

# IR Spectroscopy and physicochemical effects on astrophysical ices produced by energetic ions collisions

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## INTERNATIONAL SYMPOSIUM AND WORKSHOP ON ASTROCHEMISTRY

Understanding extraterrestrial molecular complexity through experiments and observations



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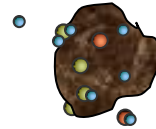
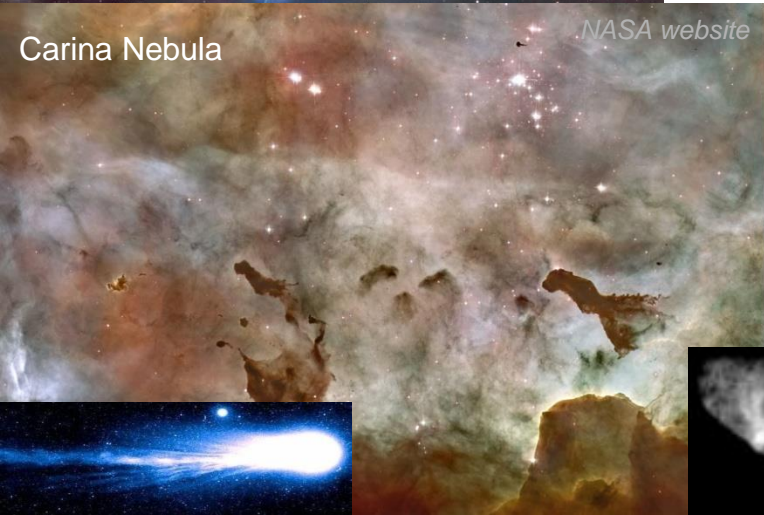
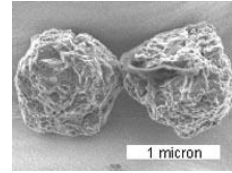
Pontifícia Universidade Católica  
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**Enio F. da Silveria**

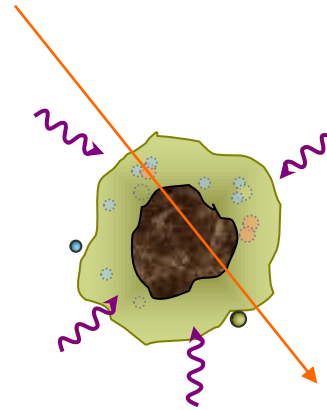
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# Astrophysical ices

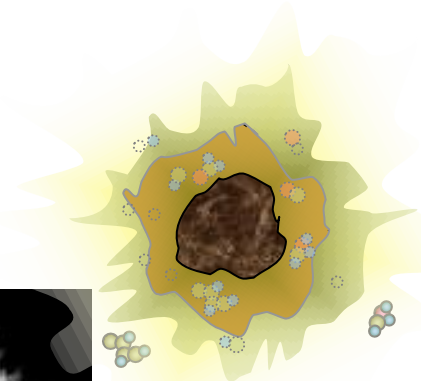


The grains are covered with an icy mantle formed from simple molecules ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , etc).



Energetic processes induced by:

- photons,
- electrons (high and low-energy),
- ions (cosmic rays, solar wind).



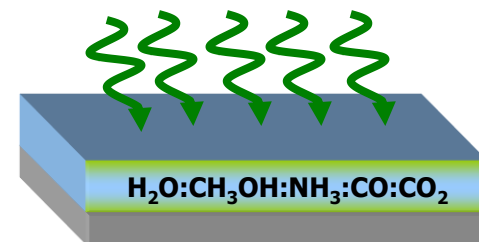
Irradiation induces chemical modification and desorption of species from the ice.



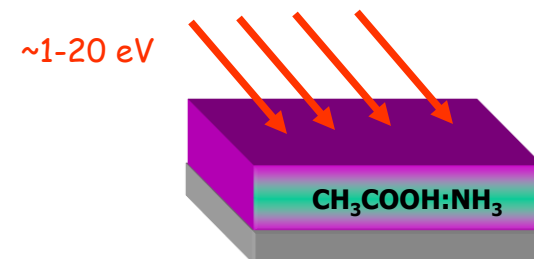
# Astrophysical ices: energetic processes - state of the art

## Projectiles:

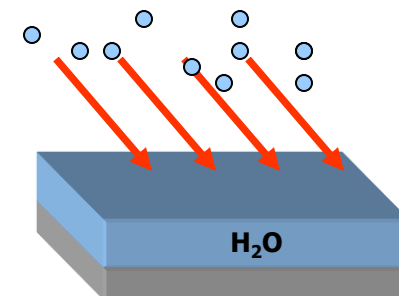
- photons  
(e.g. new molecules, destruction/formation cross sections, photodesorption)
- electrons (low and high energy range)  
(e.g. same as Photons)
- ions  
(mainly **H**, **He**, **C**, **O** ions in **~50 keV** and **~2 MeV** energy range)  
(e.g. new molecules, destruction/formation cross sections, sputtering)



