INTERNATIONAL SYMPOSIUM AND WORKSHOP ON ASTROCHEMISTRY

Understanding extraterrestrial molecular complexity through experiments, observations and models

JULY 3rd – 8th, 2016
CAMPINAS, SP, BRAZIL

www1.univap.br/gaa/iswa

Few examples on data treatment applied to astrochemistry

Prof. Dr. Sergio Pilling

www1.univap.br/spilling

sergiopilling@yahoo.com.br

LASA
Laboratório de Astroquímica e Astrobiologia da Universidade do Vale do Paraíba

UniVap
UNIVERSIDADE DO VALE DO PARAÍBA
São José dos Campos - SP

P&D

Probing some energetic processes in the interstellar medium inside the lab

i) GAS PHASE (TOF-MS)
Production of H_3^+ via photodissociation of organic molecules;

ii) SOLID PHASE /ICE (FTIR)
Unsaturation induced by cosmic rays at hydrocarbon-rich ices.

PAPER I

Mon. Not. R. Astron. Soc. **375,** 1488–1494 (2007) doi:10.1111/j.1365-2966.2006.11415.x

Production of H_3^+ via photodissociation of organic molecules in interstellar clouds

S. Pilling,[1★] D. P. P. Andrade,[2,3] R. Neves,[2] A. M. Ferreira-Rodrigues,[2,3] A. C. F. Santos[4] and H. M. Boechat-Roberty[2]

[1] *Laboratório Nacional de Luz Síncrotron, Caixa Postal 6192, CEP 13084-971, Campinas, SP, Brazil*
[2] *Observatório do Valongo, Universidade Federal do Rio de Janeiro – UFRJ, Ladeira Pedro Antônio, 43, CEP 20080-090, Rio de Janeiro, RJ, Brazil*
[3] *Instituto de Química, Universidade Federal do Rio de Janeiro – UFRJ, Ilha do Fundão, CEP 21949-900, Rio de Janeiro, RJ, Brazil*
[4] *Instituto de Física, Universidade Federal do Rio de Janeiro – UFRJ, Ilha do Fundão, Caixa Postal 68528, CEP 21941-972, Rio de Janeiro, RJ, Brazil*

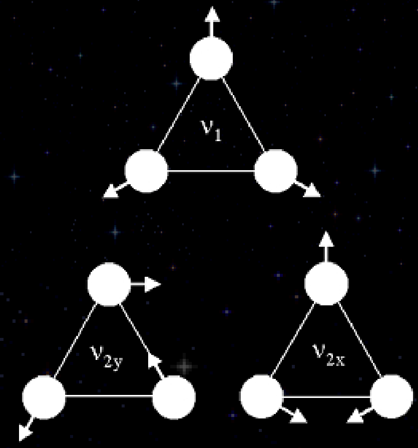
Motivation: H_3^+ in interstellar medium

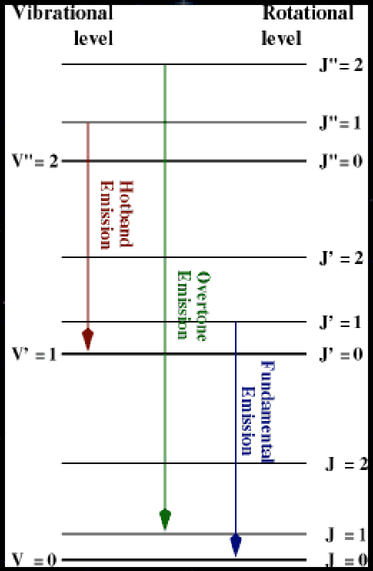
- Main reaction routes

$$H_2^+ + H_2 \longrightarrow H_3^+ + H.$$

$$H_3^+ + X \longrightarrow HX^+ + H_2,$$

$X = CO, N_2, H_2O, NH_3$, etc.

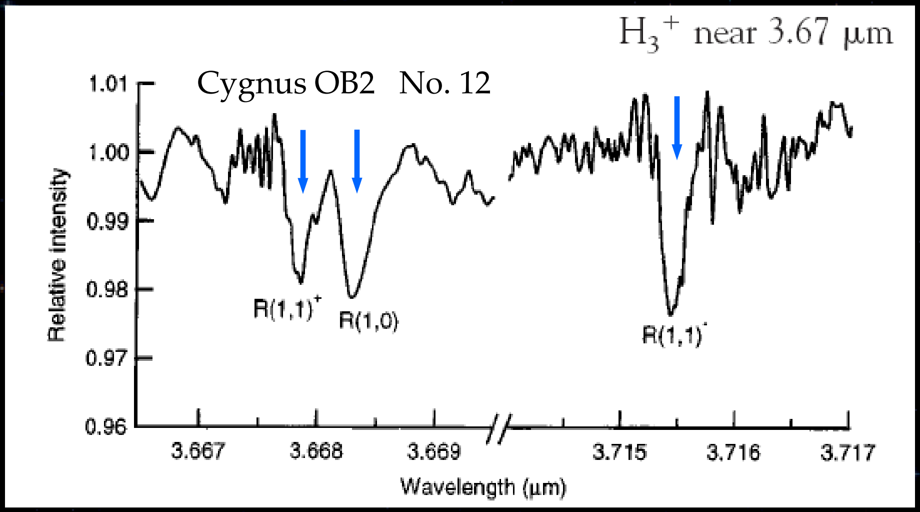




left) The motions involved in the H3+ vibrational modes, v1 and ν 2. right) Rotational and vibrational energy levels, and the associated emission features (from Tennyson and Miller, 1994)

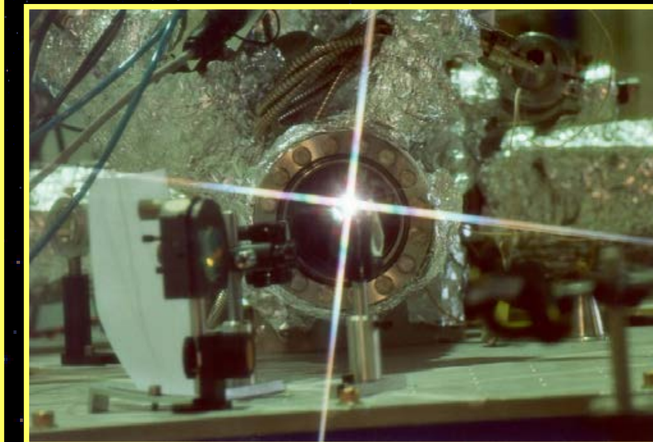
- Dense Clouds
  - $N(H_3^+) = 1\text{-}5\times10^{14}\ cm^{-2}$
  - Path length L ~ 1 pc
  - Density ~ up to $6 \times 10^4\ cm^{-3}$
  - Temperature T ~ 30 K

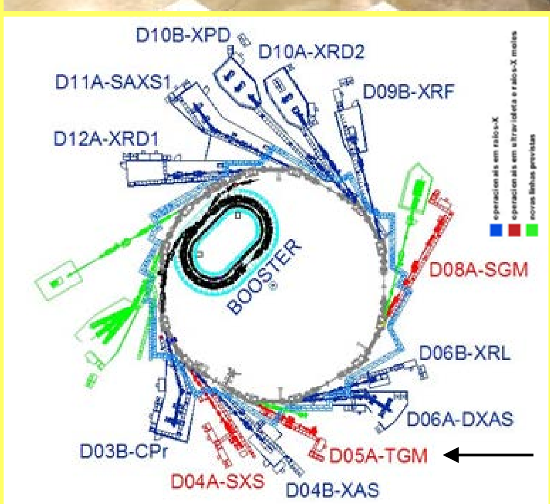
- Diffuse Clouds
  - $N(H_3^+) = 4\text{-}6\times10^{14}\ cm^{-2}$
  - Density ~ up to $4 \times 10^5\ cm^{-3}$
  - Temperature T ~ 30 K

