The role of cosmic rays in the formation of interstellar and circumstellar molecules

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Molecules in space

About 160 molecules have been detected in space (http://www.astrochymist.org/astrochymist_ism.html)

Number of atoms												
2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**>13**
CH	H_2O	NH_3	HC_3N	CH_3OH	CH_3CHO	$HCOOCH_3$	$(CH_3)_2O$	$(CH_3)_2CO$	HC_9N	C_6H_6	$HC_{11}N$	C_{60}
CN	HCO^+	H_2CO	$HCOOH$	CH_3CN	CH_3CCH	CH_3C_3N	CH_3CH_2OH	$HOCH_2CH_2OH$	CH_3C_6H	$CO(CH_2OH)_2$		C_{70}
CH^+	HCN	$HNCO$	CH_2NH	NH_2CHO	CH_3NH_2	C_7H	CH_3CH_2CN	CH_3CH_2CHO	C_2H_5OCHO	C_3H_7CN		
OH	OCS	H_2CS	NH_2CN	CH_3SH	CH_2CHCN	CH_3COOH	HC_7N	CH_3C_5N				
CO	HNC	C_3N	H_2CCO	C_2H_4	HC_5N	H_2C_6	CH_3C_4H	NH_2CH_2COOH				
H_2	H_2S	$HNCS$	C_4H	C_5H	C_6H	CH_2OHCHO	C_8H					
SiO	N_2H^+	$HOCO^+$	SiH_4	CH_3NC	$c\text{-}C_2H_4O$	C_6H_2	CH_3CONH_2					
CS	C_2H	C_3O	$c\text{-}C_3H_2$	HC_2CHO	CH_2CHOH	CH_2CHCHO	C_8H^-					
SO	SO_2	C_3H	CH_2CN	H_2CCCC	C_6H^-	CH_2CCHCN	CH_2CHCH_3					
SiS	HDO	$HCNH^+$	C_5	HC_3NH^+		NH_2CH_2CN						
NS	HCO	H_3O^+	SiC_4	C_5N								
C_2	HNO	C_3S	H_2CCC	C_4H_2								
NO	OCN^-	$c\text{-}C_3H$	CH_4	HC_4N								
HCl	HCS^+	C_2H_2	$HCCNC$	$c\text{-}H_2C_3O$								
$NaCl$	HOC^+	HC_2N	$HNCCC$	CH_2CNH								
$AlCl$	$c\text{-}SiC_2$	H_2CN	H_2COH^+	C_5N^-								
KCl	$MgNC$	SiC_3	C_4H^-									
AlF	C_2S	CH_3	$CNCHO$									
PN	C_3	C_3N^-										
SiC	CO_2	PH_3										
CP	CH_2	$HCNO$										
NH	C_2O	$HOCN$										
SiN	NH_2	$HSCN$										
SO^+	$NaCN$	$HOOH$										
CO^+	N_2O											
HF	$MgCN$											
LiH	H_3^+											
SH	$SiCN$											
FeO	$AlNC$											
N_2	$SiNC$											
CF^+	HCP											
PO	CCP											
AlO	$AlOH$											
CN^-	H_2O^+											
OH^+	H_2Cl^+											
SH^+	KCN											
O_2	$FeCN$											

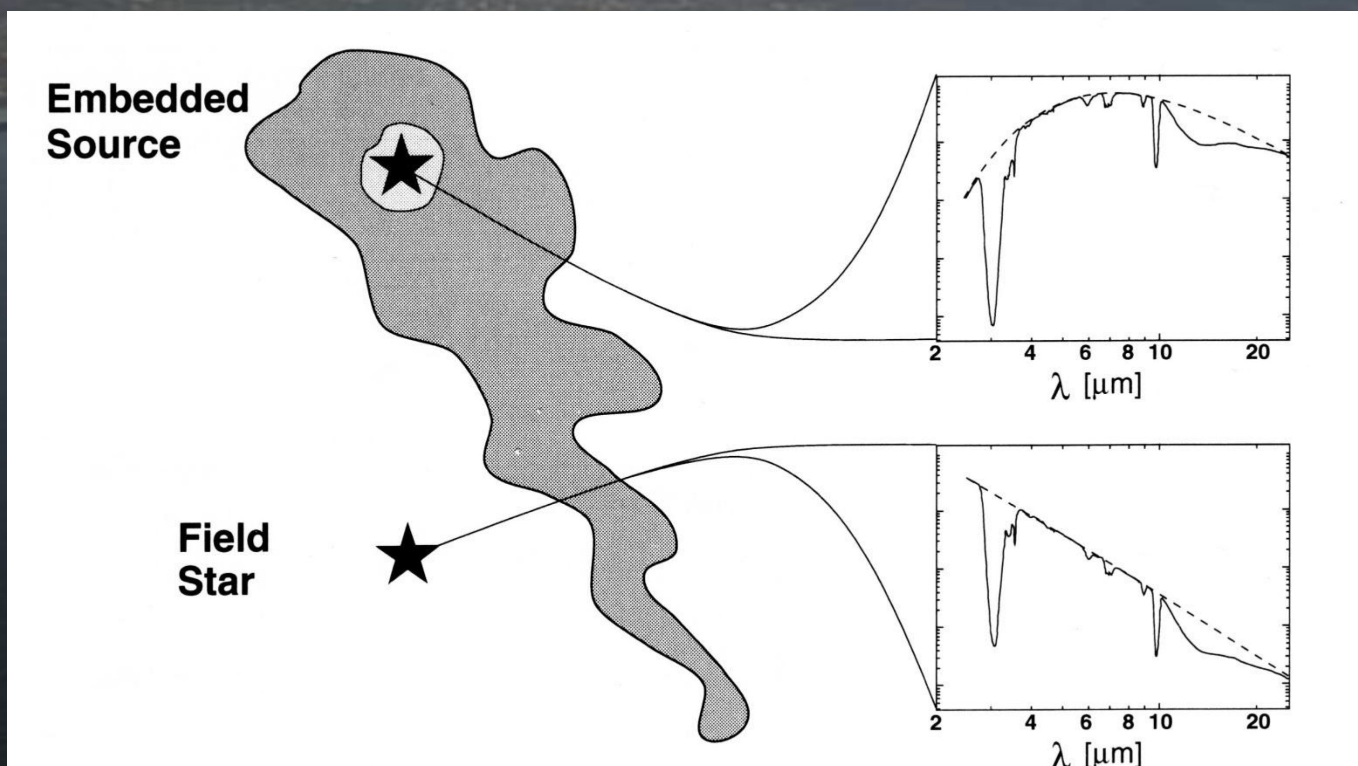
Ices in the Solar System

Planet **Satellite**	**Observed Species**
Jupiter	
Io	SO_2, H_2S, H_2O
Europa	H_2O, SO_2, CO_2, H_2O_2
Ganymede	H_2O, O_2 , O_3, CO_2
Callisto	H_2O, SO_2, CO_2
Saturn	
Mimas	H_2O
Enceladus	H_2O
Tethys	H_2O
Dione	H_2O, O_3
Rhea	H_2O, O_3
Hyperion	H_2O
Iapetus	H_2O

Planet **Satellite**	**Observed Species**
Uran	
Miranda	H_2O
Ariel	H_2O
Umbriel	H_2O
Titania	H_2O
Oberon	H_2O
Neptune	
Triton	N_2,CH_4,CO,CO_2,H_2O
Pluto*	
Pluto	N_2, CH_4, CO, H_2O
Charon	H_2O

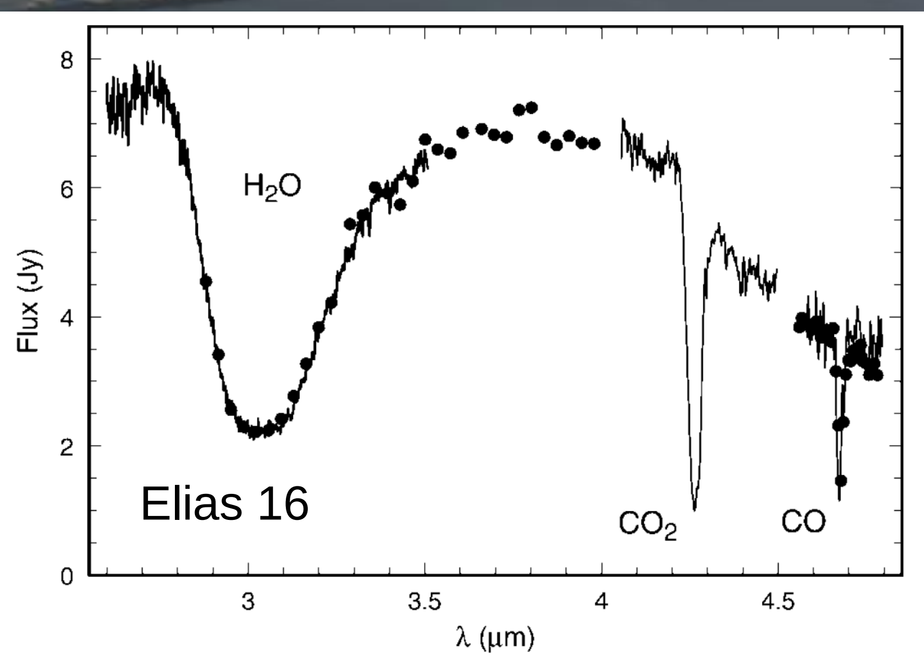
* After IAU resolution, in 2006, Pluto is a dwarf planet and is recognized as the prototype of trans-Neptunian objects.