Muñoz Caro *et al.*, Nature **416** (2002) 403



Lafosse *et al.*, PCCP **8** (2006) 5564



Strazzulla & Baratta, Europhysics  
Letter **18** (1992) 517

**In this work H<sup>+</sup> and He<sup>+</sup> at 1.5 MeV...**



# PUC - Van de Graaff Accelerator

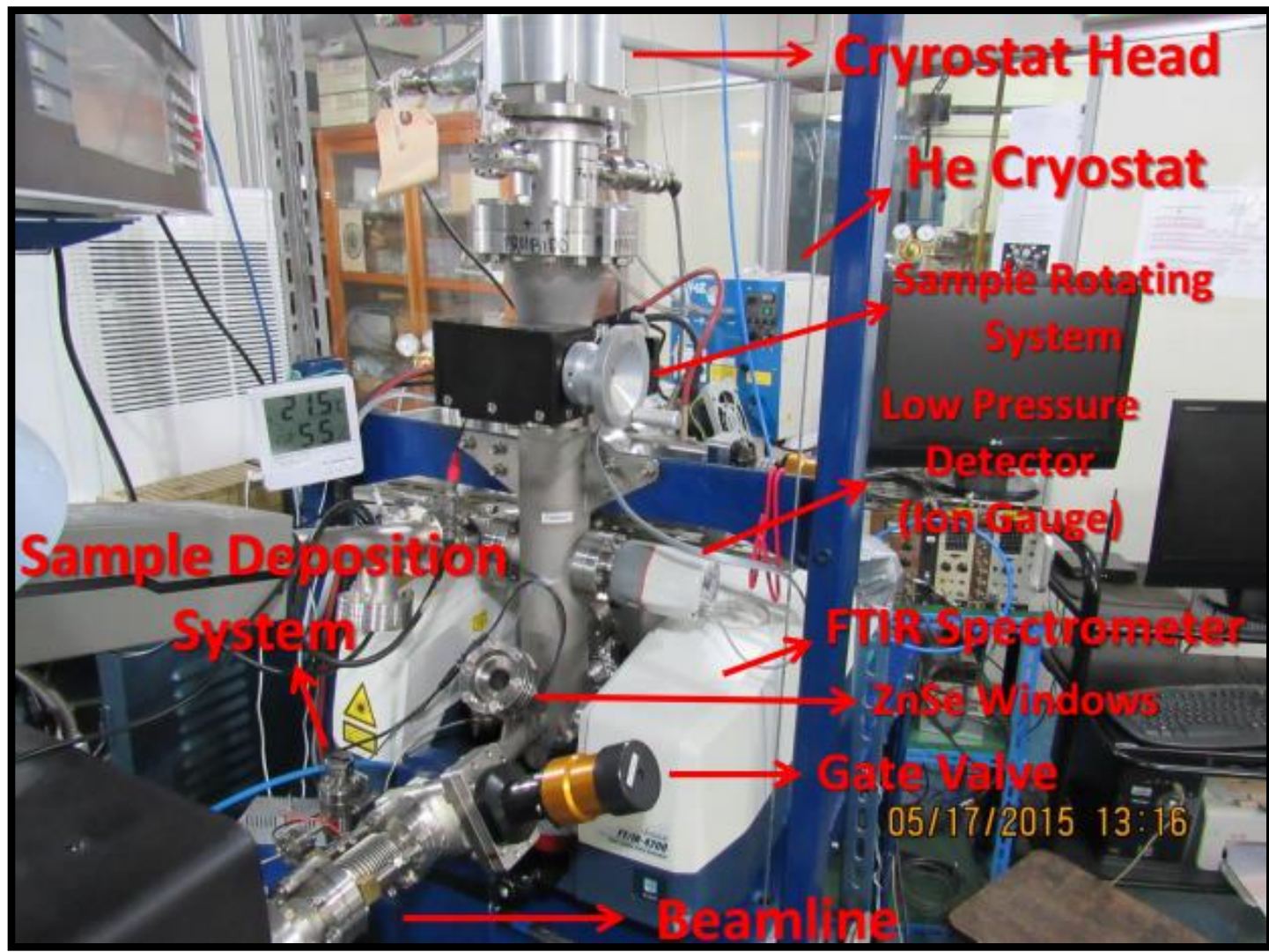
Rio de Janeiro, Brazil



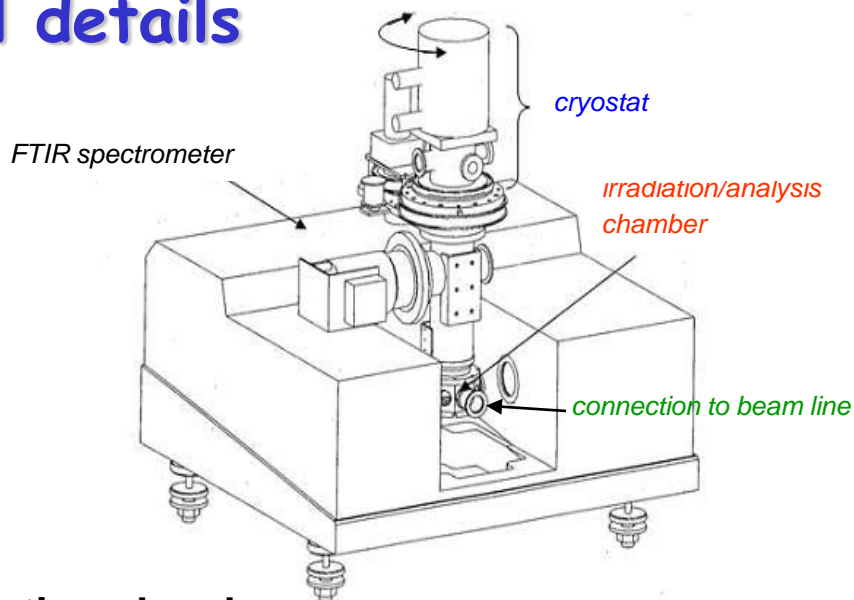


# PUC - Van de Graaff Accelerator

## FTIR Beamline UHV Chamber Overview



# Experimental details



## Substrate

Kbr window

## Temperature

$T = 10 \text{ K}$

## Pressure in irradiation chamber

$\sim 2 \times 10^{-8} \text{ mbar}$  ( $\sim 10 \text{ K}$ )

## Samples (ices- $\text{N}_2\text{O}$ )

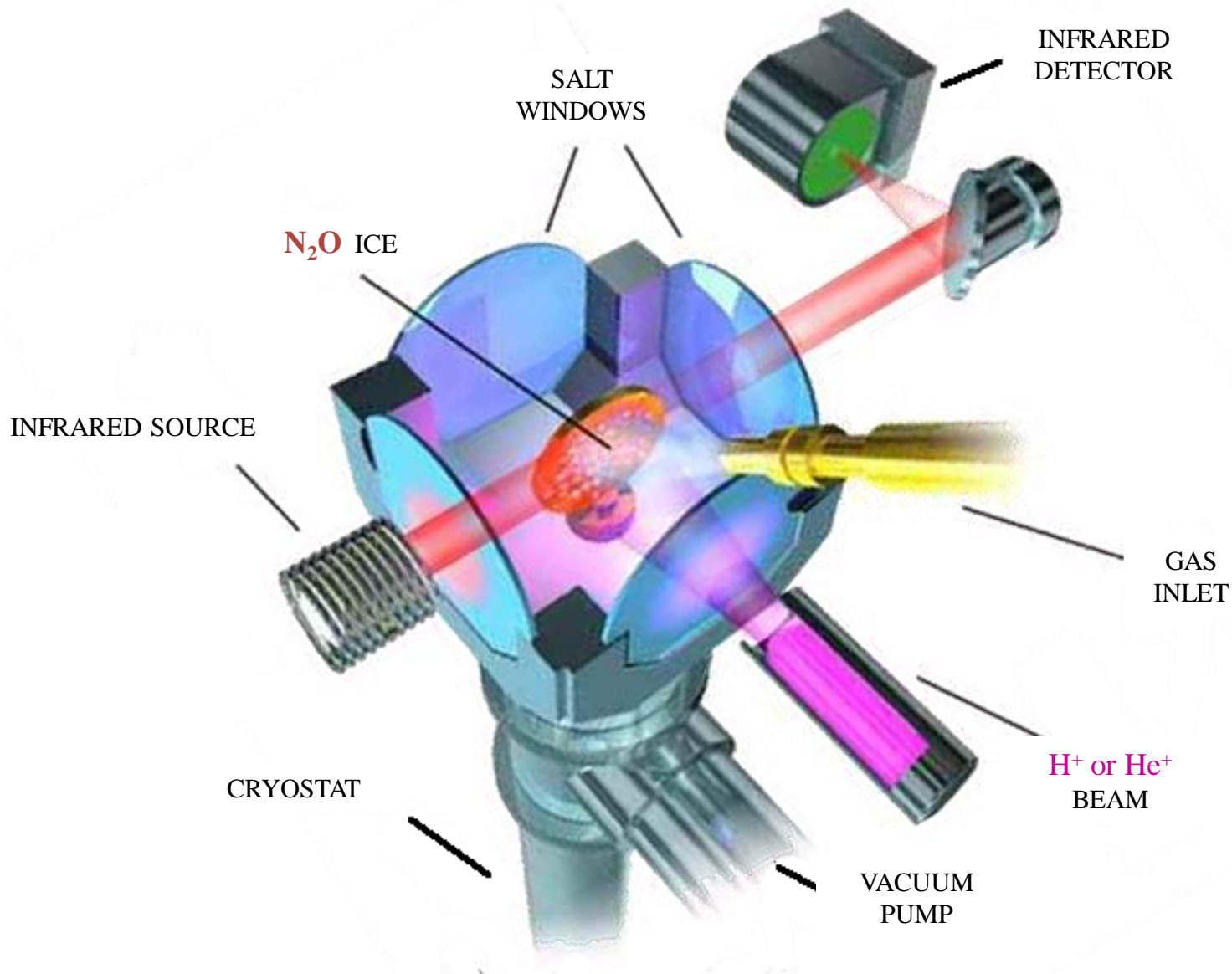
- *in situ* gas deposition
- thickness  $\sim 0.1 - 2 \mu\text{m}$  ( $10^{16}$ - $10^{17}$  molecules/ $\text{cm}^2$ )
- ion penetration depth  $>$  ice thickness