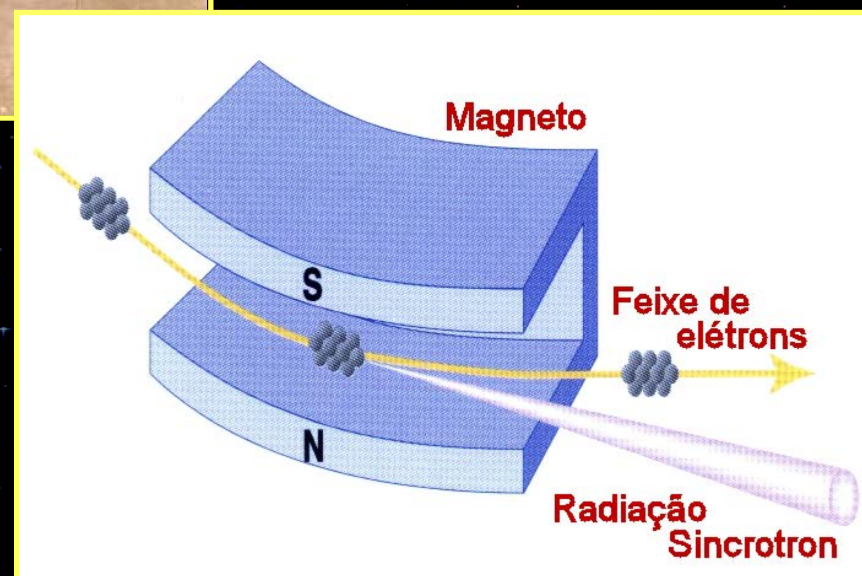


McCall et al, 1998, Science, 279, 1910. McCall et al, 1999, ApJ 522,338.

Experimental setup – LNLS (Campinas, SP, Brazil)