Observations of dense molecular clouds

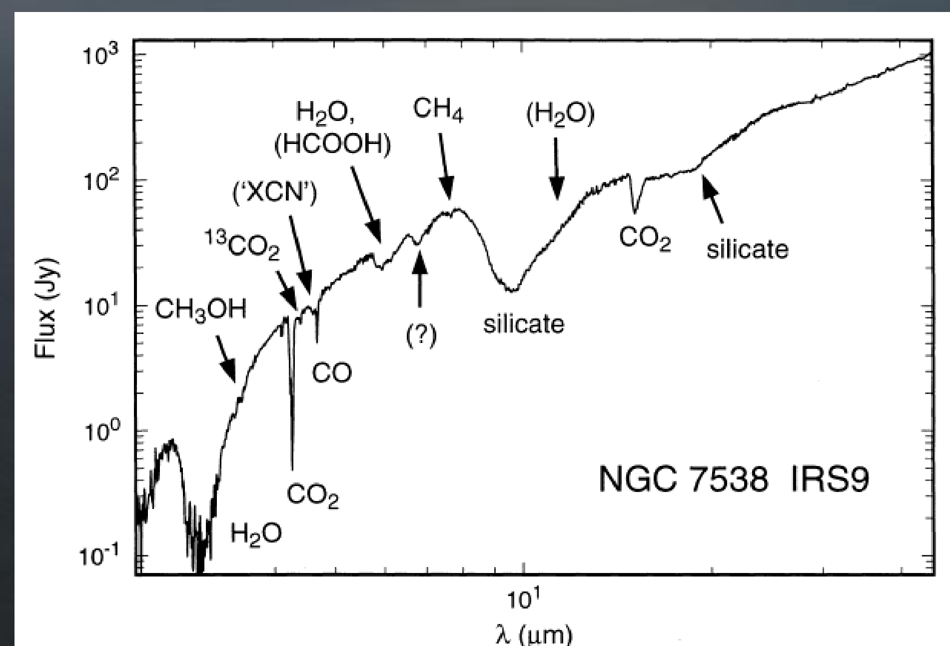


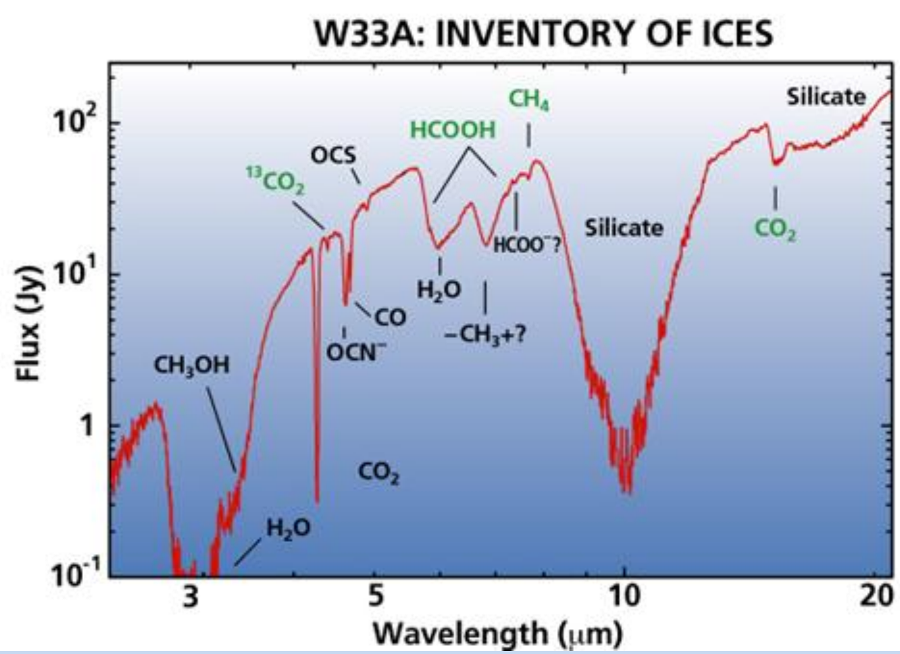
Solid-phase species in dense molecular clouds

Field star



High-mass young stellar object





Abundance of solid-phase molecules

(with respect to H_2O=100)

species	abundance	references
H_2O	100	
CO	0-144	Chiar et al. 1994; Pontoppidan et al. 2003
CO_2	10-32	Gerakines et al. 1999 ; Pontoppidan et al. 2008
CH_3OH	3-30	Allamandola et al. 1992; Dartois et al. 1999; Boogert et al. 2008
CH_4	2-10	Boogert et al. 1997; Oberg et al. 2008
NH_3	5-10	Tielens 1984; Lacy et al. 1998
H_2CO	3-7	Schutte 1994
OCN^-	1-8	Tegler et al. 1995
SO_2	0.3-0.8	Boogert et al. 1997
OCS	0.04-0.1	Palumbo et al. 1997

It is generally accepted that other molecules are also present in icy grain mantles

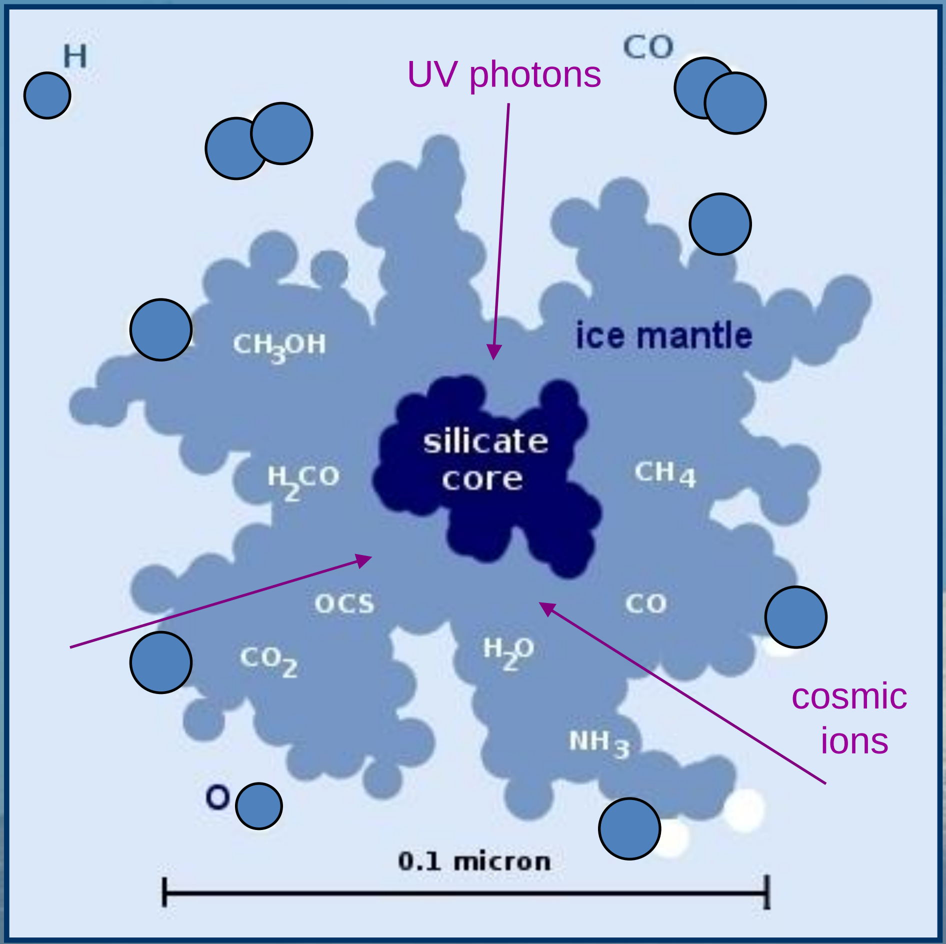
Origin of interstellar molecules

Gas-phase reactions

Solid phase
- → **Grain-surface reactions**
- → **Energetic processing of icy mantles**

(molecules released to the gas phase after desorption of ices)

Icy grain mantles



- **Freeze out of gas phase species (CO)**
- **Grain surface reactions (H_2O, CH_3OH, CH_4, H_2S)**
- **Energetic processing of icy mantles (CO_2 , OCS)**

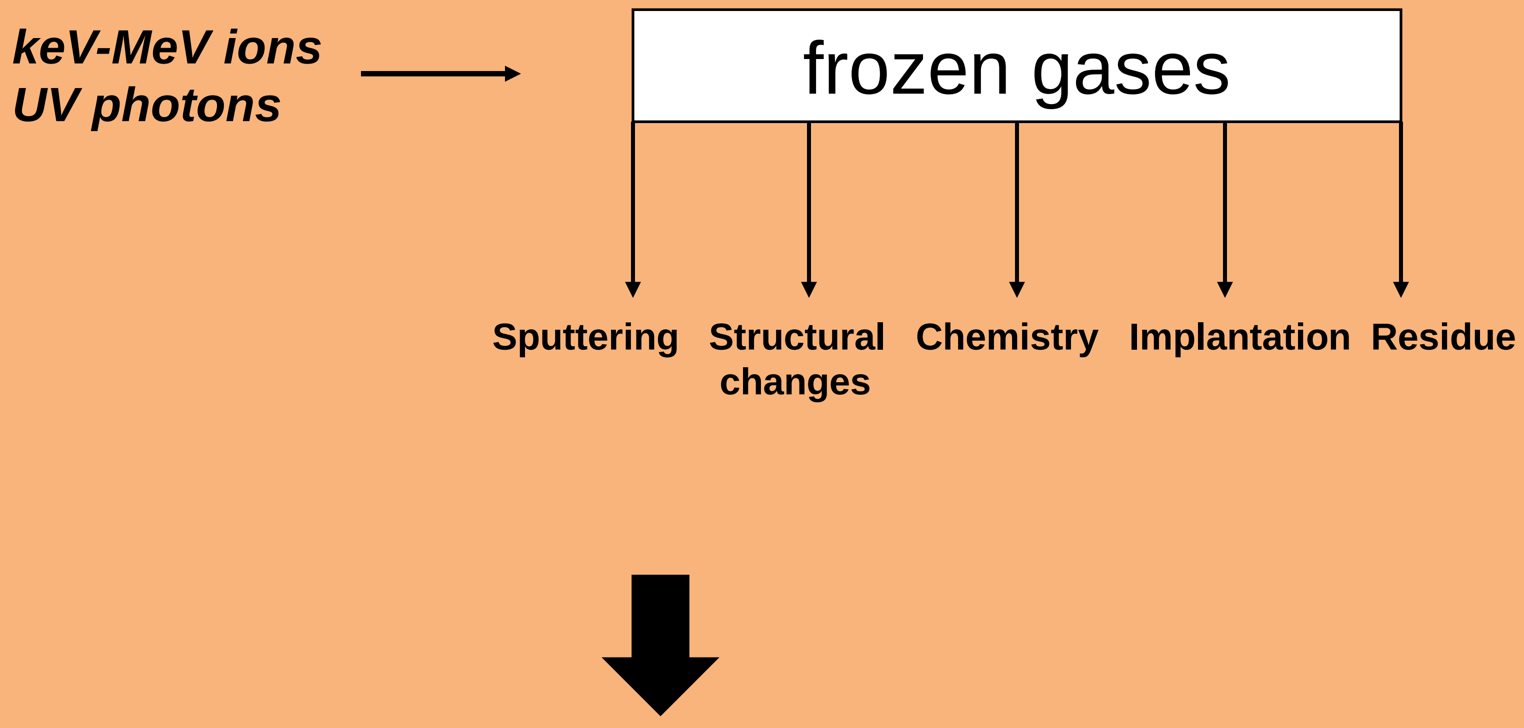
Energetic processing

High density and high extinction → stellar radiation does not penetrate molecular clouds

Interaction of cosmic rays with molecular clouds

low-energy cosmic rays	electrons	UV photons
↓	↓	↓
E = keV - MeV	E = keV	E = 6.9-13.6 eV