## Ion beam

- 1.5 MeV  $\text{H}^+$  and  $\text{He}^+$
- flux  $\sim 10^9$  ion/ $\text{cm}^2 \text{ s}$
- fluence up to  $2.0 \times 10^{13}$  ions/ $\text{cm}^2$

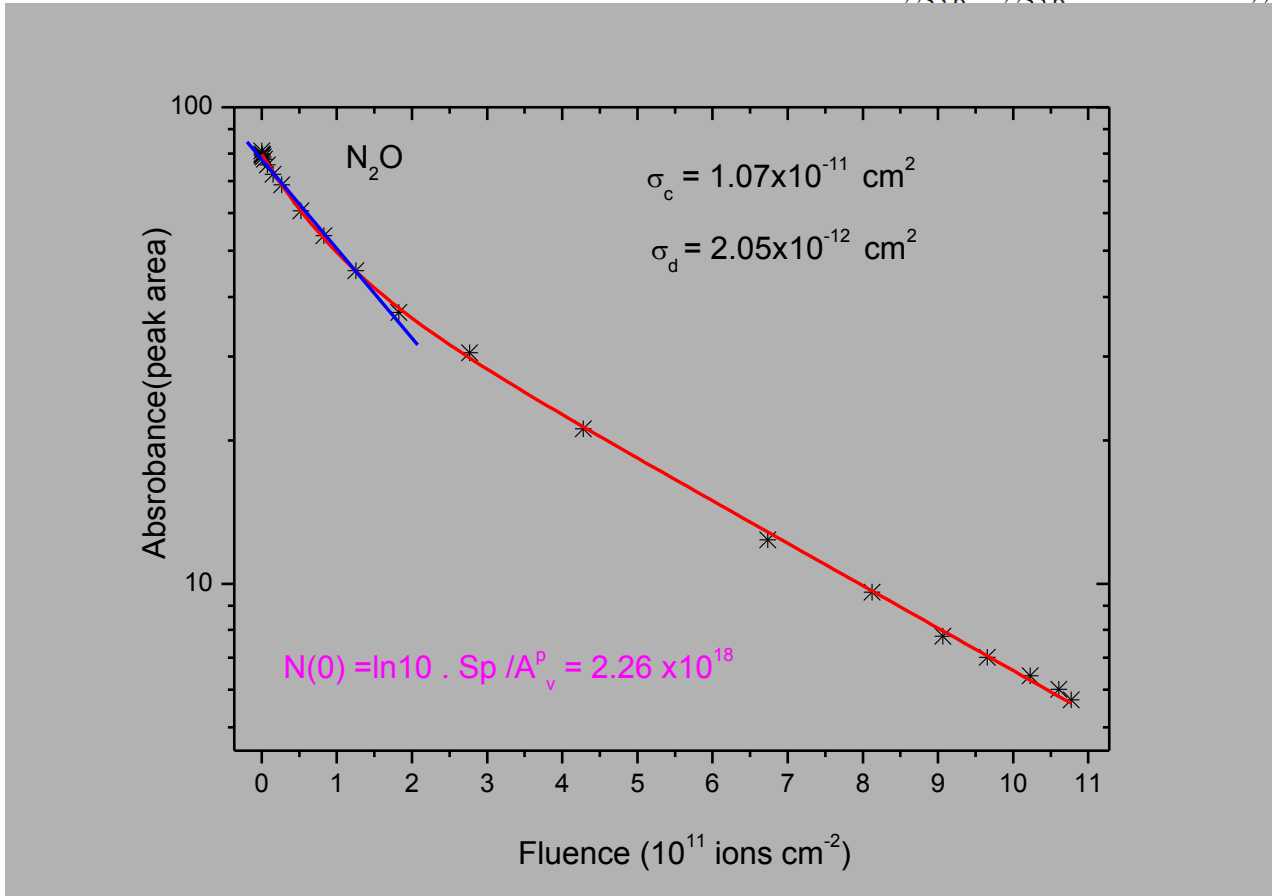


# Irradiation Process

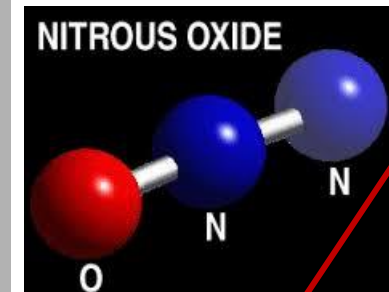


# FTIR spectrum of N<sub>2</sub>O ice

11 K	Absorption 80 K	<sup>a</sup> Fulvio	(cm <sup>-1</sup> ) <sup>b</sup> Ioppolo	<sup>c</sup> L'apiski	Vibration	Isotopomers	A-value This work
589.2	589.2	-	-	588.8	$\nu_2$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	3.1
1165.5	1165.5	1166	1167	-	$2\nu_2$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	0.32
1297.8	1297.8	-	-	-	$\nu_1$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	2.7
1293.5	1293.5	1295	1290	1291.2	$\nu_1$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	<b>10.7<sup>a</sup></b>
2187.5	-	-	-	2185.7	$\nu_3$	<sup>14</sup> N <sup>15</sup> N <sup>17</sup> O	0.26
2196.1	2196.1	-	-	2194.0	$\nu_3$	<sup>15</sup> N <sup>14</sup> N <sup>18</sup> O	0.32
2221.0	2221.0	-	-	2200.1	$\nu_3$	<sup>14</sup> N <sup>14</sup> N <sup>17</sup> O	3.0
2235.6	2235.6	-	2235	2235.6	$\nu_3$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	41
-	-	-	-	-	$\nu_3$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	56
2465.0	$2\nu_1$	-	-	-	$2\nu_1$	<sup>15</sup> N <sup>14</sup> N <sup>18</sup> O	0.34
2565.2	$\nu_1 + 2\nu_2$	-	-	-	$\nu_1 + 2\nu_2$	<sup>14</sup> N <sup>15</sup> N <sup>16</sup> O	0.58
2575.3	$2\nu_1$	-	-	-	$2\nu_1$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	1.9
-	$\nu_2 + \nu_3$	-	-	-	$\nu_2 + \nu_3$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	0.09
-	$2\nu_2 + \nu_3$	-	-	-	$2\nu_2 + \nu_3$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	0.08
3499.3	$\nu_1 + \nu_3$	-	-	-	$\nu_1 + \nu_3$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	0.35
-	$\nu_1 + \nu_3$	-	-	-	$\nu_1 + \nu_3$	<sup>14</sup> N <sup>14</sup> N <sup>16</sup> O	1.81



Ioppolo et al. (2014), L'apiski et al. (2001)

