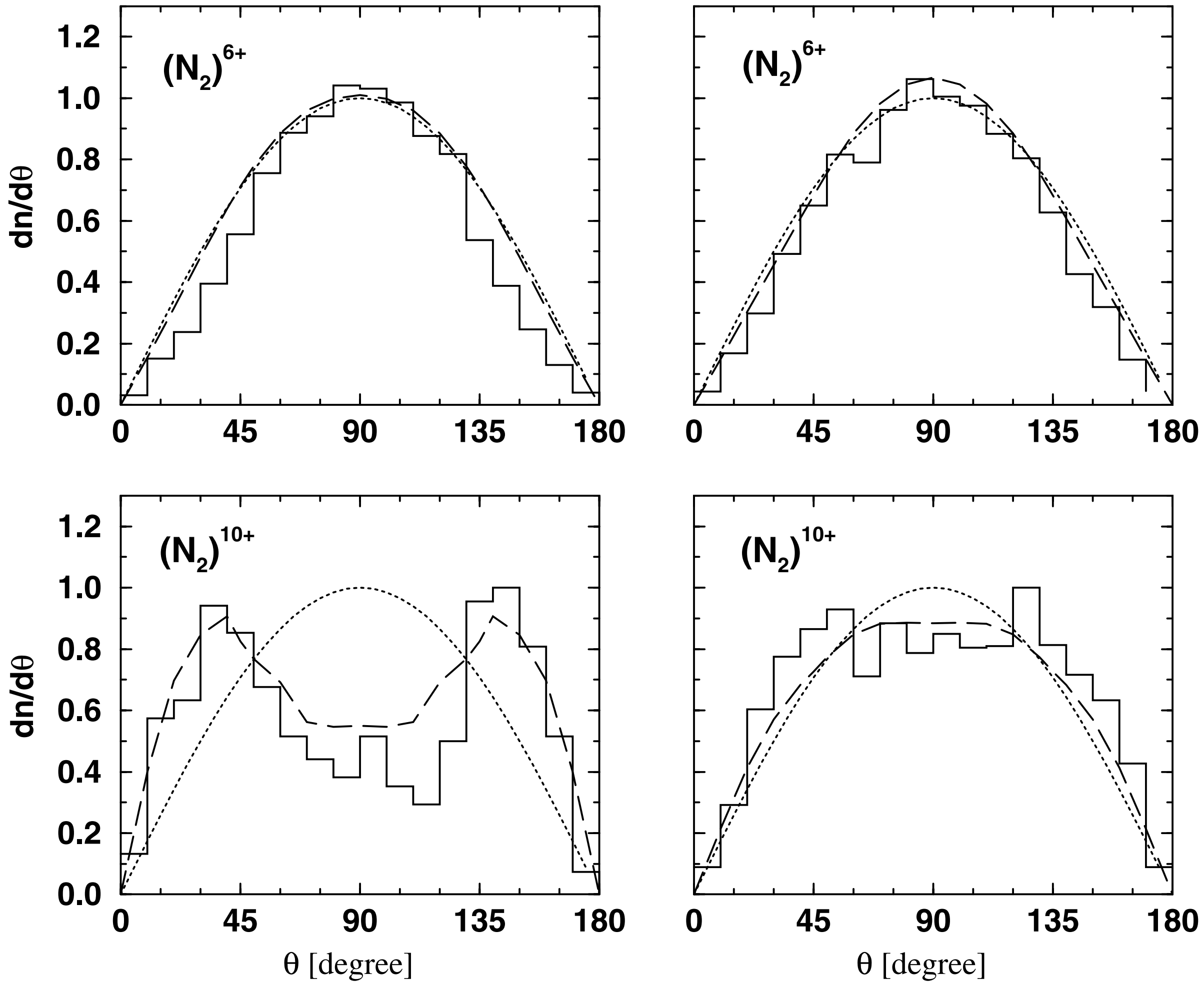
Mizuno 2007 JPCS : separating capture and loss channels