Effects of energetic processing



Laboratory experiments

Laboratories worldwide

Energetic processing driven chemistry

University of Hawaii, Honolulu (USA)
NASA/Ames Research Center (USA)
NASA/Goddard Space Flight Center (USA)
University of Virginia, Charlottesville (USA)
AT&T Bell Lab, NJ (USA)
Leiden Observatory (NL)
University of Paris, Orsay (F)
CIMAP-CIRIL-Ganil, Caen (F)
Forschungszentrum Jülich (D)
Catania Astrophysical Observatory (I)

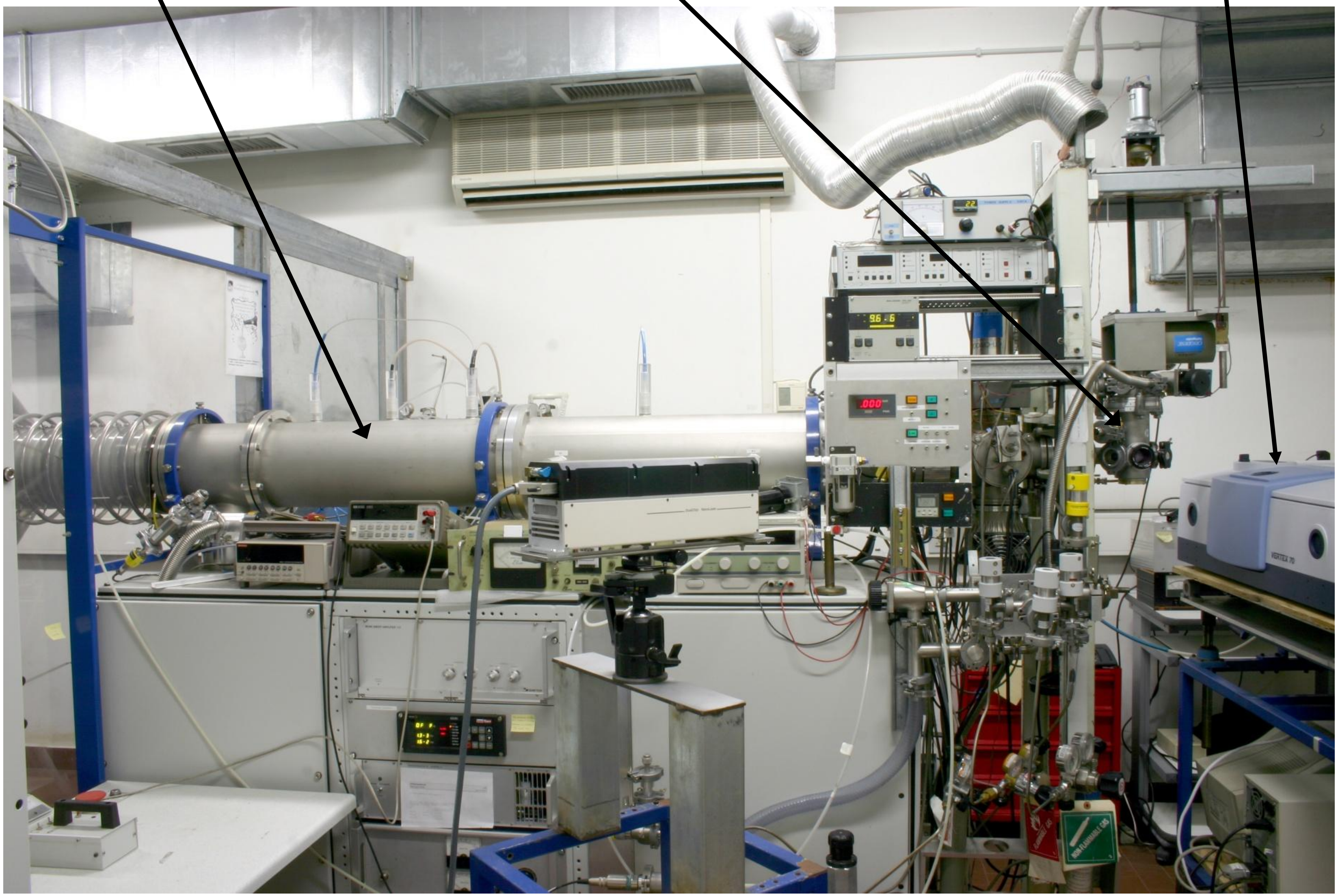
etc.

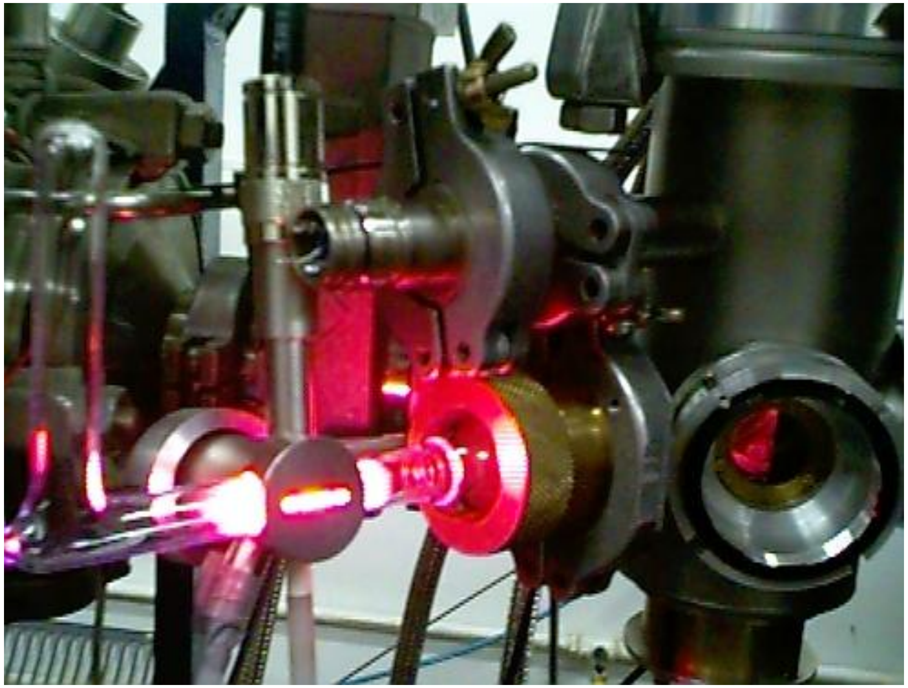
Laboratorio di Astrofisica Sperimentale
Catania

Ion beam

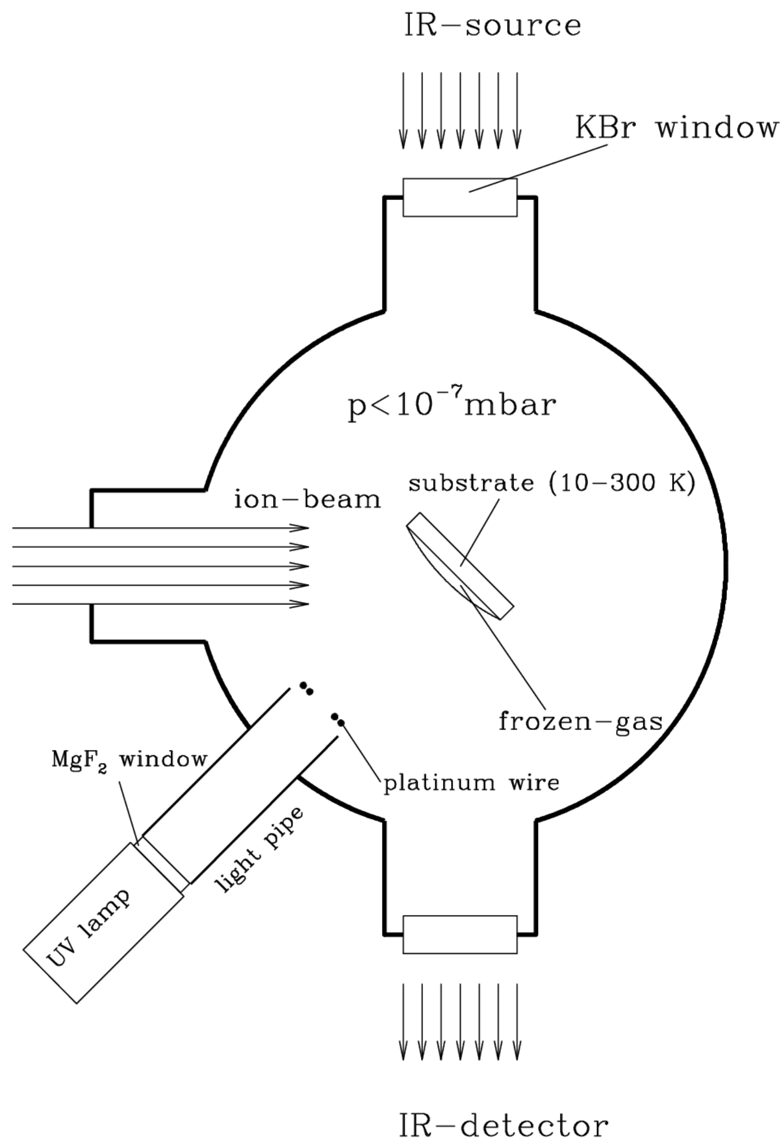
Vacuum chamber

FTIR spectrometer





Vacuum chamber

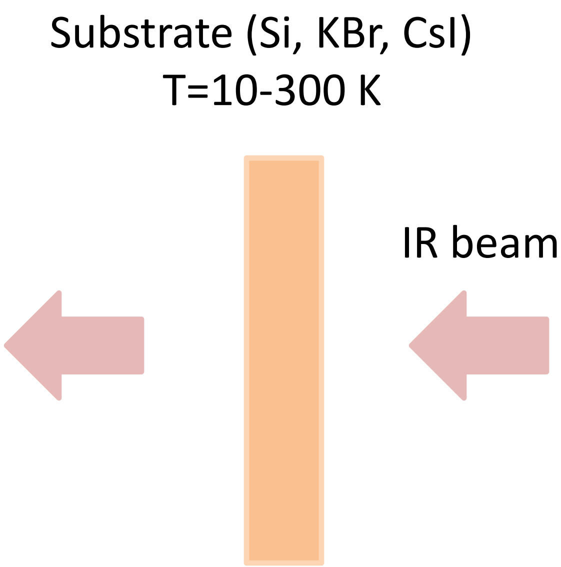


Analysis:

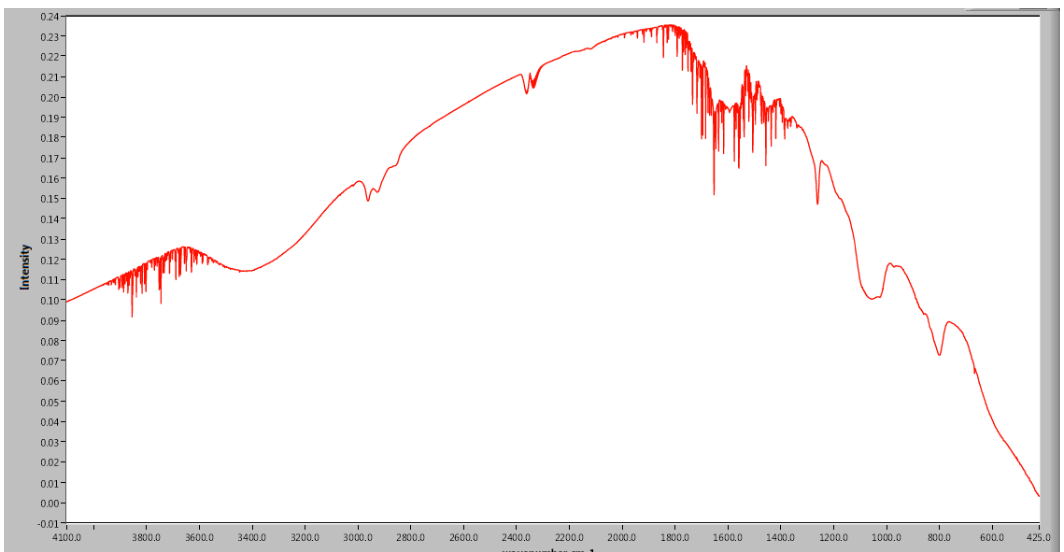
IR spectroscopy

Raman spectroscopy

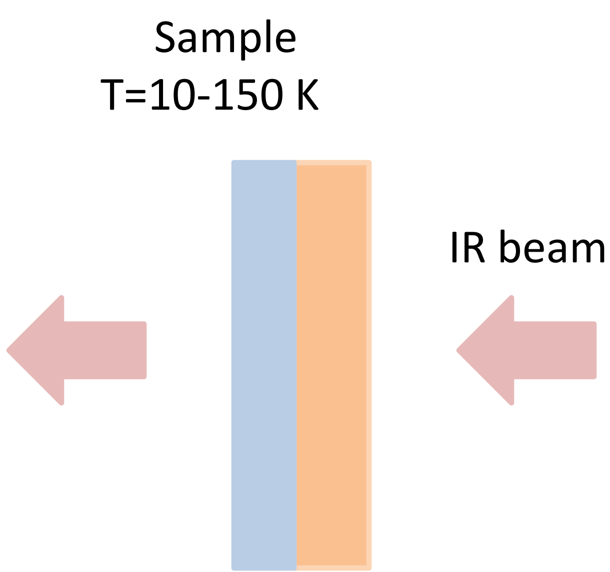
Experimental procedure



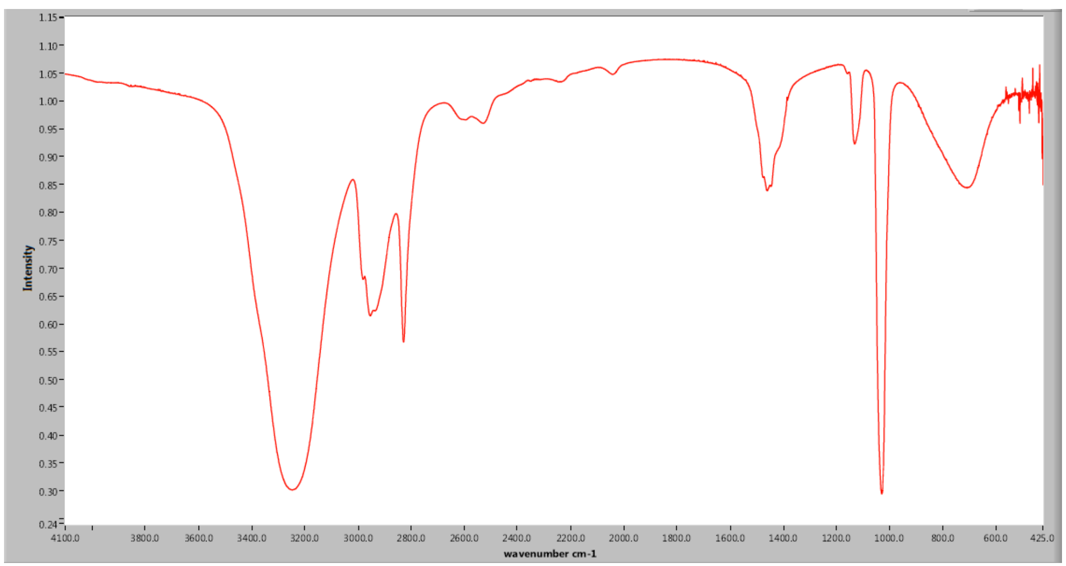
Background (mid-infrared) at 16 K
(KBr substrate)



Experimental procedure

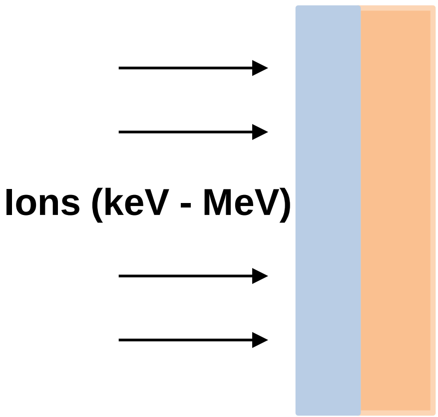


Mid-IR spectrum of the sample as deposited
(CH_3OH at 16 K)