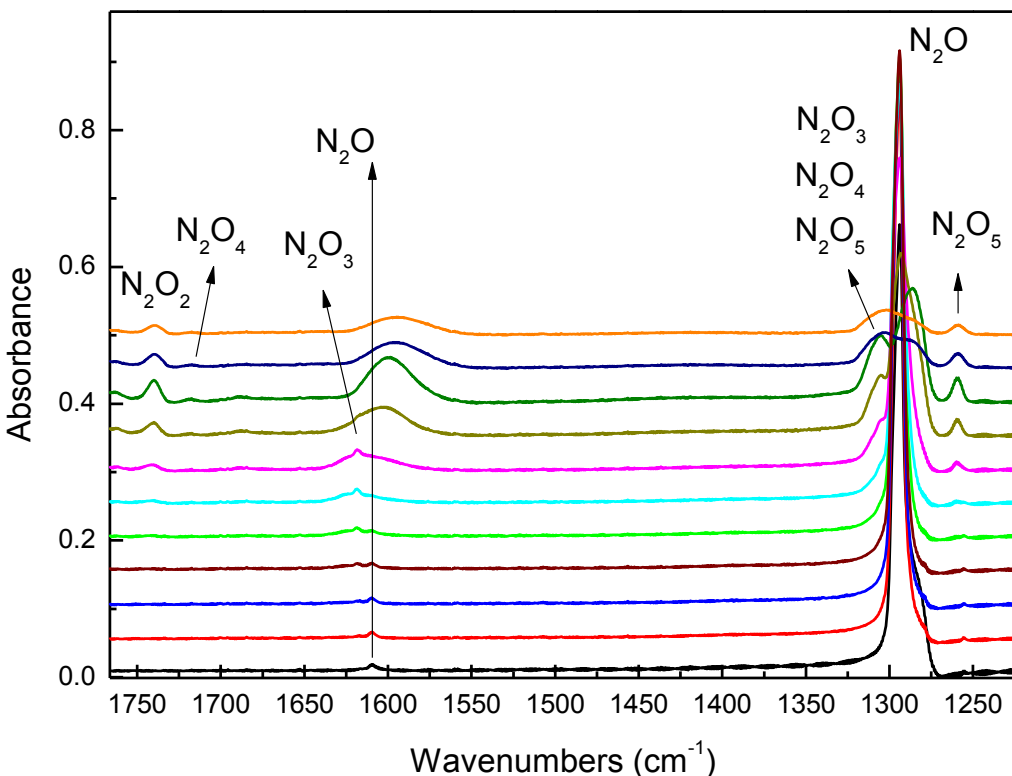


$$N = \ln(10) \frac{\int \text{Absorbance} \cdot d\nu}{A(\text{cm} / \text{molecule})}$$

Abs( $\nu$ ) – total band absorbance  
A – integrated absorbance



# Observed Daughter Species

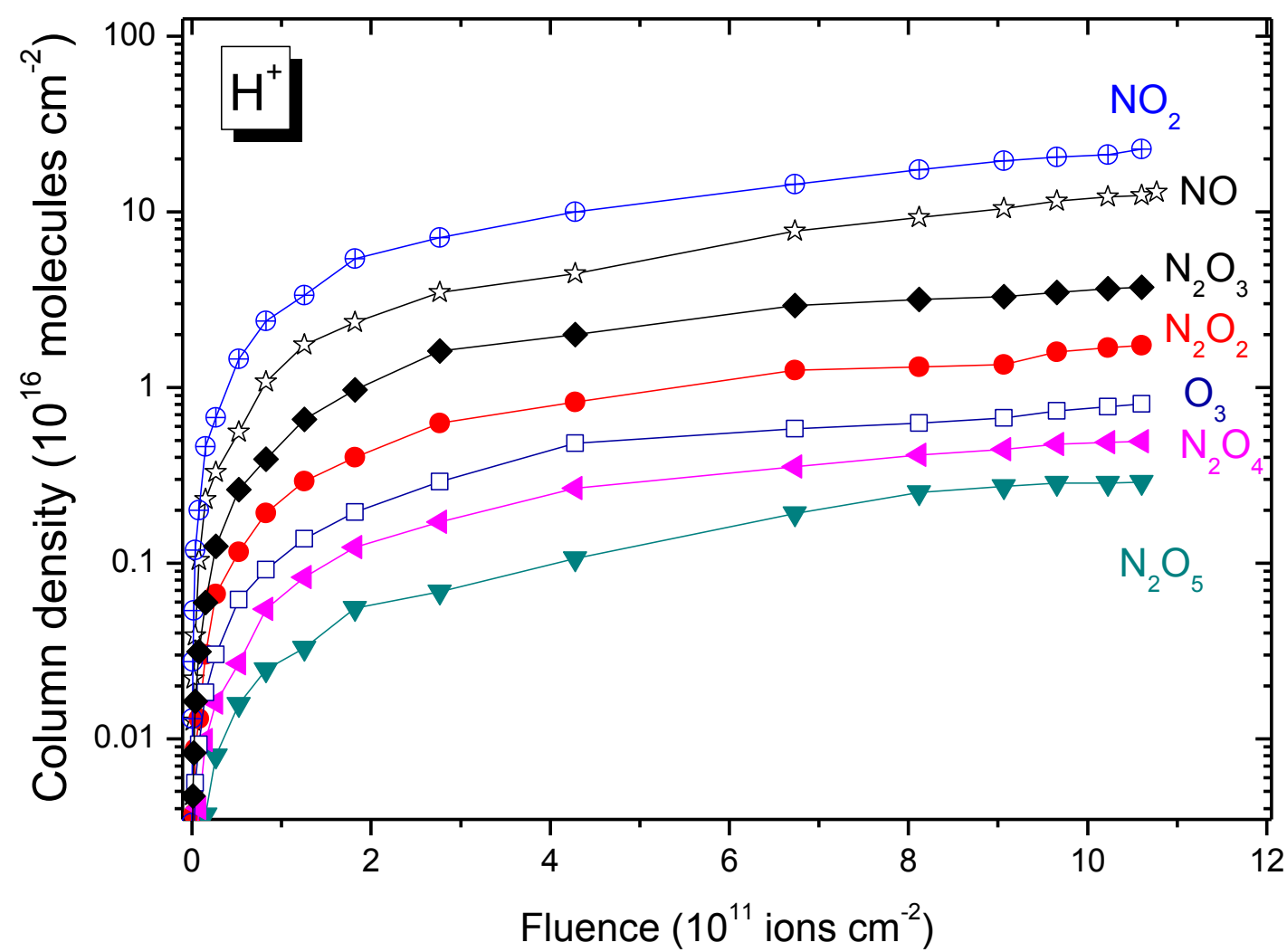


Species	Position (cm <sup>-1</sup> )	Vibration	A-value	Ref.
NO	1889.3	$\nu_1$	0.68	[2]†
NO <sub>2</sub>	752.4	$\nu_2$	-	[4]
	1613.4	$\nu_3$	6.36* /6.24	[2]/[5]
N <sub>2</sub> O <sub>2</sub>	1740.5	$\nu_5$	2.72	[2]
	1765.8	$\nu_5$	15	[2]
	1866.0	$\nu_1$	-	[2]
N <sub>2</sub> O <sub>3</sub>	784.7	$\nu_4$	6.0	[4,6]
	1305.9	$\nu_1/\nu_3$	4.63	[2]
	1653.2	$\nu_2$	6.24	[2]
N <sub>2</sub> O <sub>4</sub>	1259.4	$\nu_{11}$	8.5	[2]
	1305.9	$\nu_3$	5.60	[2]
	1627.5	$\nu_2$	5.95	[2]
	1719.5	$\nu_7/\nu_5$	-	[5]
	1861.3	$\nu_4 + \nu_5/\nu_1$	-	[5]
N <sub>2</sub> O <sub>5</sub>	752.4	$\nu_{11}$	-	[6]
	1243.2	$\nu_{10}$	-	[4]
	1305.9	$\nu_2$	0.7	[2]
	1740.5	$\nu_1$	2.75	[2]
O <sub>3</sub>	1039.7	$\nu_3$	1.40	[2]†

[1]Zheng et al. (2008), [2]Jamieson et al. (2005),[3]Hudson & Moore (2002), [4]Manion et al., [5]Fulvio et al. (2009), [6]Ioppolo et al. (2014). † Not seen at 80 K. \*Value used in the current work.