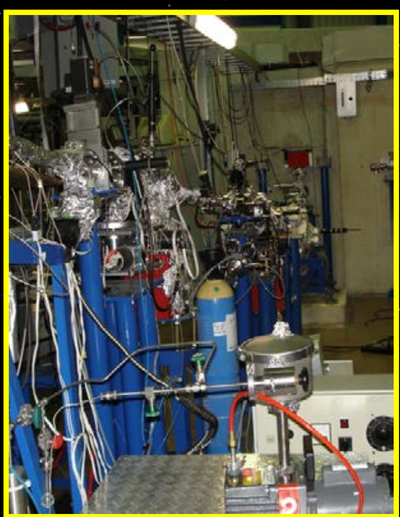




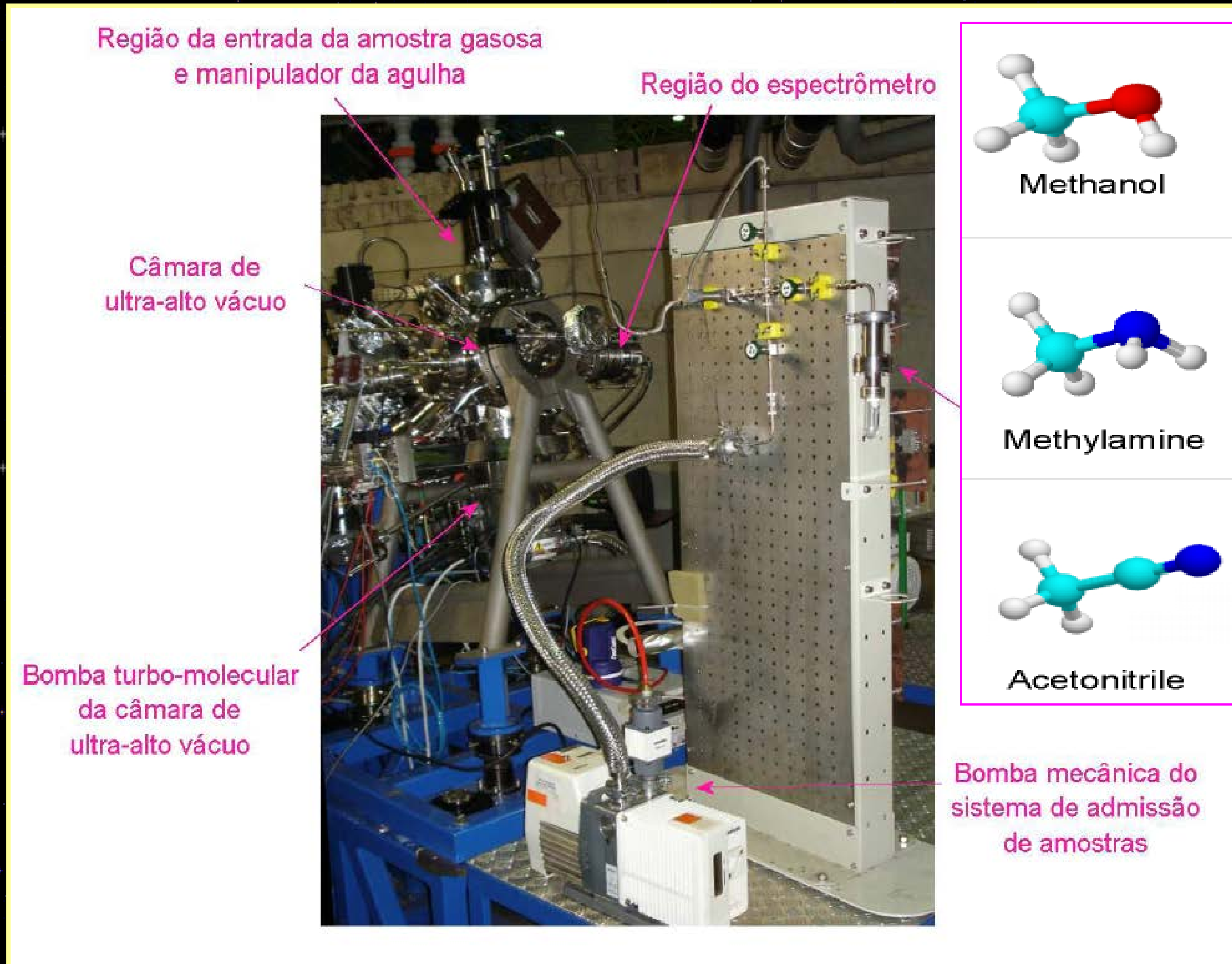


The TGM (thoroidal grating monochromator) beamline

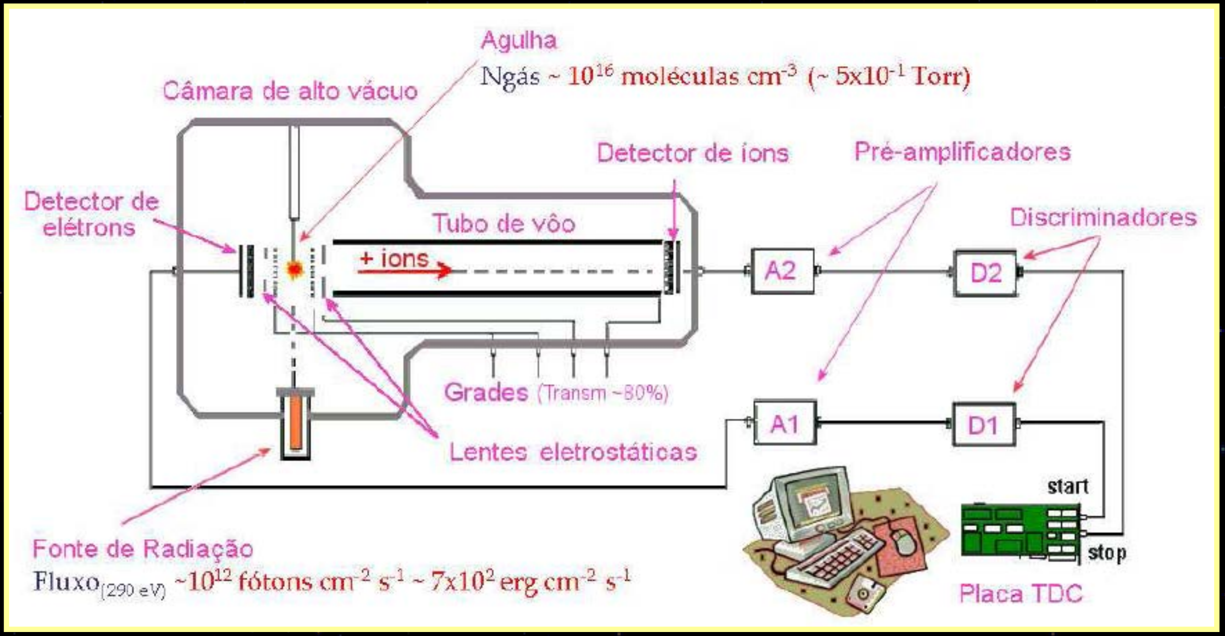
Eletronics

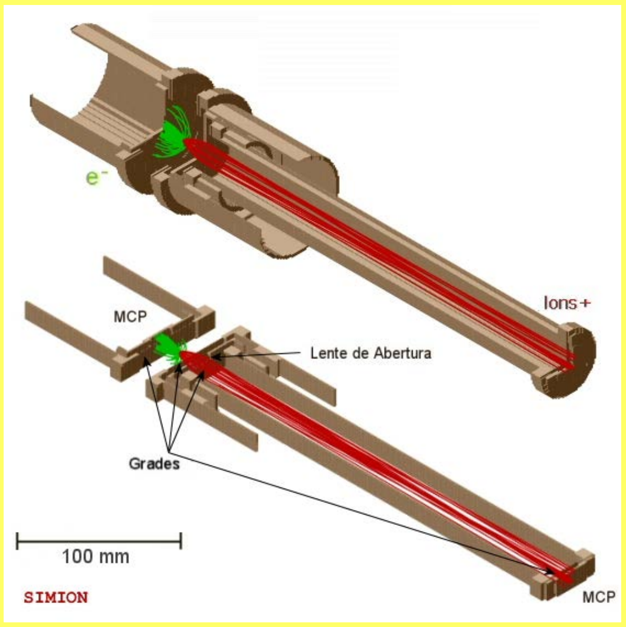


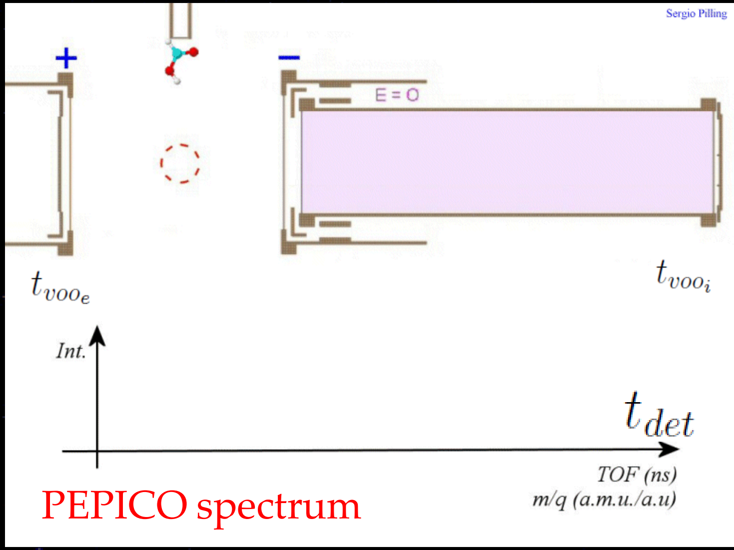
TGM Beamline

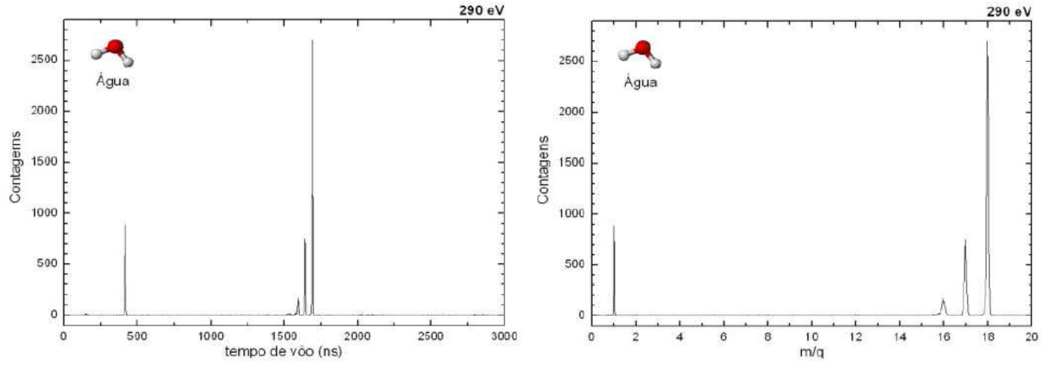


The technique and the spectrometer



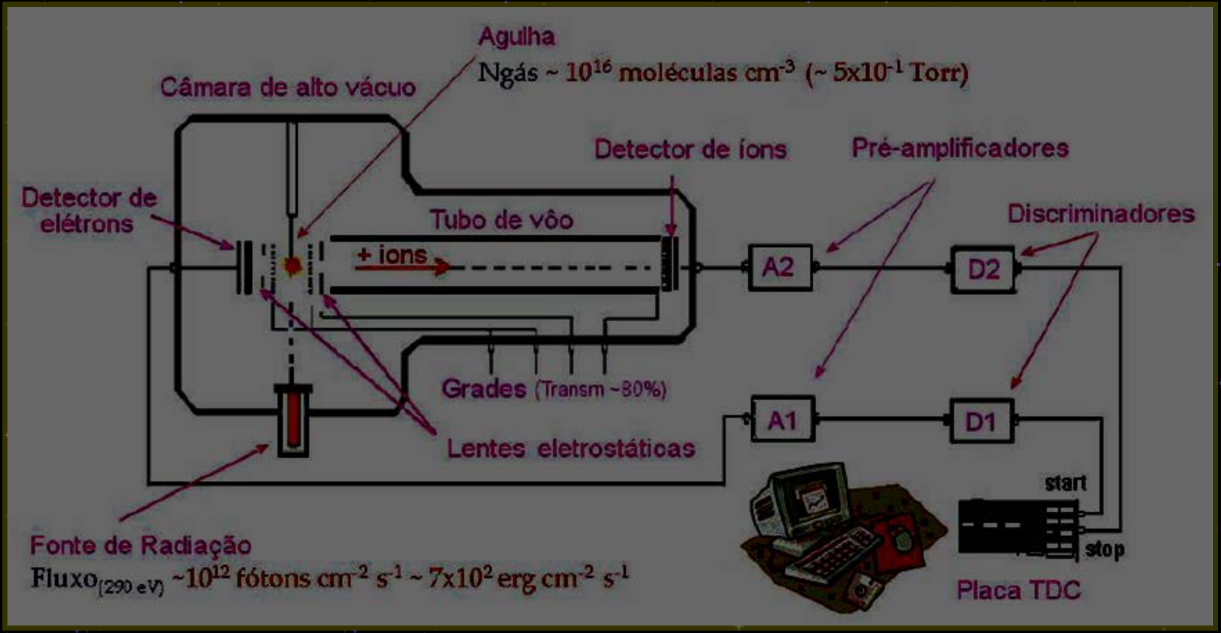


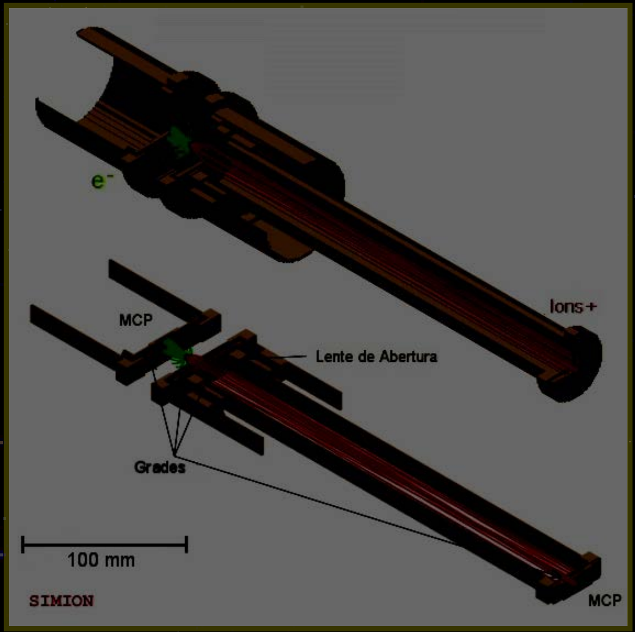


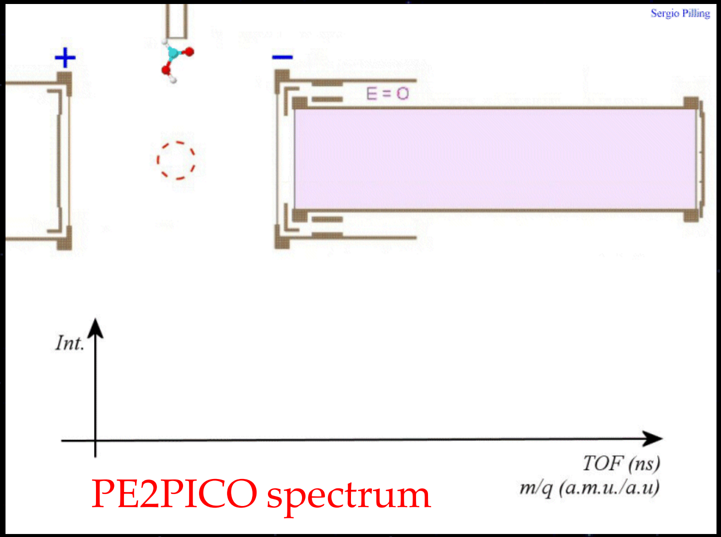