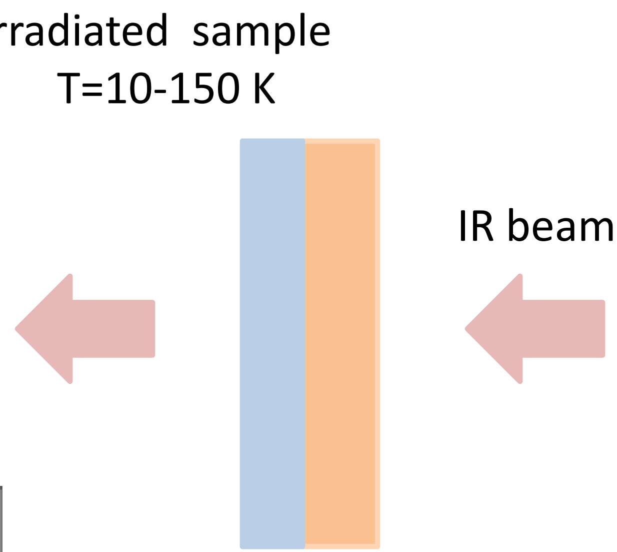


Experimental procedure

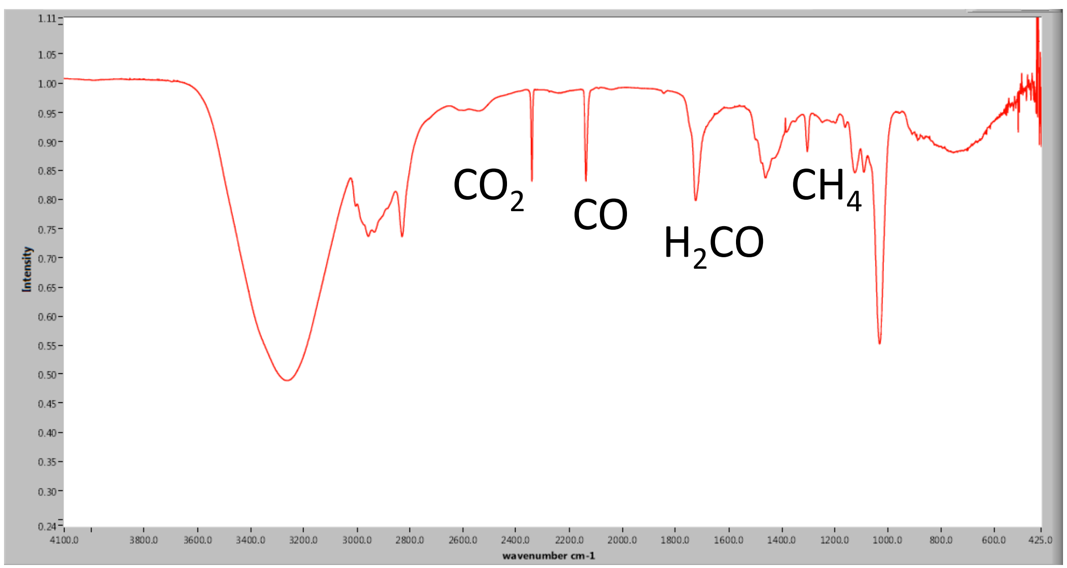
Irradiation of the sample
T=10-150 K



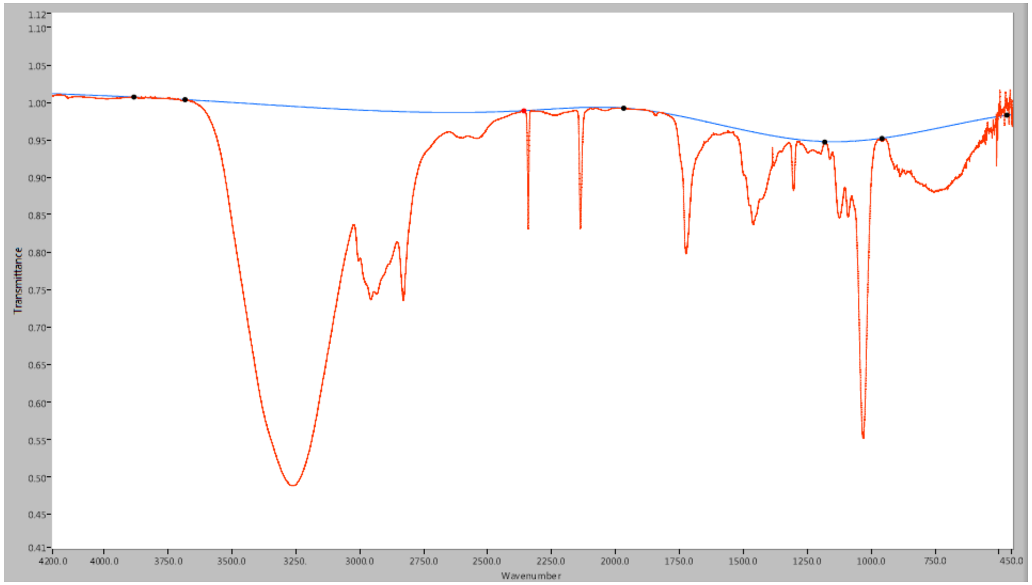
Experimental procedure

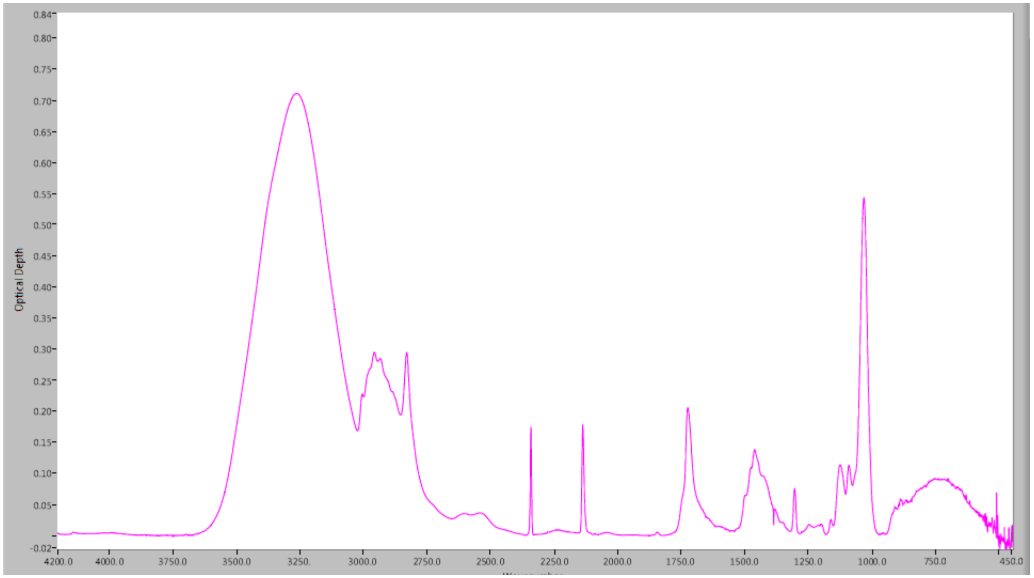


Mid-IR spectrum of the sample after irradiation
(CH_3OH + 200 keV H^+ at 16 K)

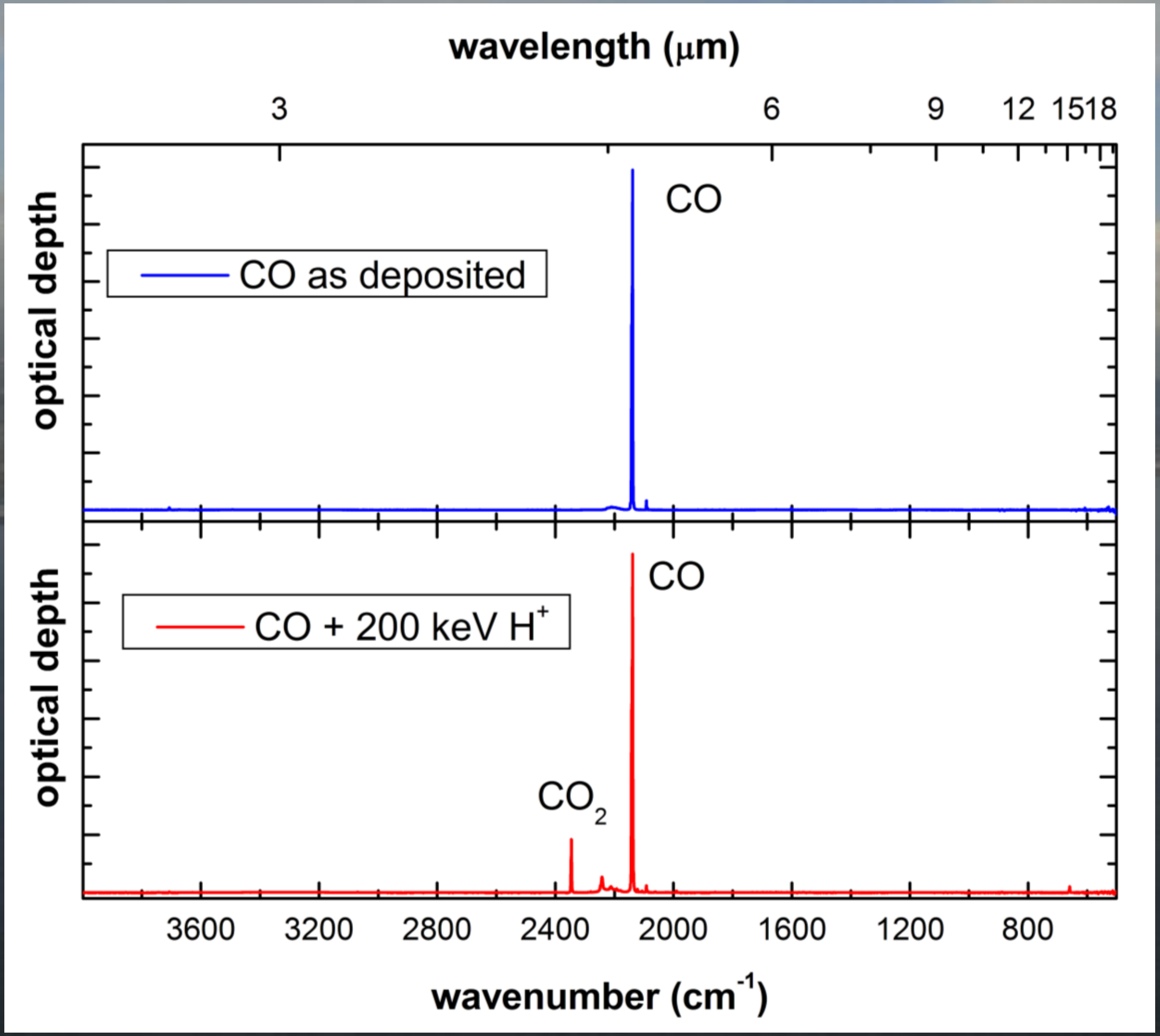


Experimental procedure



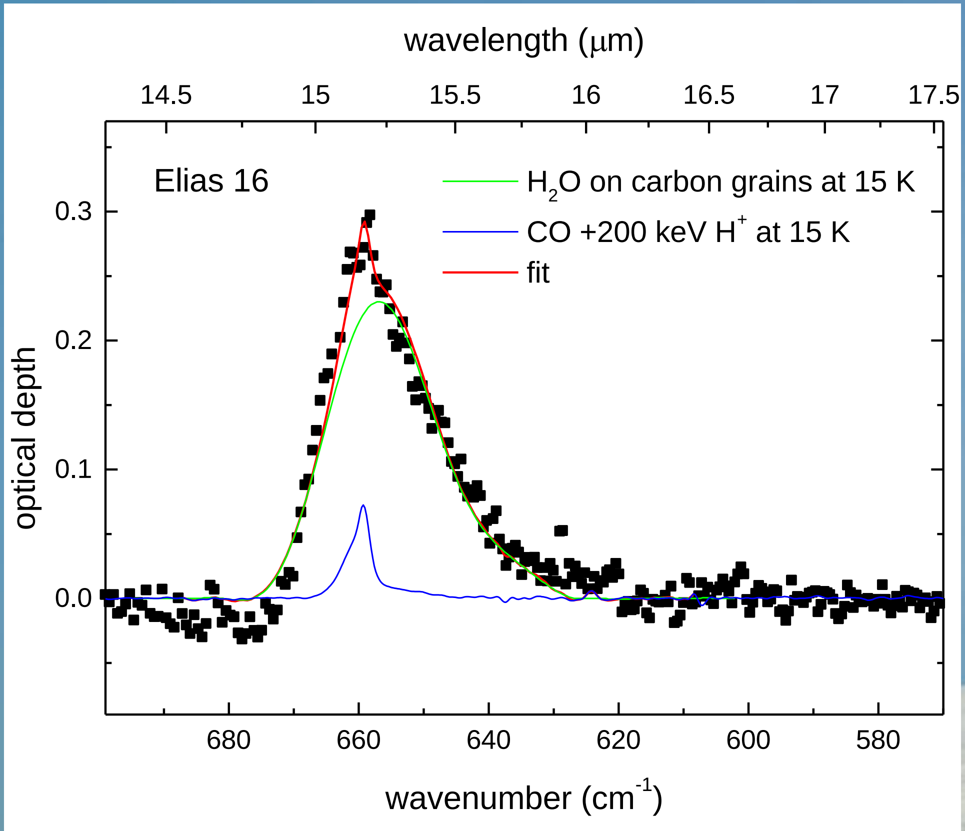


Solid CO



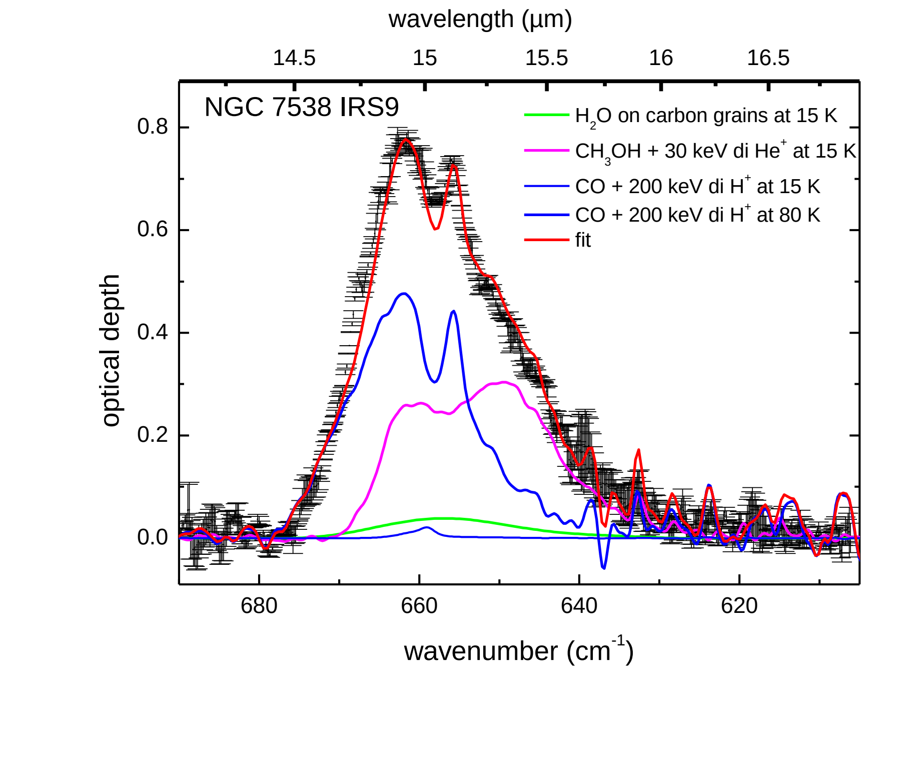
Loeffler, Baratta, Palumbo, Strazzulla, Baragiola, 2005, A&A 435, 587