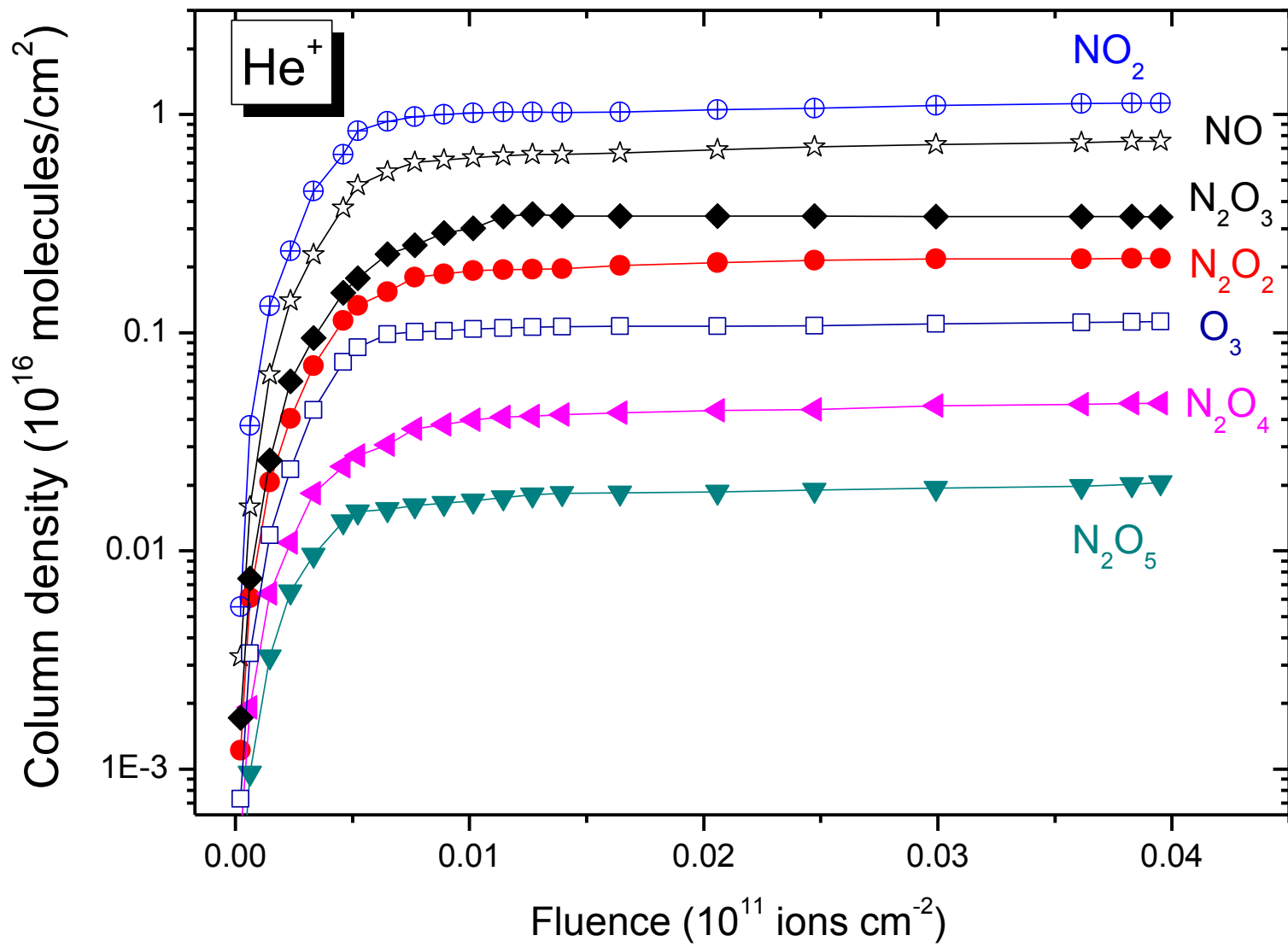
# Daughter Species 1.5 MeV $H^+ \rightarrow N_2O$







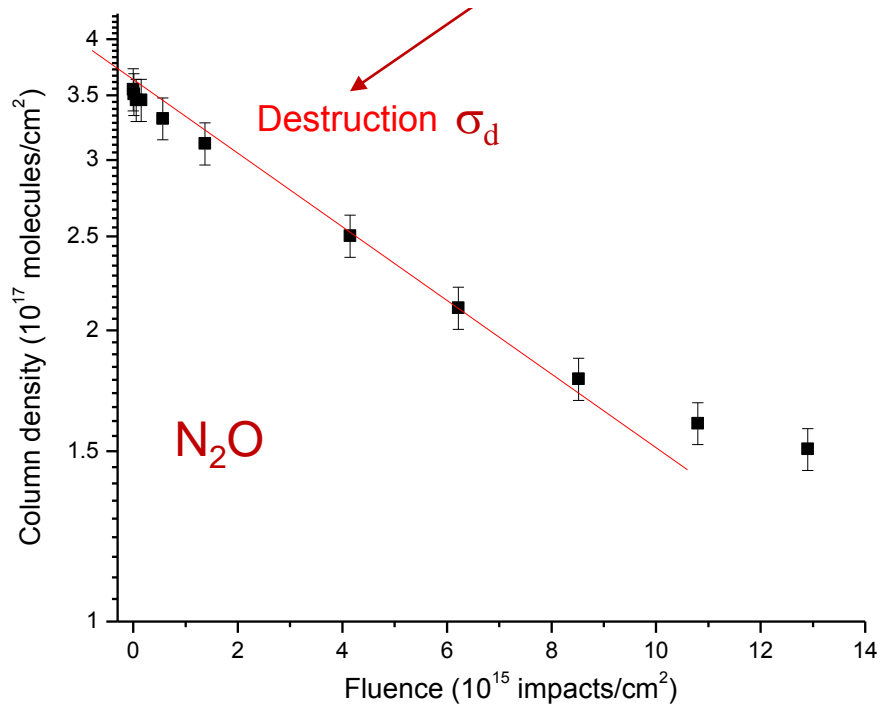
# Daughter Species 1.5 MeV He<sup>+</sup> → N<sub>2</sub>O