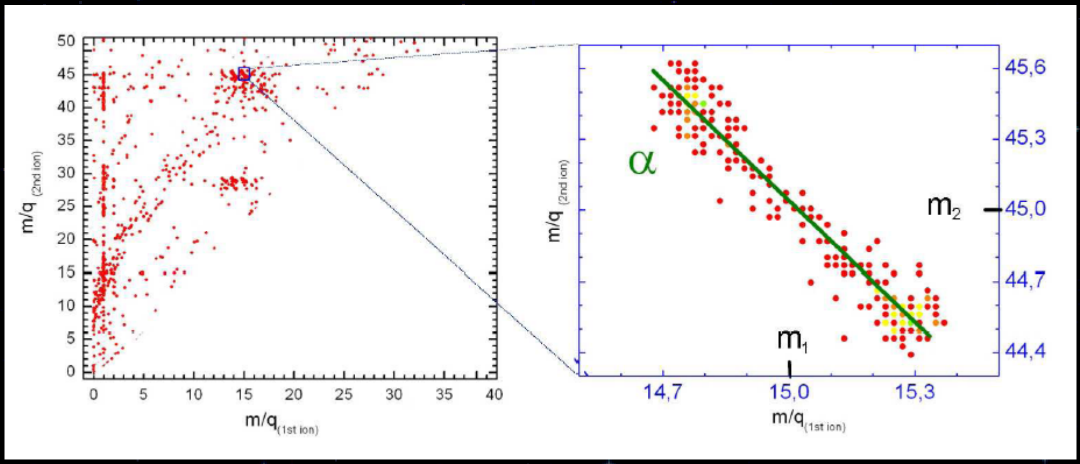
$$t_{det} = t_{voo_i} - t_{voo_e} \Rightarrow \frac{m}{q} = at_{det}^2 + bt_{det} + c$$

The technique and the spectrometer









PEPICO spectra

$$\begin{aligned} M + h\nu &\longrightarrow M^{+} + e^{-} \\ M^{+} &\longrightarrow M_1^{+} \ (+\ \text{neutros}). \end{aligned}$$

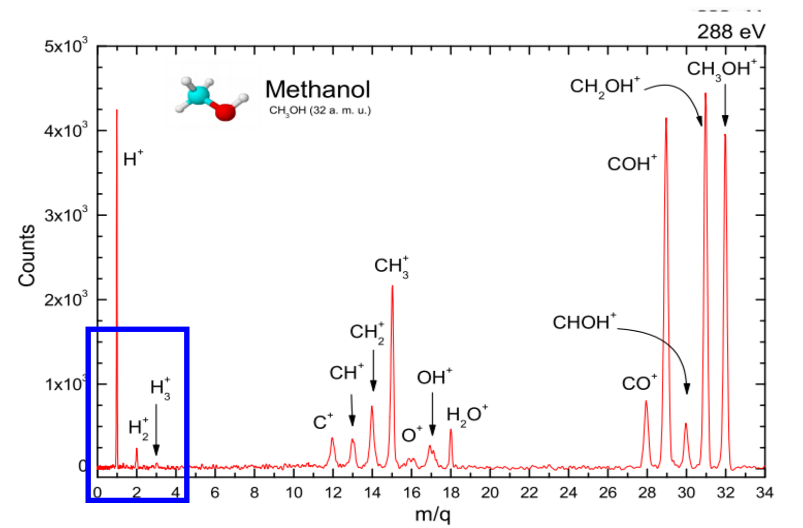
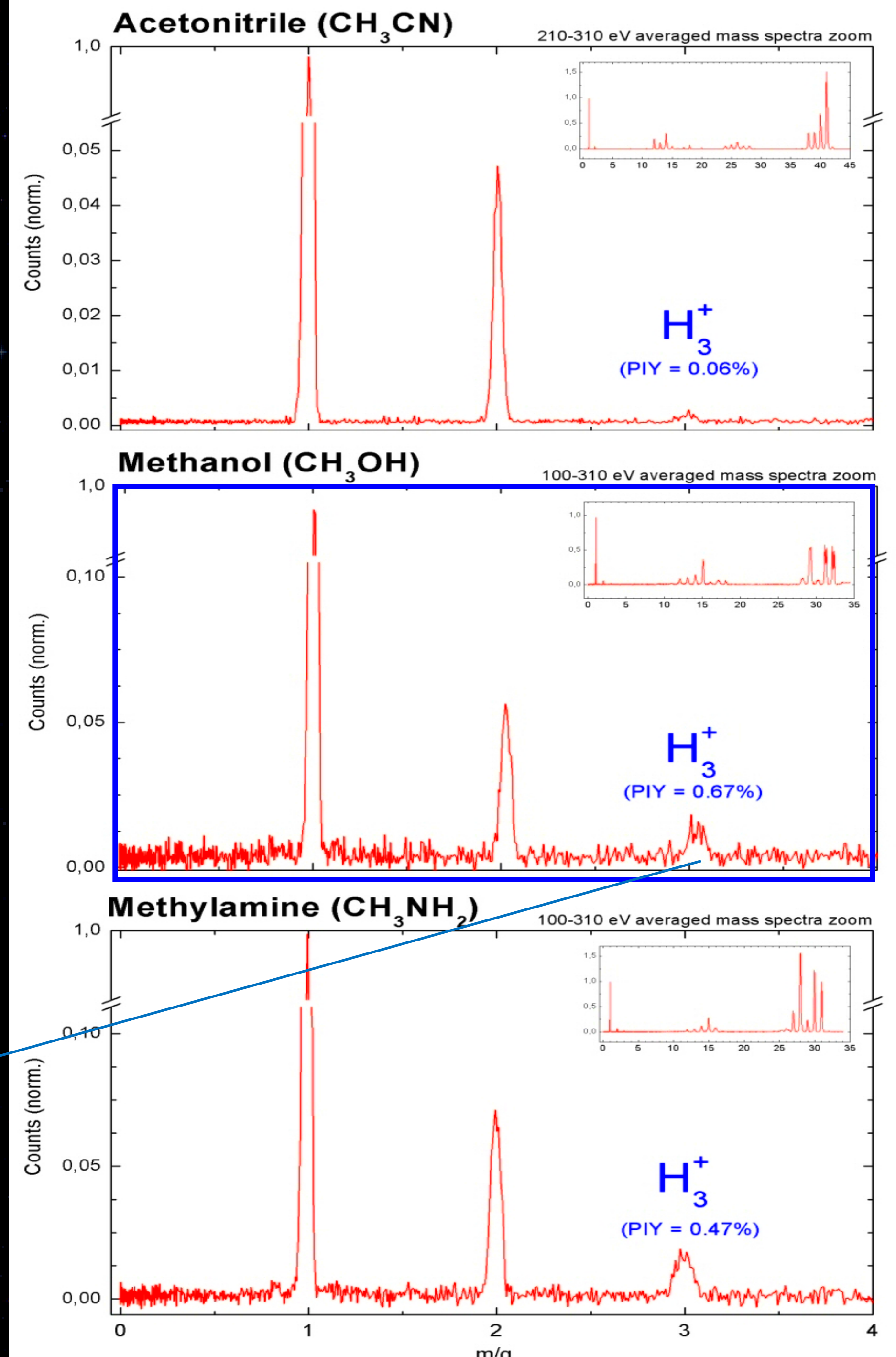


Fig. 1. Time-of-flight mass spectrum of methanol after exposure to 288.3 eV X-ray.