Comparison with IR observations

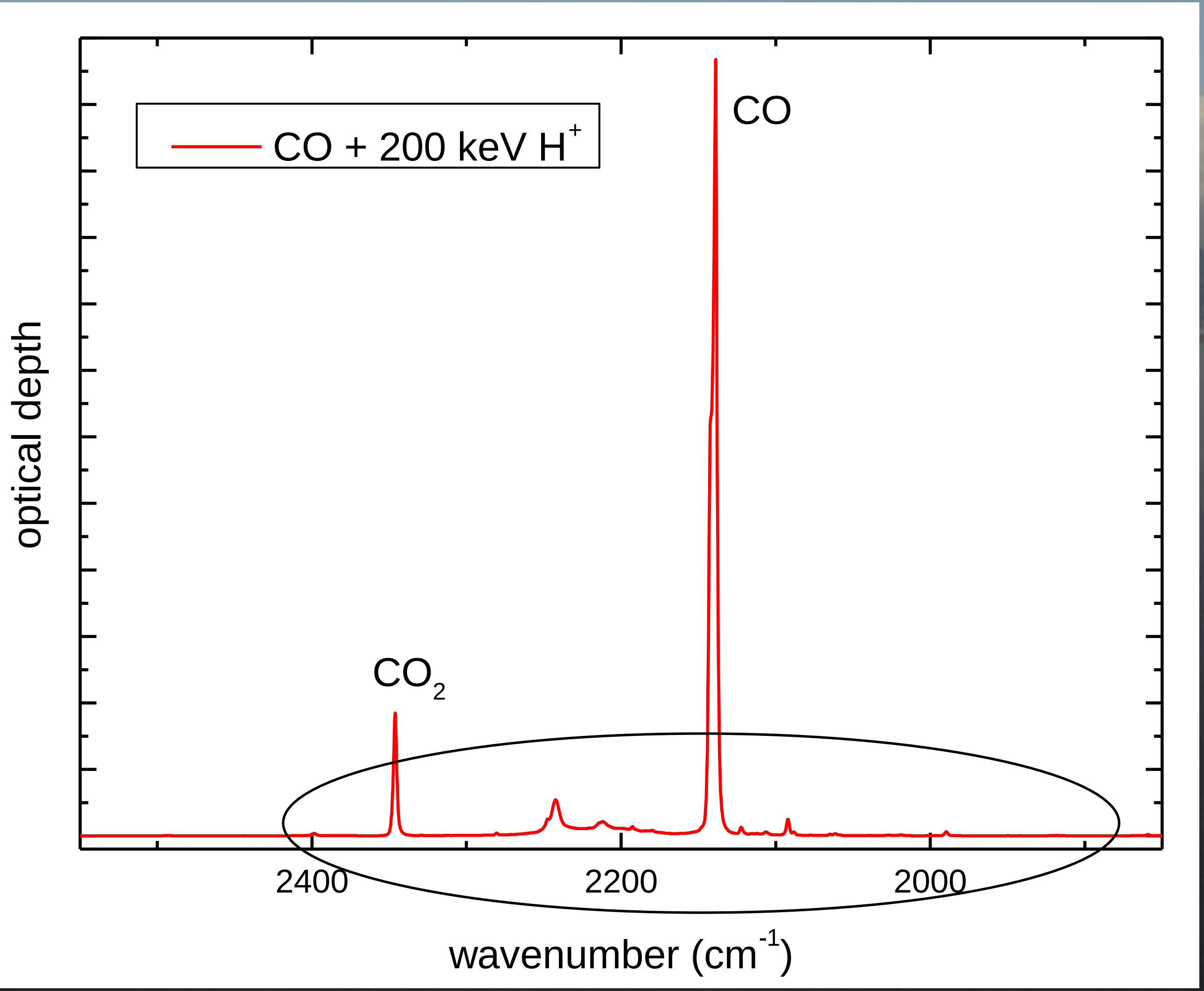


Elias 16 (field star)
Mennella, Baratta, Palumbo, Bergin, 2006, ApJ 643, 923

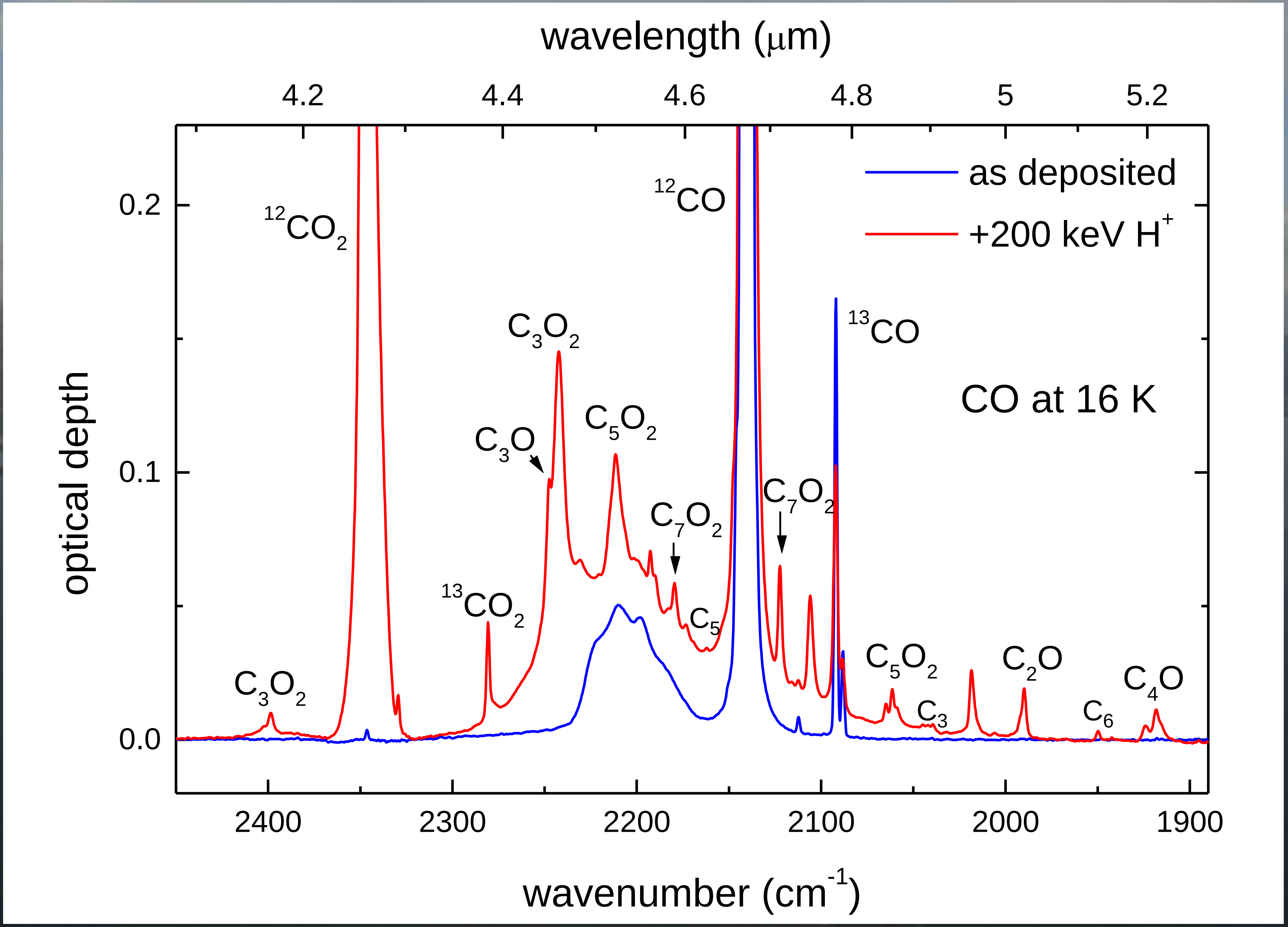
NGC7538 IRS9 (high-mass YSO)
Ioppolo, Palumbo, Baratta, Mennella, 2009, A&A 493, 1017