Precursors Integrated (Destruction +

) Cross Sections

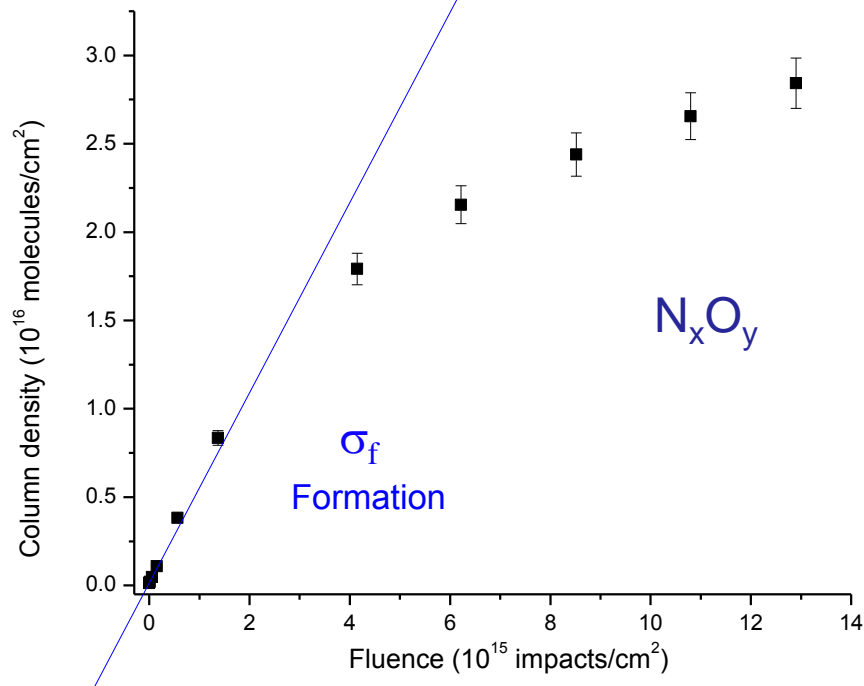
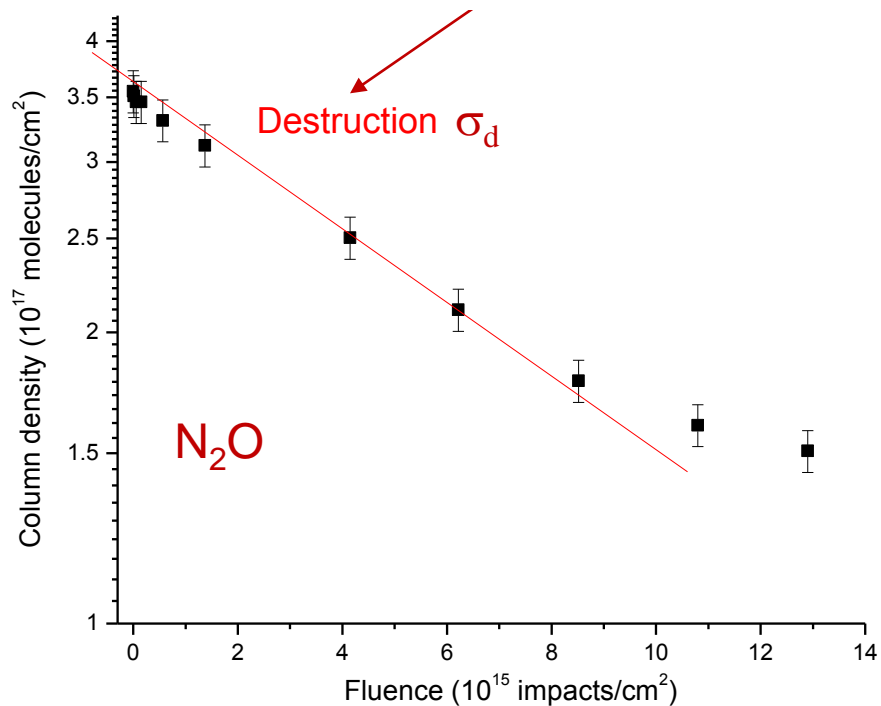






Precursors Integrated (Destruction +

) Cross Sections



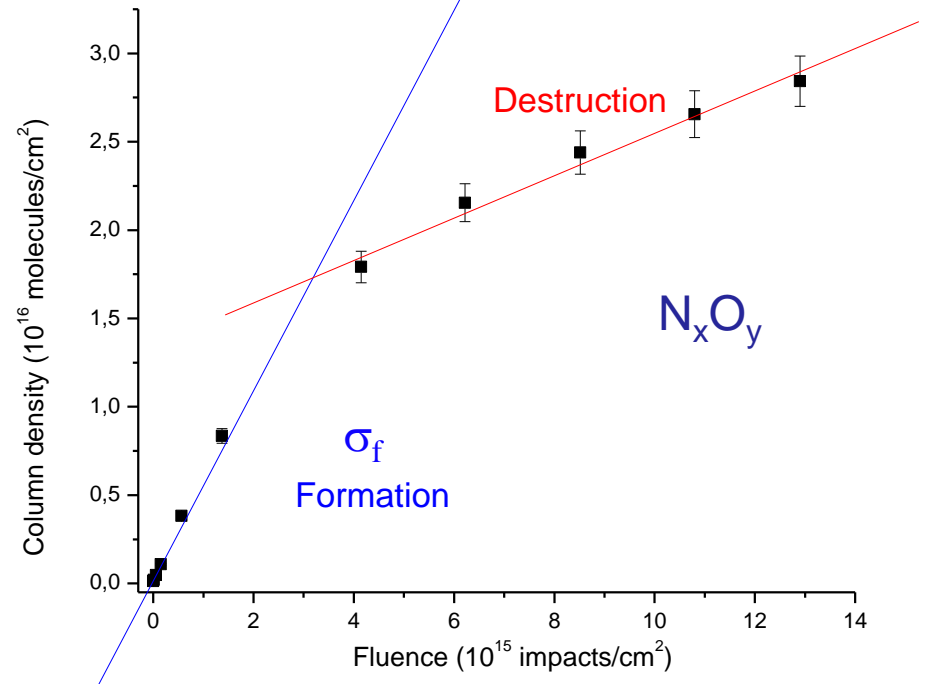
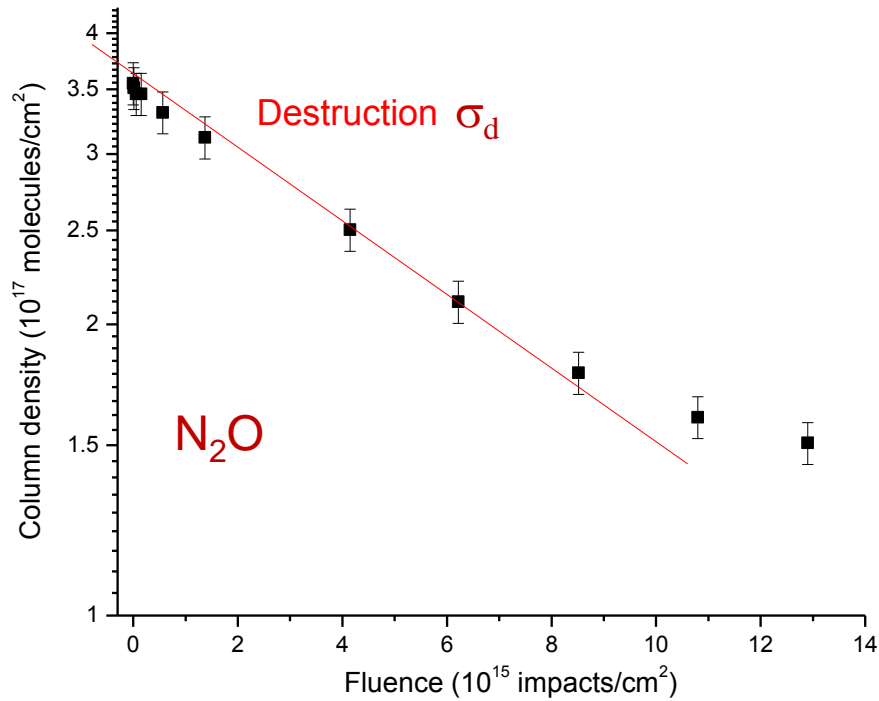
$N_xO_y$  (Formation +