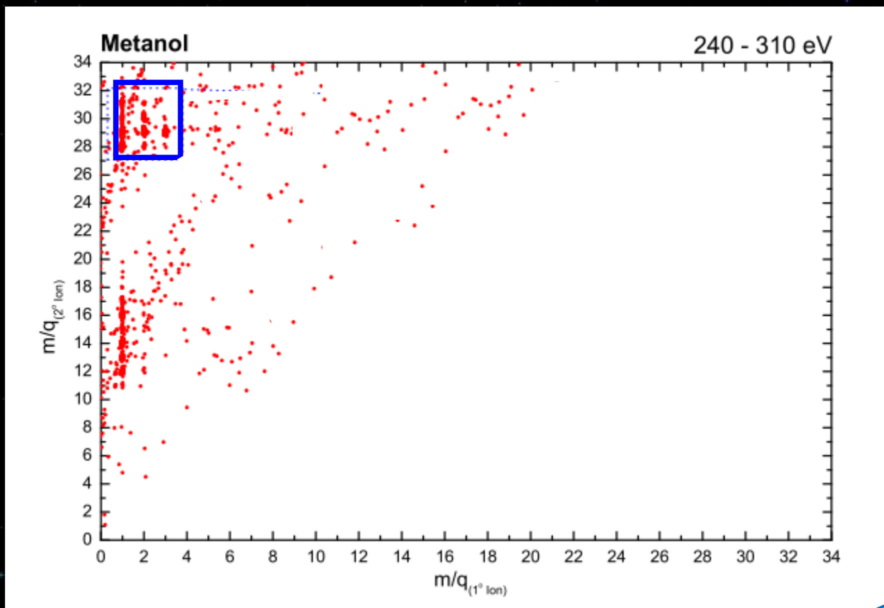
Partial Ion Yield

$$PIY_i = \left(\frac{A_i}{A_t^+} \pm \frac{\sqrt{A_i} + A_i \times ER/100}{A_t^+} \right) \times 100\%$$

Total peaks´s area

PE2PICO spectra

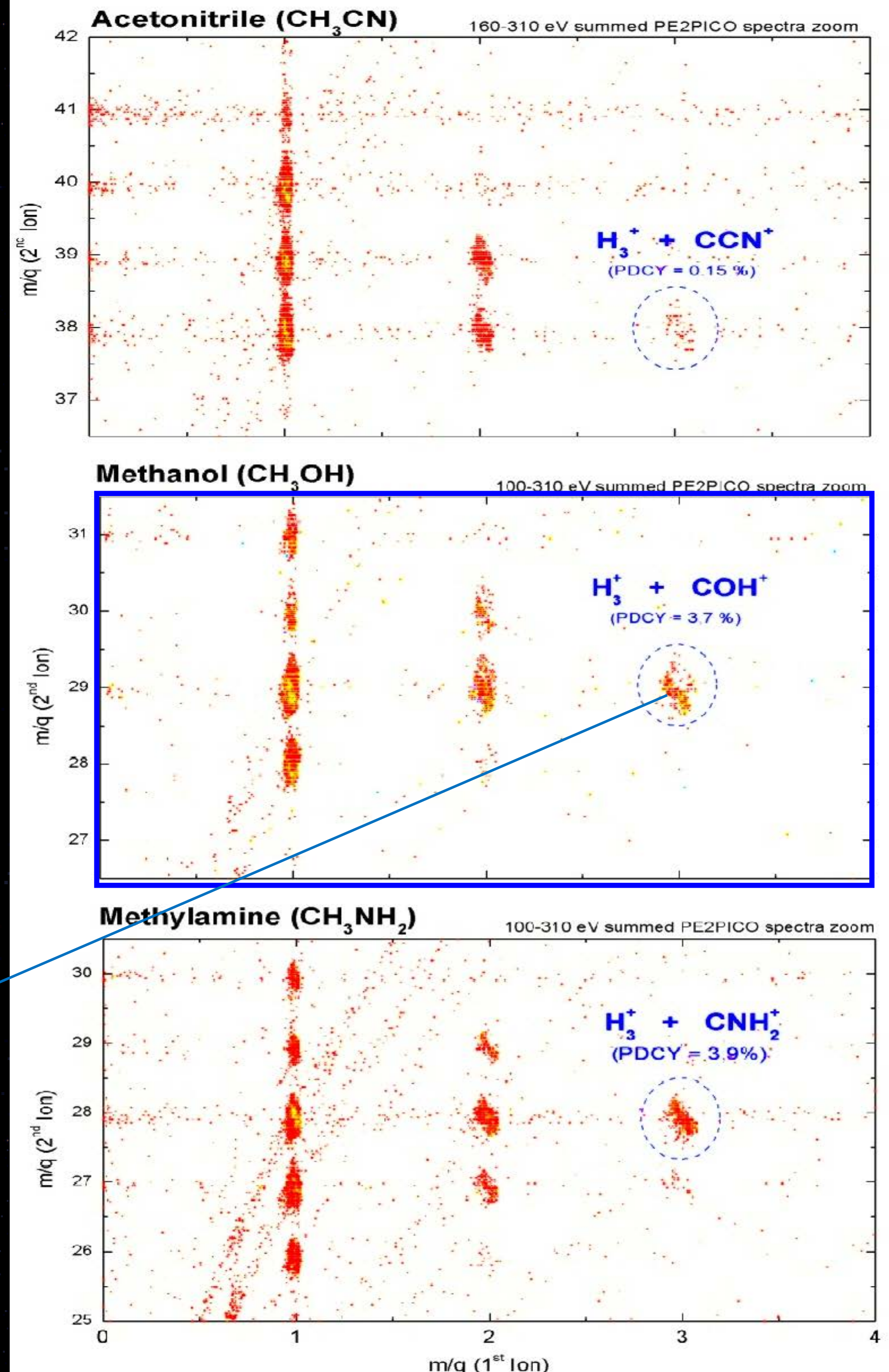
$$\begin{array}{lcl} M + h\nu & \longrightarrow & M^{+} + e^{-} \\ M^{+} & \xrightarrow{Auger} & M^{++} + e^{-} \\ M^{++} & \longrightarrow & M_1^{+} + M_2^{+} \ (+ \text{neutros}). \end{array}$$