Chemistry in solid CO



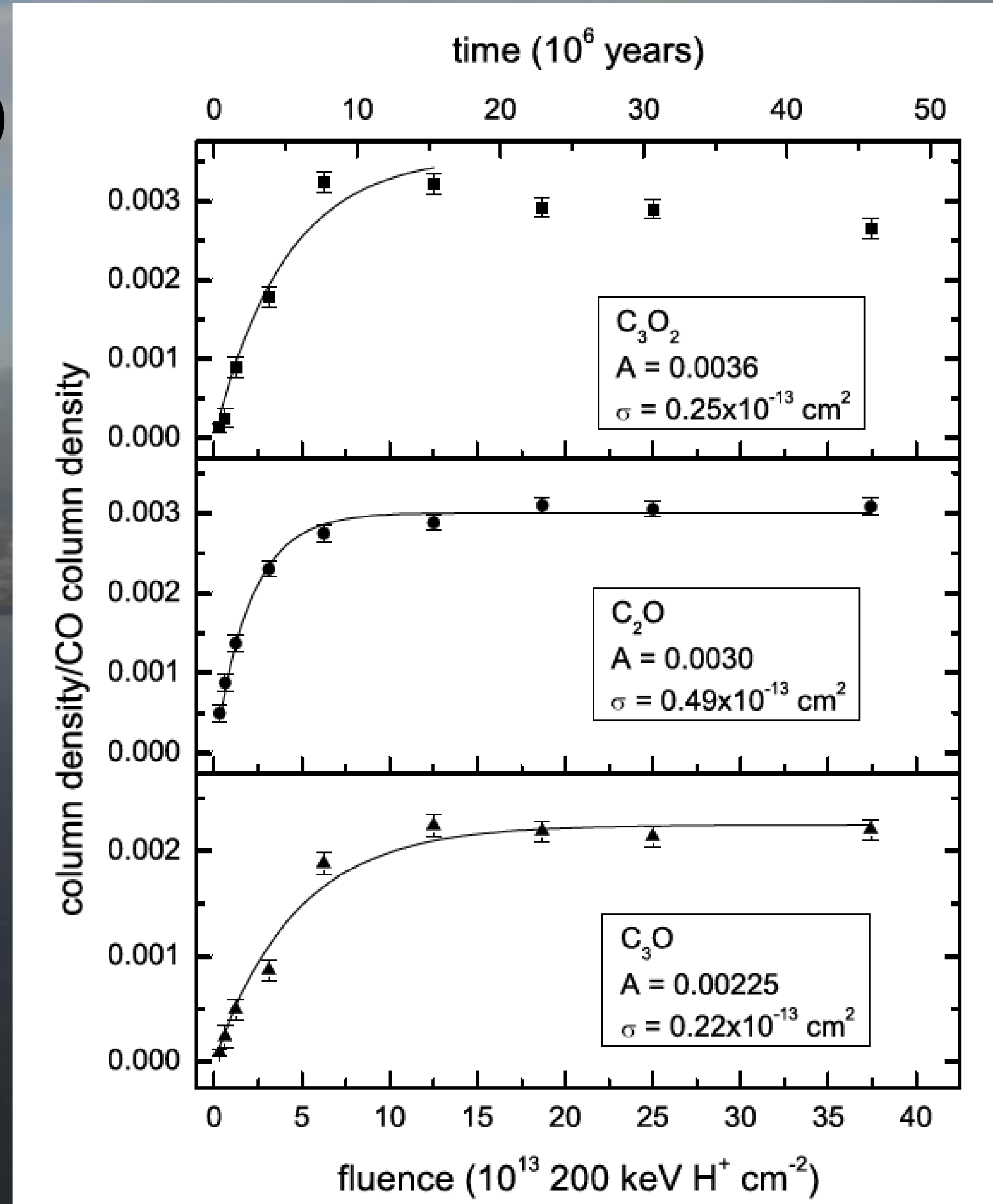
Formation of carbon chains



Palumbo, Leto, Siringo, Trigilio, 2008, ApJ 685, 1033

C_3O_2, C_2O and C_3O

$CO + 200$ keV H^+
T=16 K

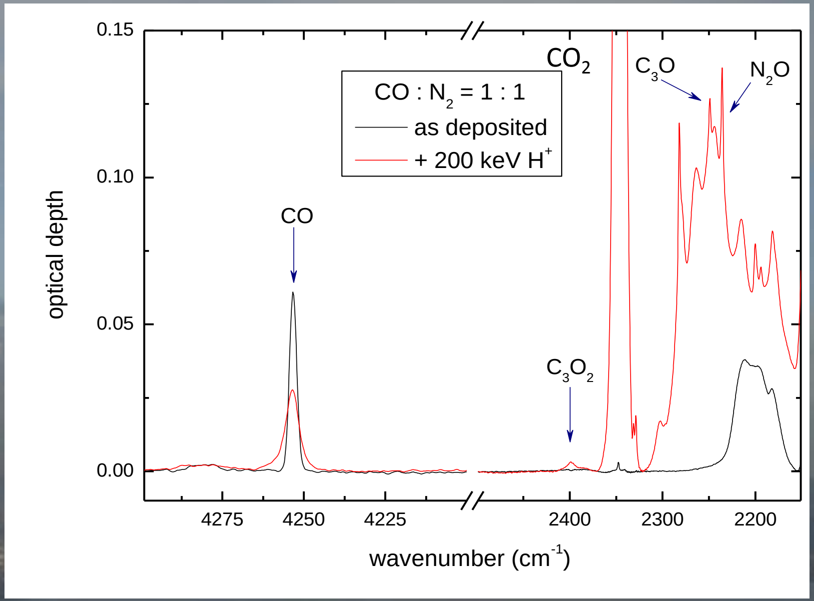


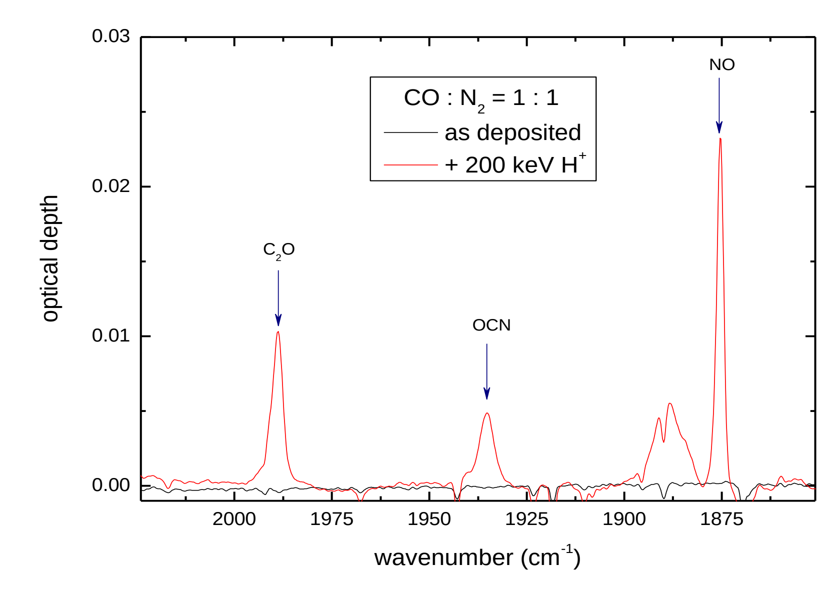
Palumbo et al. 2008

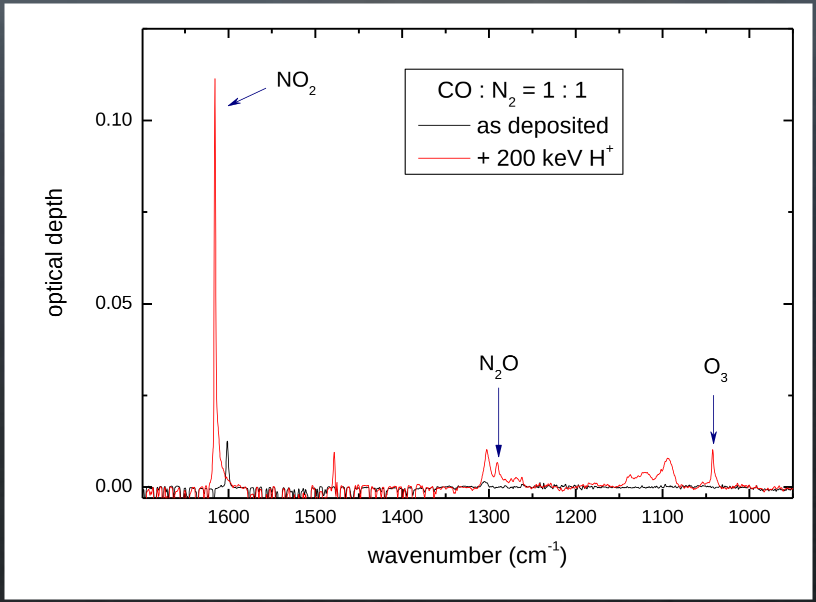
$CO:N_2$ mixtures

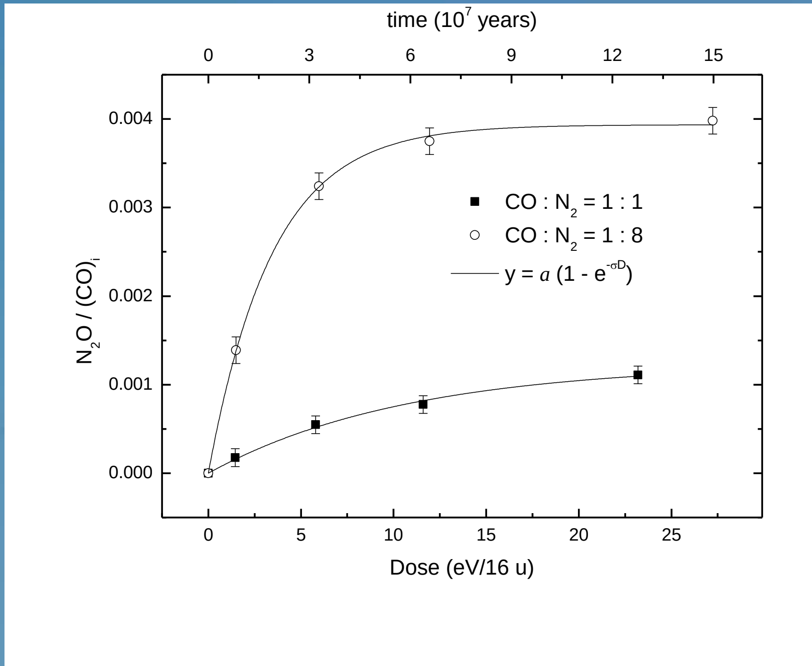
T = 16 K

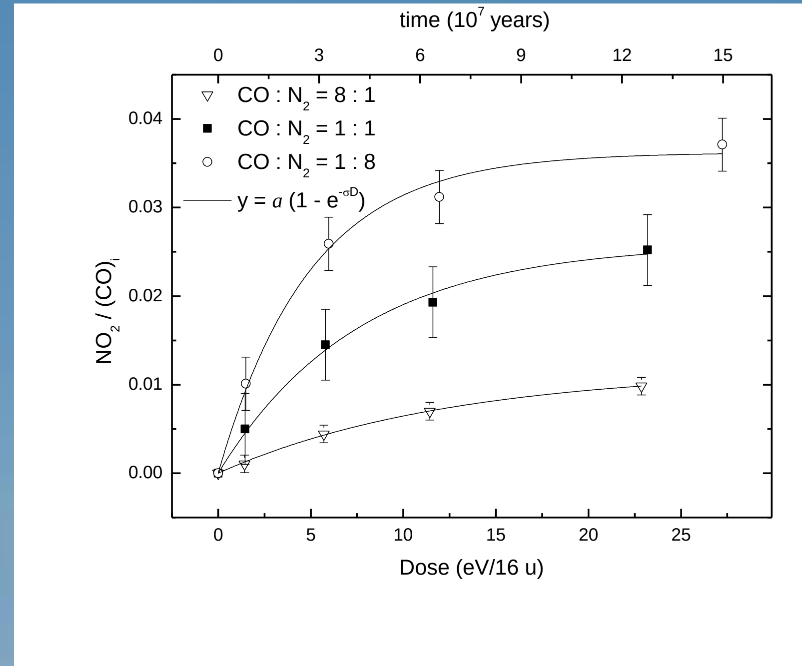
Sicilia et al. *in preparation*

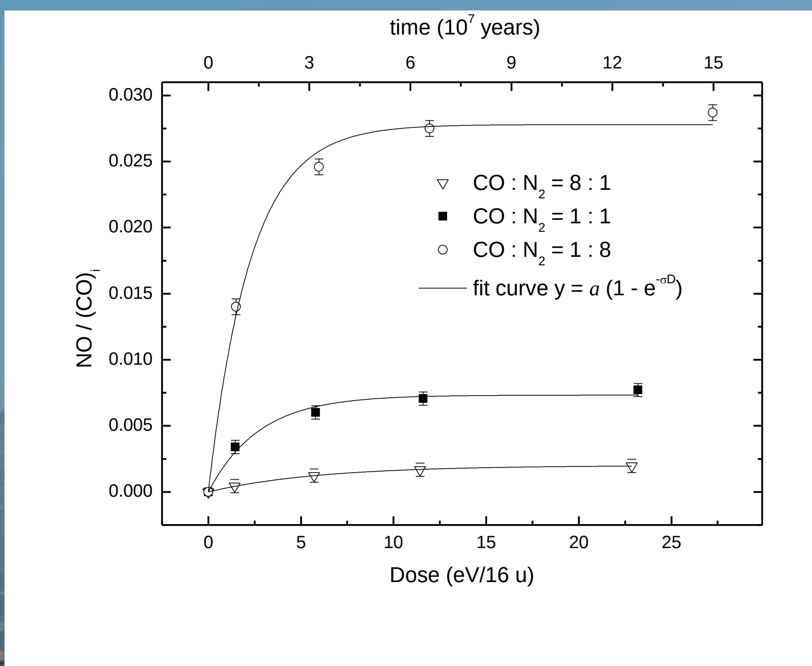












Nitrogen oxides

Sicilia et al. *in preparation*

Experimental results

After irradiation of CO and CO:N_2 ice mixtures:

✓ **$CO_2/CO_i \sim 0.1$ (Ioppolo et al. 2009)**

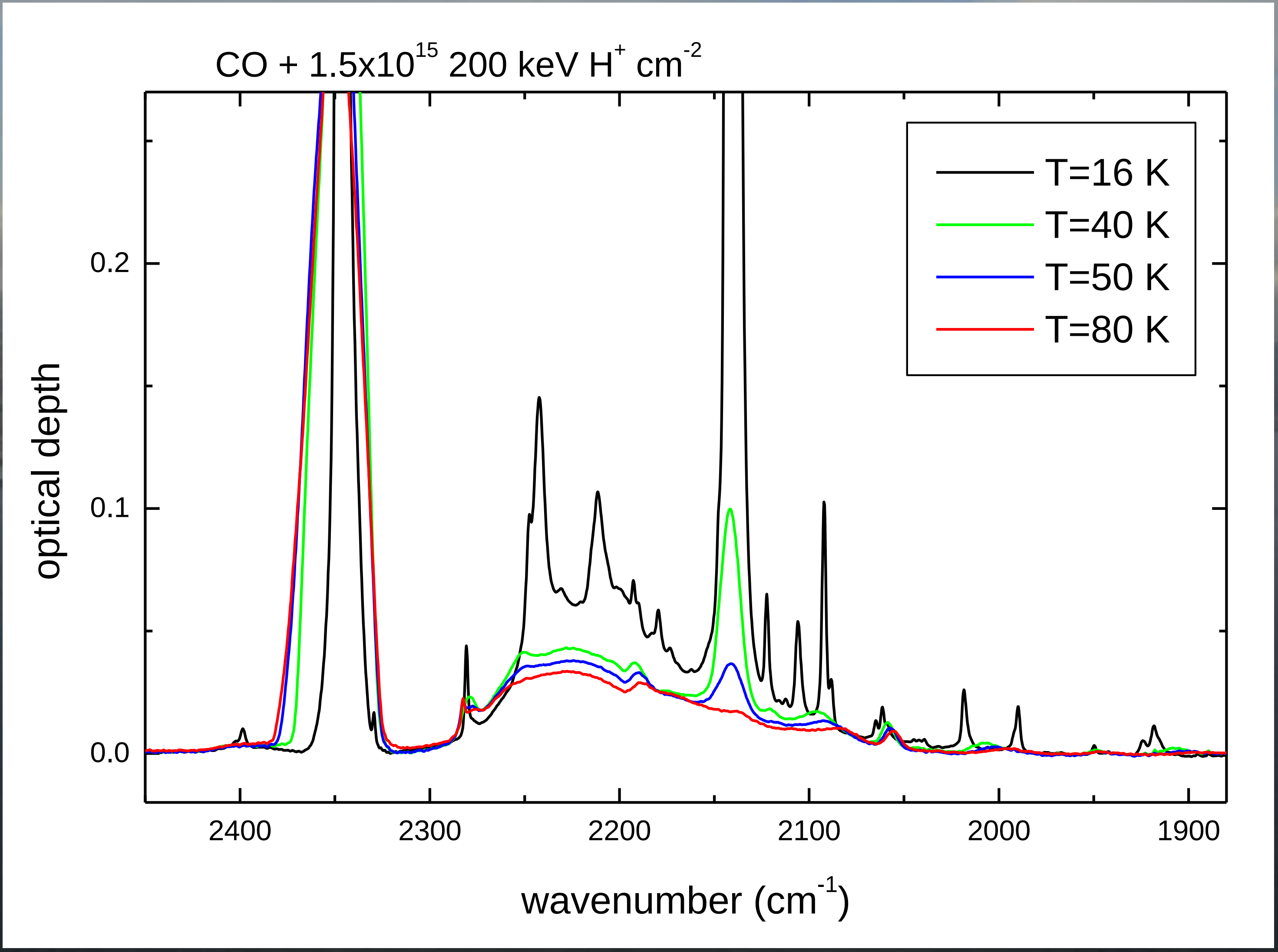
✓ **carbon-chain oxides/CO_i $\sim 2\text{-}3 \times 10^{-3}$ (Palumbo et al. 2008)**

✓ **NO/CO_i $\sim 10^{-2} - 10^{-3}$ (Sicilia et al. *in preparation*)**

✓ **N_2O/CO_i $\sim 1\text{-}4 \times 10^{-3}$**

✓ **NO_2/CO_i $\sim 1\text{-}3 \times 10^{-2}$**

Sublimation



Palumbo, Leto, Siringo, Trigilio, 2008, ApJ 685, 1033

Carbon chain oxides in the ISM

gas phase C_2O and C_3O detected towards

TMC-1CP	*cold molecular cloud (Brown et al. 1985)*
L1498	*starless core (Palumbo et al. in preparation)*
IRAS 16293-2422	*hot corino (Ceccarelli, priv. comm.)*
Elias 18	*class II protostar (Palumbo et al. 2008)*

These sources cover different phase of low-mass star formation.
Observations towards L1498 and Elias 18 triggered by laboratory results.
We expect ALMA will detect carbon-chain oxides towards a large number of sources.

$C_2O/H_2 = 6\times10^{-11}$

$C_3O/H_2 = 1.4\times10^{-10}$

(e.g., Brown et al. 1985; Ohishi et al. 1991; Palumbo et al. 2008)

Origin of C_2O and C_3O

- ✓ Gas phase reactions
- ✓ Ion irradiation of CO-rich icy mantles

In IS clouds: $CO/H_2 = 9.5\times10^{-5}$ (*Frerking et al. 1982*)

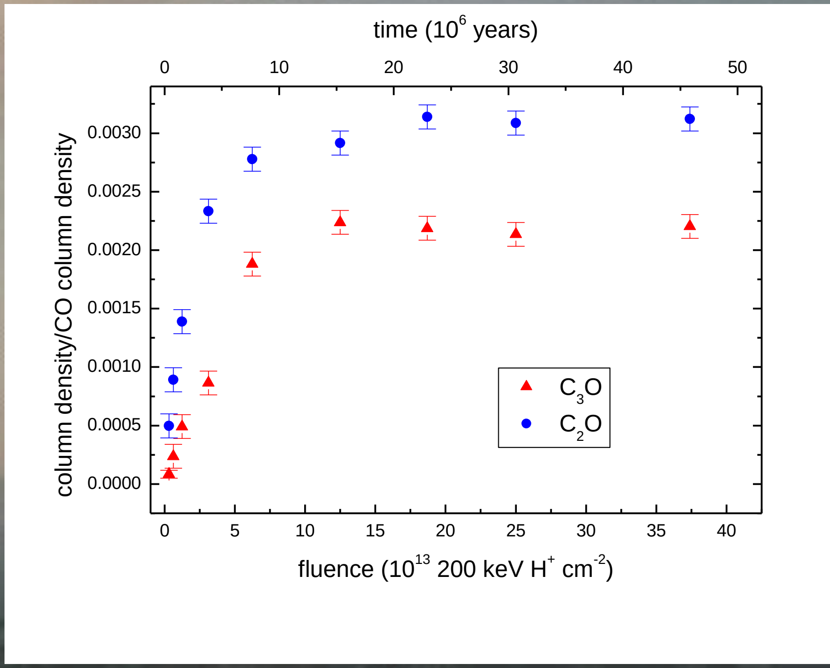
$C_2O/CO = 6.3\times10^{-7}$

$C_3O/CO = 1.5\times10^{-6}$

Experimental highest values

$C_2O/CO = 3\times10^{-3}$

$C_3O/CO = 2\times10^{-3}$



Assuming:

✓High depletion

✓Φ(1 MeV) = 1 cm^{-2} s^{-1} (*Mennella et al. 2003*)

⇓

Observed C_2O and C_3O can be formed after 10^2-10^3 years (Palumbo et al. 2008)

Nitrogen oxides in the ISM

Sagittarius B2 (Halfen et al. 2001)

$NO/H_2 \sim 10^{-8}$

$N_2O/H_2 \sim 10^{-9}$ (two orders of magnitude higher than predicted by chemical models)

$NO_2/H_2 < 3.3 \times 10^{-9}$

CO depletion at $n_H \geq 10^4$ cm^{-3}
N depletion at $n_H \geq 10^6$ cm^{-3}

Nitrogen oxides formed in the solid phase after ion irradiation of icy grain mantles and released to the gas phase after desorption of icy mantles.

We expect ALMA will detect nitrogen oxides towards a large number of sources.

C_3O in carbon star IRC +10216

Tenenbaum et al. 2006, ApJ 649, L17

IRC +10216 is an asymptotic giant branch star

C_3O column density = 1.2×10^{12} cm^{-2}

an order of magnitude higher than predicted

Other detected O-bearing molecules:

H_2O (Melnick et al. 2001; Hasegawa et al. 2006)

OH (Ford et al. 2003)

H_2CO (Ford et al. 2004)

C_3O origin in IRC +10216

Gas phase reactions (Tenenbaum et al. 2006)

Sublimation of icy bodies (Melnick et al. 2001)

Search for carbon-chain oxides in icy Solar System objects

(Comets, Pluto and Kuiper Belt objects)

Tentative detection of carbon suboxide (C_3O_2) in **comet Halley** (Huntress et al. 1991; Crovisier et al. 1991).
We would need almost a Hale-Bopp like comet to be able to detect some C_3O lines with ALMA (Jeremie Boissier , priv. comm.)

New Horizons (http://pluto.jhuapl.edu/)
Launched in January 2006, will encounter Pluto-Charon in 2015 and other Kuiper Belt objects in 2016-2020.

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