) Cross Sections



Precursors Integrated (Destruction +

) Cross Sections

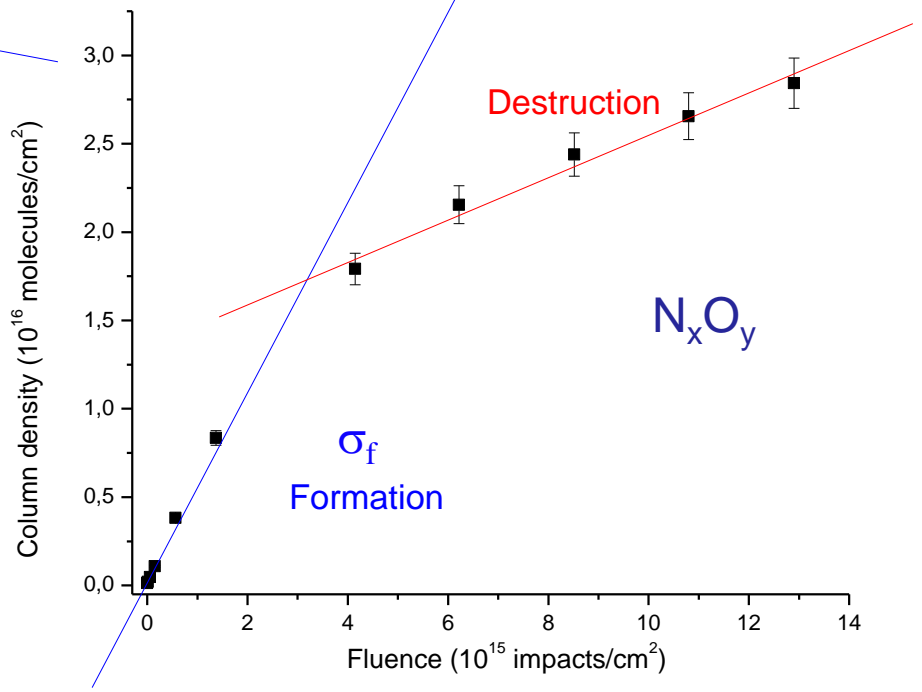
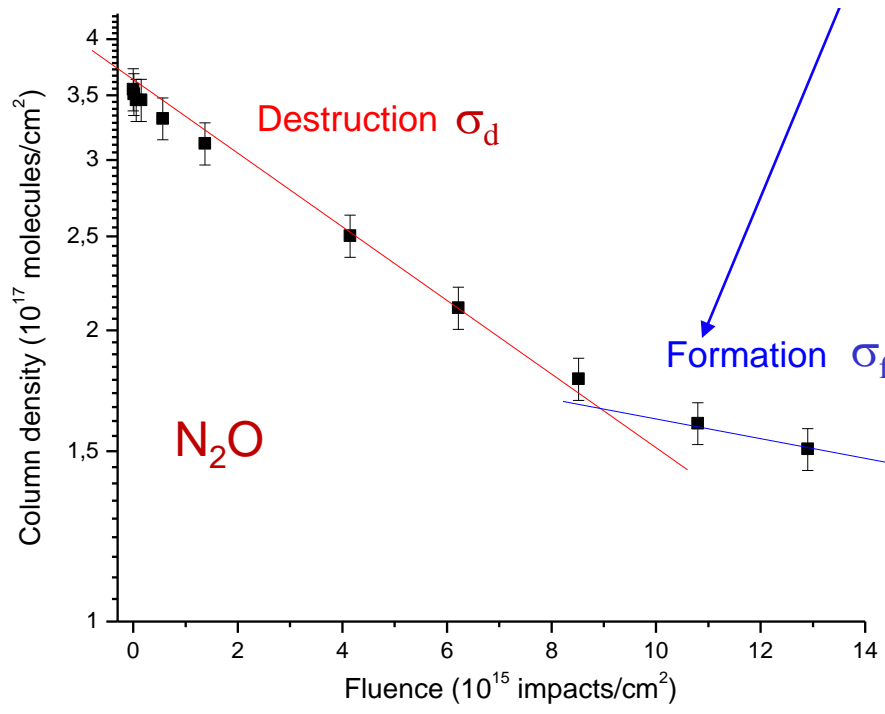