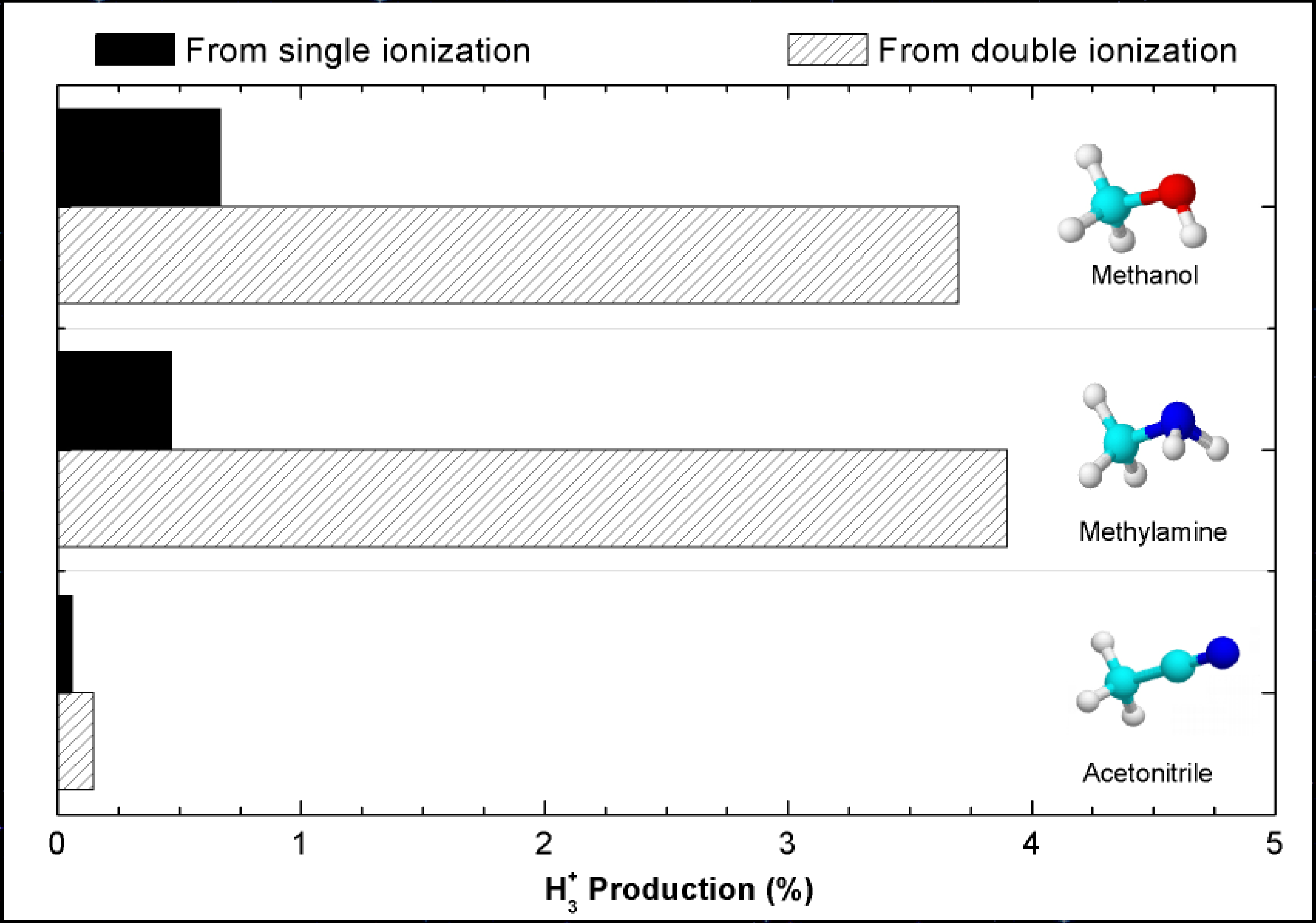
Partial Double Coincidence Yield

$$PDCY_{i,j} = \left(\frac{A_{i,j}}{A_t^{2+}} \pm \frac{\sqrt{A_{i,j} + A_{i,j} \times ER/100}}{A_t^{2+}} \right) \times 100\%$$

Total peaks´s area



H_3^+ production from X-ray photodissociation organic molecules (CH_3-X type)



Cross Sections and Photoproduction rates

(employing X-rays around YSO AFGL25 91; e.g. Stauber et al 2005)

Yields

$$\mathrm{PIY}_{\mathrm{H}_3^+} = \left(\frac{A_{\mathrm{H}_3^+}}{A_t^+} \pm \frac{\sqrt{A_{\mathrm{H}_3^+}} + A_{\mathrm{H}_3^+} \times \mathrm{ER}/100}{A_t^+} \right) \times 100 \text{ per cent},$$

$$\mathrm{PDCY}_{\mathrm{H}_3^+} = \left(\frac{A_{i,\mathrm{H}_3^+}}{A_t^{2+}} \pm \frac{\sqrt{A_{i,\mathrm{H}_3^+}} + A_{i,\mathrm{H}_3^+} \times \mathrm{ER}/100}{A_t^{2+}} \right) \times 100 \text{ per cent},$$

Cross Sections

$$\sigma^+_{\mathrm{H}_3^+} = \sigma^+ \frac{\mathrm{PIY}_{\mathrm{H}_3^+}}{100} \quad \text{and} \quad \sigma^{++}_{\mathrm{H}_3^+} = \sigma^{++} \frac{\mathrm{PDCY}_{\mathrm{H}_3^+}}{100},$$

Rates

The H_3^+ photoproduction rate due to the dissociation of methyl compound molecules by soft X-rays (200–310 eV) is given by the simple expression

$$k_{\mathrm{ph}} = \int \sigma_{\mathrm{H}_3^+}(\varepsilon) F(\varepsilon)\, \mathrm{d}\varepsilon \sim \sigma_{\mathrm{H}_3^+} F_{\mathrm{softX}} \quad (\mathrm{s}^{-1}), \tag{6}$$

where $\sigma_{\mathrm{H}_3^+} = \sigma^+_{\mathrm{H}_3^+} + \sigma^{++}_{\mathrm{H}_3^+}$ and F_{softX} is the averaged H_3^+ photoproduction cross-section and photon flux over the soft X-ray energy (200–310 eV).

Table 2. Averaged H_3^+ photoproduction cross-section and photoproduction rate for an X-ray luminosity of $L_X \gtrsim 10^{31}$ erg s^{-1} (Stäuber et al. 2005), from the dissociation of methanol, methylamine and acetonitrile by soft X-ray photons over the C1s edge (200–310 eV). See details in text.

CH_3-X molecule	$\sigma^+_{\mathrm{H}_3^+}$ ($\times 10^{-19}$ cm^2)	$\sigma^{++}_{\mathrm{H}_3^+}$ ($\times 10^{-19}$ cm^2)	$\sigma_{\mathrm{H}_3^+} = \sigma^+_{\mathrm{H}_3^+} + \sigma^{++}_{\mathrm{H}_3^+}$ ($\times 10^{-18}$ cm^2)	k_{ph} ($\times 10^{-15}$ s^{-1})
Acetonitrile	2.0	0.2	~0.2	$\gtrsim 40^b$; $\gtrsim 0.05^c$
Methanol	12.0	2.0	1.4	$\gtrsim 300^b$; $\gtrsim 0.4^c$
Methylamine[a]	8.0	3.0	1.1	$\gtrsim 200^b$; $\gtrsim 0.3^c$

[a]Estimated value. [b]At a distance $r \sim 200$ au (2.5×10^{15} cm) from the central source; $F_{\mathrm{softX}} \gtrsim 2 \times 10^5$ photons cm^{-2} s^{-1}. [c]$r \sim 5000$ au (7×10^{16} cm); $F_{\mathrm{softX}} \gtrsim 3 \times 10^2$ photons cm^{-2} s^{-1}.

Column densities (H_3^+ from methanol photodissociation)

$$CH_3OH^+ + h\nu \xrightarrow{k_{ph}} H_3^+ + COH \quad \left(\text{or } H_3^+ + CO^+\right),$$

$$H_3^+ + CO \xrightarrow{k_{CO}} COH^+ + H_2,$$

$$\frac{d[H_3^+]}{dt} = k_{ph}[CH_3OH] - k_{CO}[CO] = 0,$$

$$N_{H_3^+}^{ph} \sim \frac{k_{ph}}{k_{CO}[CO]} N_{CH_3OH},$$

Table 3. The H_3^+ column density due to the photodissociation of methanol by soft X-rays, $N_{H_3^+}^{ph}$, in some dense molecular clouds. The observed column density of CH_3OH and H_3^+ in each region are also given. The last column represents the fraction of the produced H_3^+ due to CH_3OH photodissociation, $N_{H_3^+}^{ph}/N_{H_3^+}$. See details in text.