C^{+}:O^{+} C^{2+}:O^{+} C^{+}:O^{2+}

Previous Experimental Result : N_2

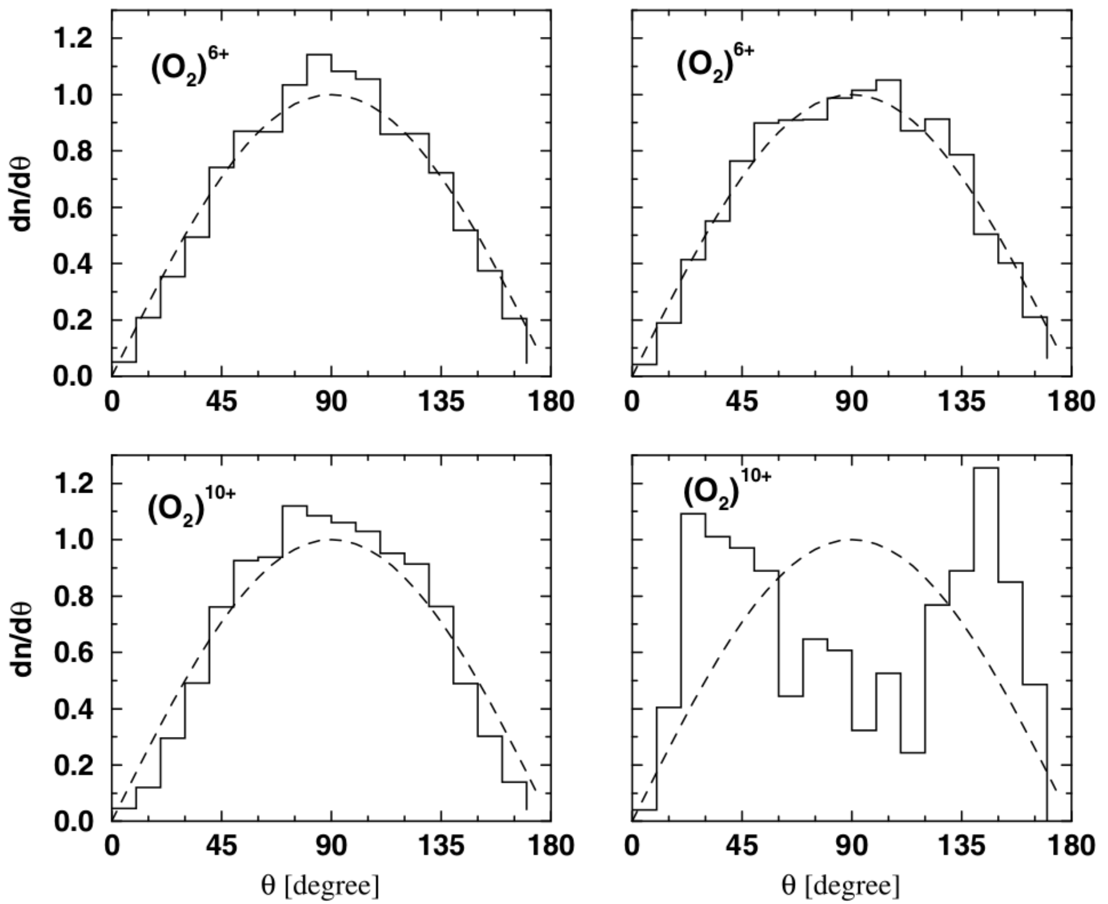
Siegmann et al 2003 NIM(B):



5.9 MeV/u Xe^{18+} 5.9 MeV/u Xe^{43+}

Previous Experimental Result : O_2

Siegmann et al 2003 NIM(B):



360 keV Xe^{18+} 5.9 MeV/u Xe^{18+}

Alignment and Orientation q and v dependence

- Some of the previous results are in contrast to our observations
- There has been a lack of clarity about the distinction between orientation effects and alignment effects
- The SED explains some features for homonuclear diatomic molecules

Alignment and Orientation – Summary

- Our observations
  - ⋆ Low projectile charge leads to greater anisotropy (for the same velocity)
  - ⋆ High velocity projectile leads to greater anisotropy (for the same charge)
  - ⋆ High q/v leads to greater degree of ionisation

- Explanation: Owing to the Coulomb repulsion for a given impact parameter, larger q/v implies a larger distance of closest approach d_{min}

$$d_{min} = \frac{b}{[1 - \frac{2qU(d_{min})}{mv^2}]^{1/2}}$$

- For large d_{min}, the molecule appears to be nearly structureless – hence weak orientation effects

- However, even for large d_{min}, a large q/v ion can cause multiple ionisation