$N_xO_y$  (Formation + Destruction) Cross Sections



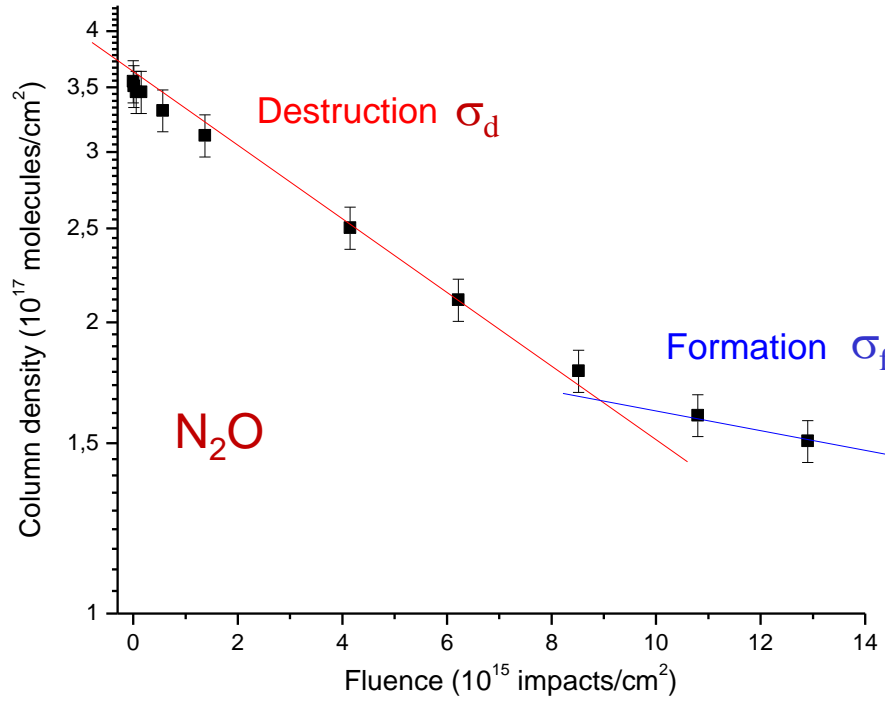


# Precursors Integrated (Destruction + Formation) Cross Sections

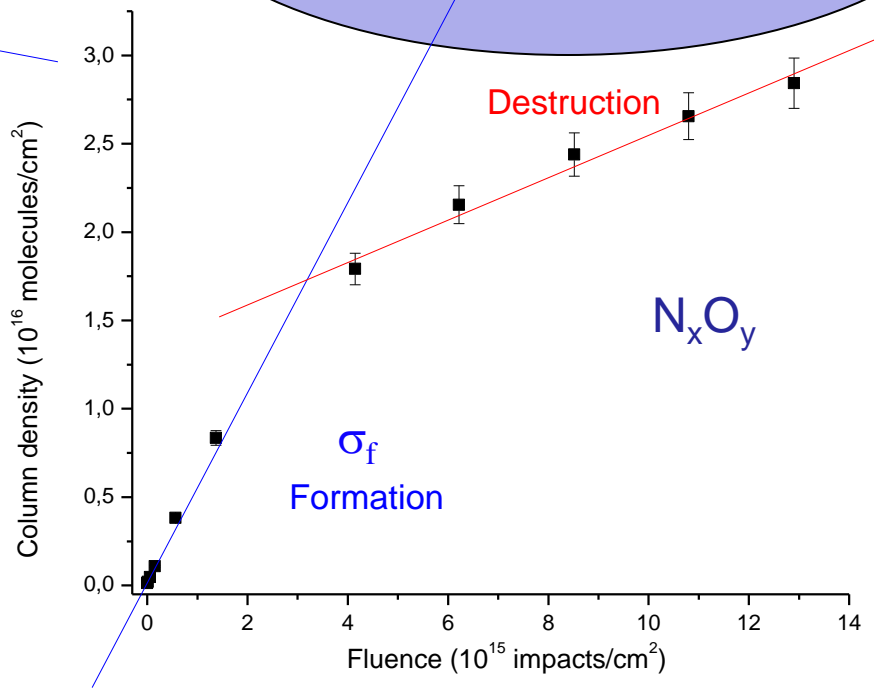




# Precursors Integrated (Destruction + Formation) Cross Sections

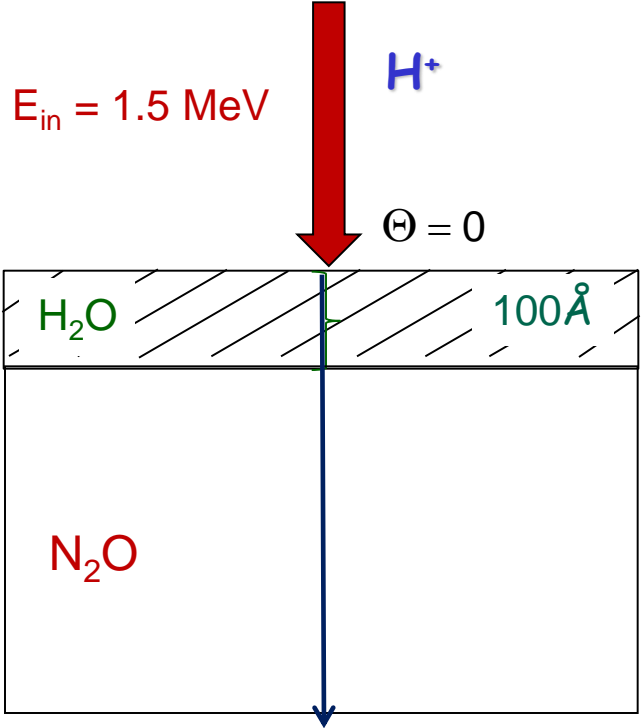


regeneration of  $N_2O$  from its daughter molecules





# Average (integrated) Cross Sections



$$\frac{dN_i}{dF} = \sum_{j \neq i} \sigma_{f,ij} N_j + \cancel{L_i} - \sigma_{d,i} N_i - \cancel{Y_i}$$

$N_i$  is the column density of molecular species  $i$ ;  
 $\sigma_f$  and  $\sigma_d$  formation and destruction cross sections;  
 ~~$L_i$  and  $Y_i$  are their layering and sputtering yields;~~

## Approximate Equations ...

Precursor molecule

$$\frac{dN_1}{dF} = \sigma_{f,1k} \sum_k N_k - \sigma_{d,1} N_1$$

Daughter molecule

$$\frac{dN_k}{dF} = \sigma_{f,k1} N_1 - \sigma_{d,k} N_k$$

# Cross Sections

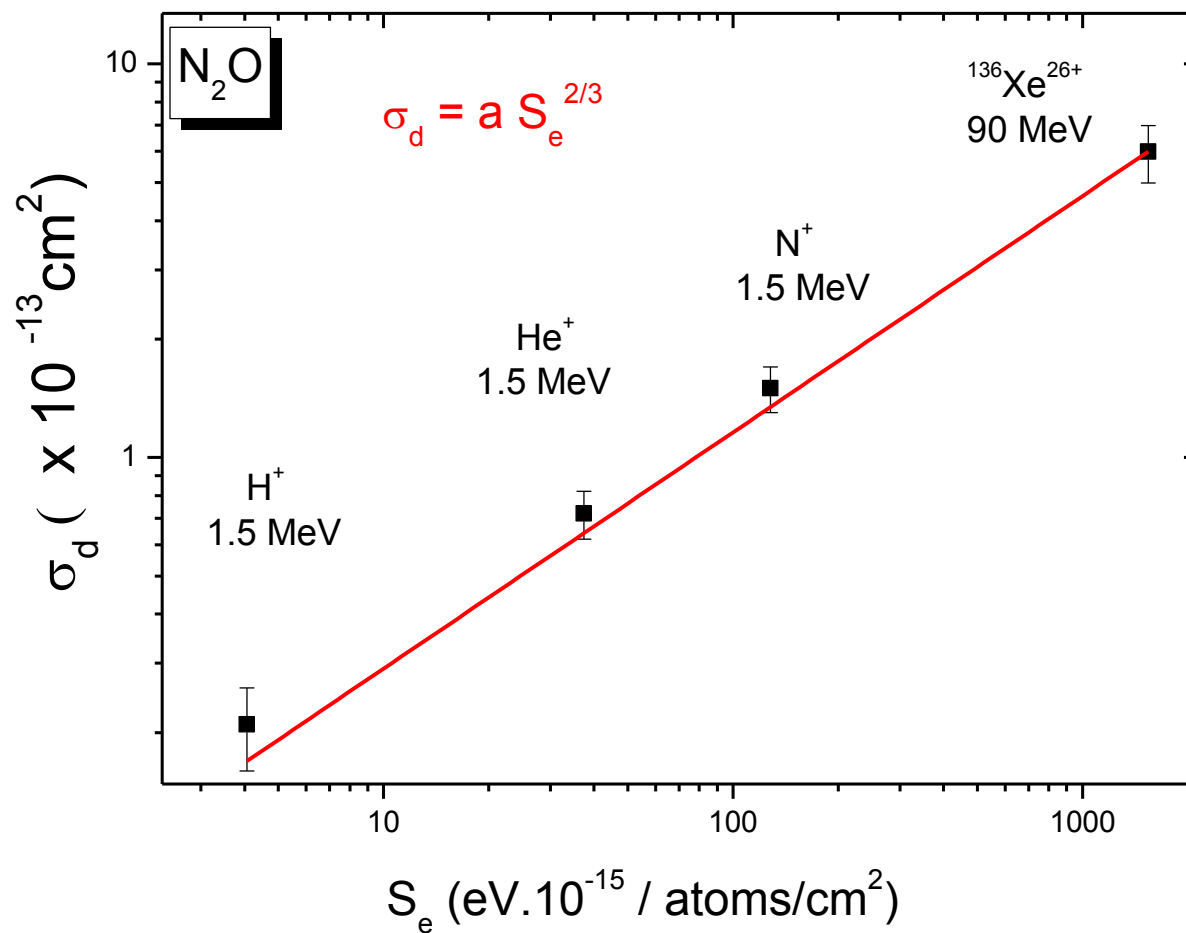
Destruction and formation cross-sections ( $10^{-14} \text{ cm}^2$ ) of  $\text{N}_2\text{O}$  with  $\text{H}^+$

	Molecules 10 K at 1.5 MeV	Formation cross-section	Destruction cross-section
Precursor	$\text{N}_2\text{O}$	-	$(2.1 \pm 0.5)$
Daughters	$\text{NO}_2$	$(1.1 \pm 0.2)$	$(1.3 \pm 0.2)$
	$\text{N}_2\text{O}_2$	$(0.09 \pm 0.01)$	$(3.1 \pm 0.6)$
	$\text{NO}$	$(0.54 \pm 0.08)$	$(1.0 \pm 0.5)$
	$\text{N}_2\text{O}_3$	$(0.25 \pm 0.02)$	$(5.4 \pm 0.7)$
	$\text{N}_2\text{O}_4$	$(0.03 \pm 0.01)$	$(3.8 \pm 0.8)$
	$\text{N}_2\text{O}_5$	$(0.02 \pm 0.01)$	$(3.3 \pm 0.8)$
	$\text{O}_3$	$(0.05 \pm 0.02)$	$(4.8 \pm 0.4)$

$\Sigma = 2.08$



The dissociation cross-sections due to 4 projectiles at different energies are determined, assuming validity of the  $\sigma_d \sim S_e^{2/3}$  power law.







## Summary

- ❑ Our experiments demonstrate that 1.5 MeV ion irradiation of nitrous oxide with  $H^+$  leads to production of molecules  $NO_2$ ,  $N_2O_2$ ,  $NO$ ,  $N_2O_3$ ,  $N_2O_4$ ,  $N_2O_5$  and  $O_3$ ;
- ❑ The most abundant daughter species are  $NO_2$  and  $NO$ ;
- ❑ Same results were observed for the  $He^+$  beam irradiation;
- ❑ The formation and destruction cross sections of both ion beams were determined;
- ❑ For the  $N_2O$  matrix, the dependence of the destruction cross section on the stopping power is found to follow a power law, i.e.,  $\sigma_d \propto S_e^n$ , where  $n \sim 2/3$ .



# Acknowledgments

# Thank you



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