Dense molecular clouds	$N_{CH_3OH}^{a}$ ($\times 10^{15}$ cm^{-2})	$N_{H_3^+}^{b}$ ($\times 10^{14}$ cm^{-2})	$N_{H_3^+}^{ph}$ ($\times 10^{8}$ cm^{-2})	$N_{H_3^+}^{ph}/N_{H_3^+}$ ($\times 10^{-5}$)
AFGL 2136	0.44	3.8	$\gtrsim 400^{c}$; $\gtrsim 0.7^{d}$	$\gtrsim 10^{c}$; $\gtrsim 0.02^{d}$
AFGL 490	0.36	1.1	$\gtrsim 400^{c}$; $\gtrsim 0.5^{d}$	$\gtrsim 30^{c}$; $\gtrsim 0.05^{d}$
W33A	2.0	5.2	$\gtrsim 2000^{c}$; $\gtrsim 3^{d}$	$\gtrsim 40^{c}$; $\gtrsim 0.06^{d}$
AFGL 2591	1.2	2.2	$\gtrsim 1000^{c}$; $\gtrsim 2^{d}$	$\gtrsim 50^{c}$; $\gtrsim 0.08^{d}$

[a] van der Tak, van Dishoeck & Caselli (2000); [b] McCall et al. (1999). [c] Assuming a photon flux in the soft X-ray range of $F_{softX} \gtrsim 2 \times 10^5$ photons cm^{-2} s^{-1}. [d] $F_{softX} \gtrsim 3 \times 10^2$ photons cm^{-2} s^{-1}.

Conclusion: Yes, a small fraction of interstellar H_3^+ may be formed this way!

PAPER II

Monthly Notices of the ROYAL ASTRONOMICAL SOCIETY

Mon. Not. R. Astron. Soc. **423,** 2209–2221 (2012) doi:10.1111/j.1365-2966.2012.21031.x

Formation of unsaturated hydrocarbons in interstellar ice analogues by cosmic rays

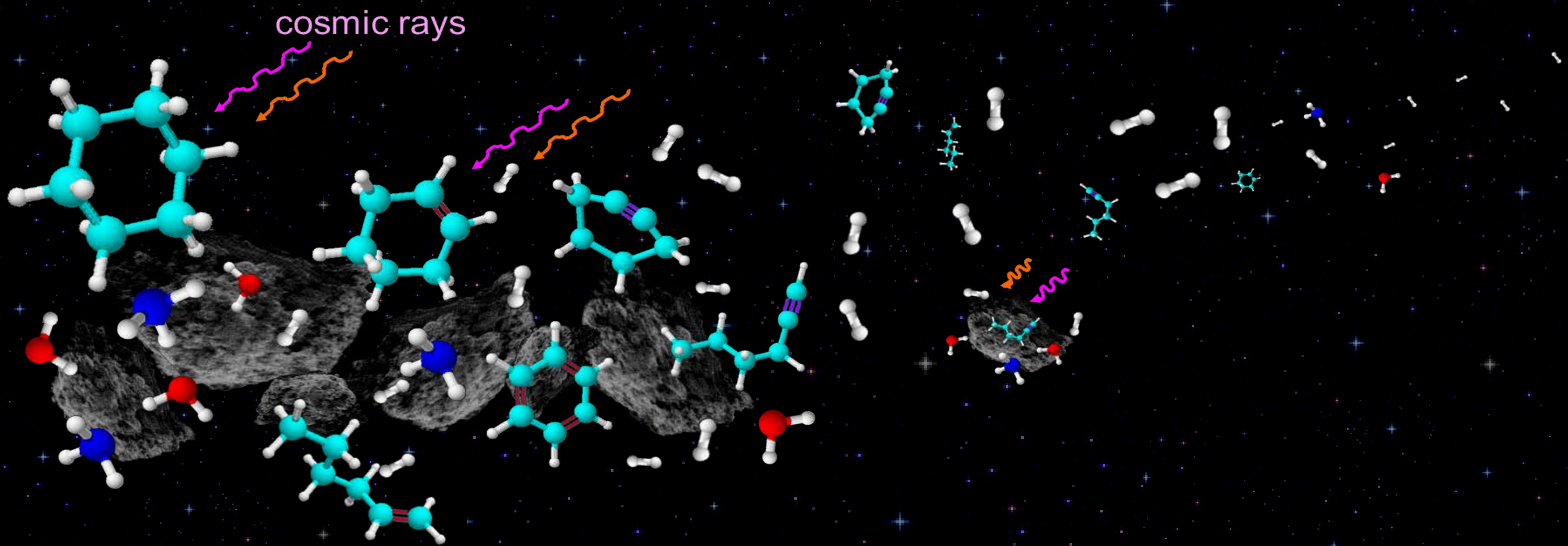
S. Pilling,[1★] D. P. P. Andrade,[1] E. F. da Silveira,[2] H. Rothard,[3] A. Domaracka[3] and P. Boduch[3]

[1] *Instituto de Pesquisa e Desenvolvimento (IP&D), Universidade do Vale do Paraíba (UNIVAP), São José dos Campos, SP 12244-000, Brazil*

[2] *Instituto de Fisica, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), Rio de Janeiro, RJ 22451-000, Brazil*

[3] *Centre de Recherche sur les Ions, les Matériaux et la Photonique CIMAP (GANIL/CEA/CNRS/ENSICAEN/Université de Caen Basse-Normandie), F-14070 Caen Cedex 05, France*

Motivation



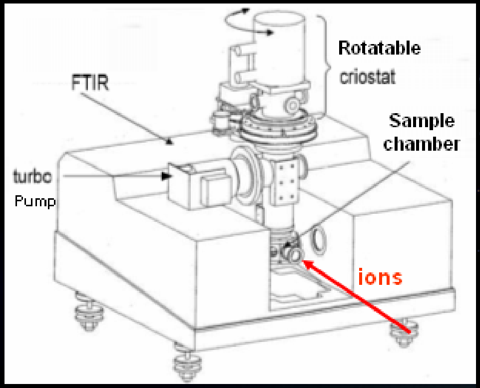
We study the formation of C=C and C≡C bonds (and dehydrogenation) from the processing of pure c-C_6H_{12} (cyclohexane) and mixed H_2O:NH_3:c-C_6H_{12} (1:0.3:0.7) ices by highly-charged, and energetic ions (219 MeV $^{16}O^{7+}$ and 632 MeV $^{58}Ni^{24+}$).

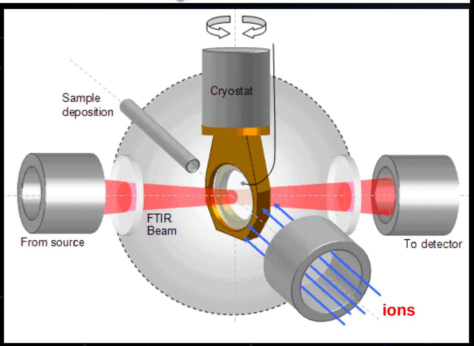
The experiments simulate the physical chemistry induced by medium-mass and heavy-ion cosmic rays at saturated hidrocarbon-rich interstellar ices.

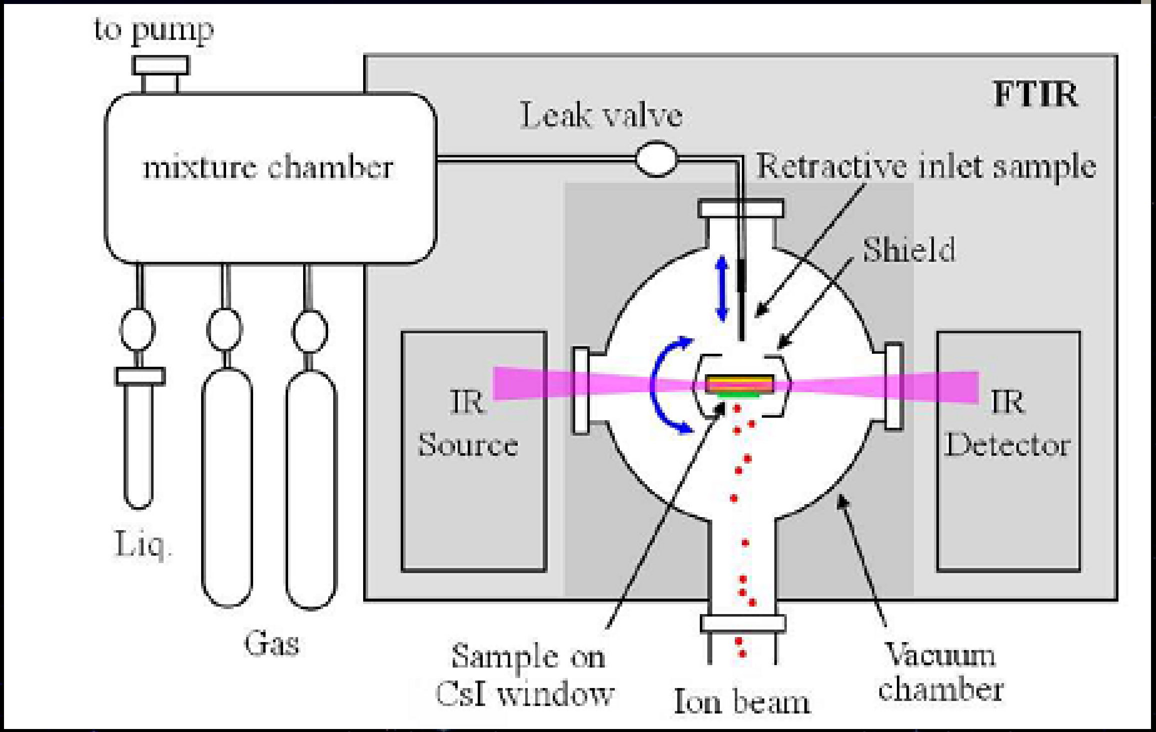
Experimental Setup (GANIL – France)

The measurements were performed inside a high vacuum chamber at the heavy ion accelerator GANIL (Grand Accelerateur National d´Ions Lourds – GANIL) in Caen, France.

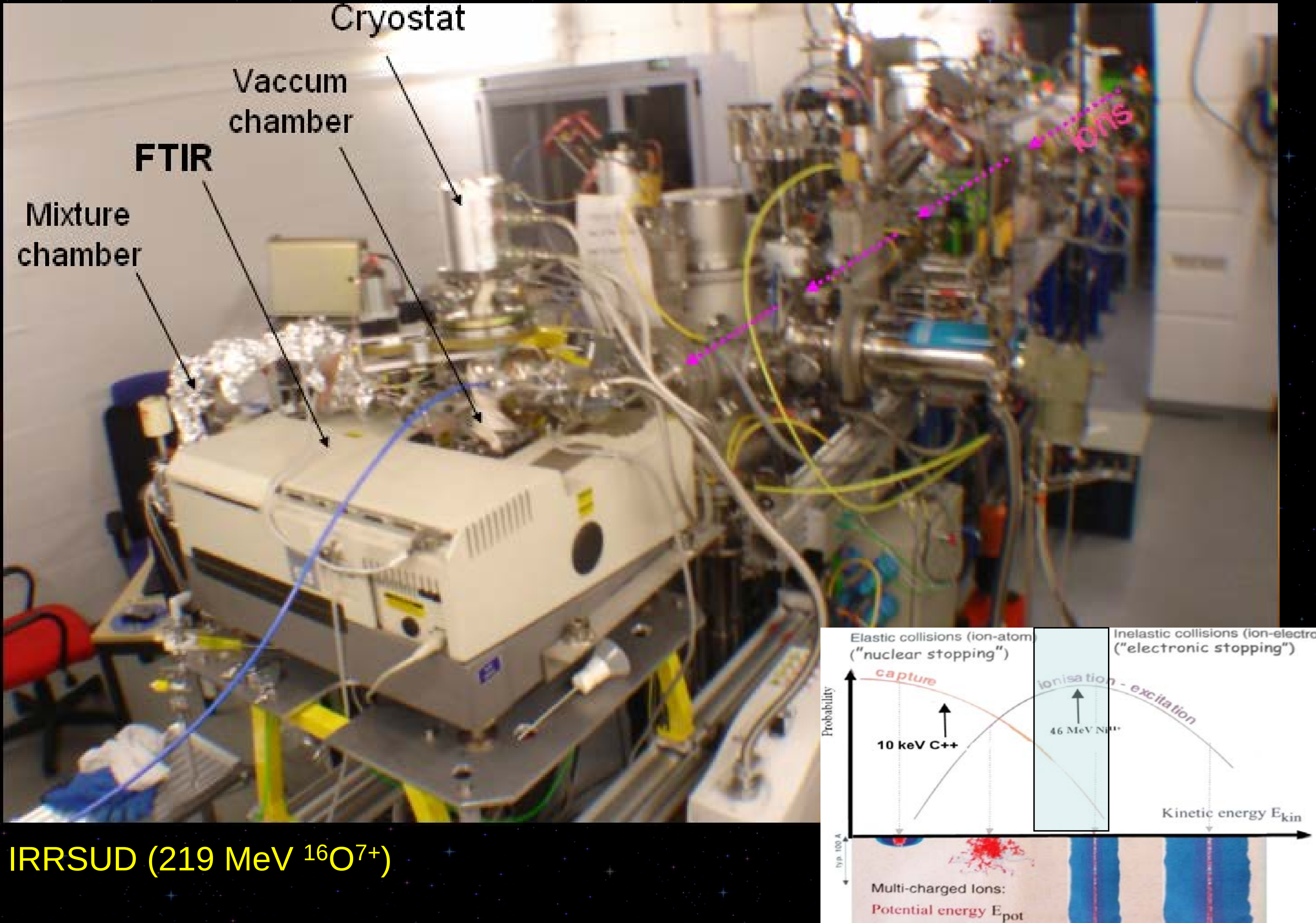
The gas samples were deposited onto a CsI substrate at 13 K. *In-situ* analysis were performed by a Fourier transform infrared (FTIR) spectrometer at different ion fluences. Cross section, Radiolysis yield and half-lives of the produced species were quantified.







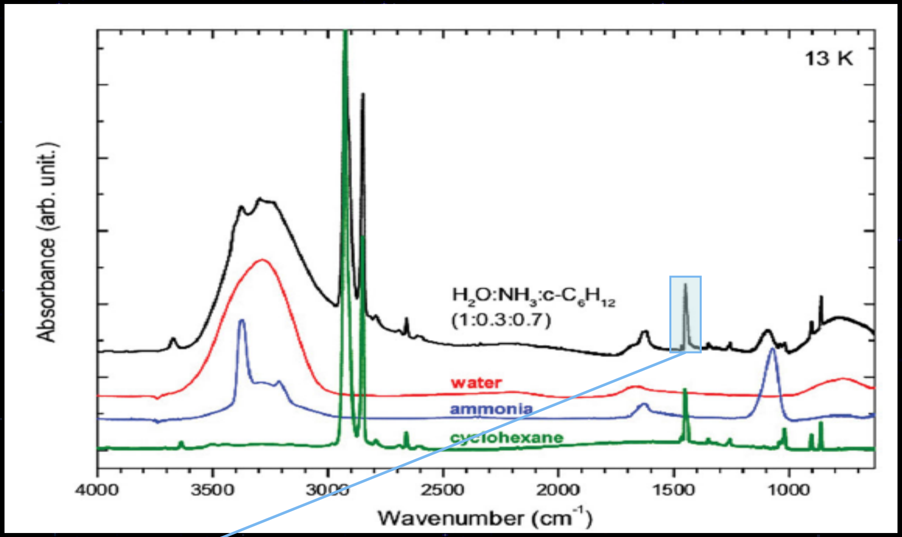
Experimental Setup (GANIL – France)



IRRSUD (219 MeV $^{16}O^{7+}$)

Basics on IR spectroscopy of astrophysical ices

e.g. IR spectra of non irradiated samples (this work)



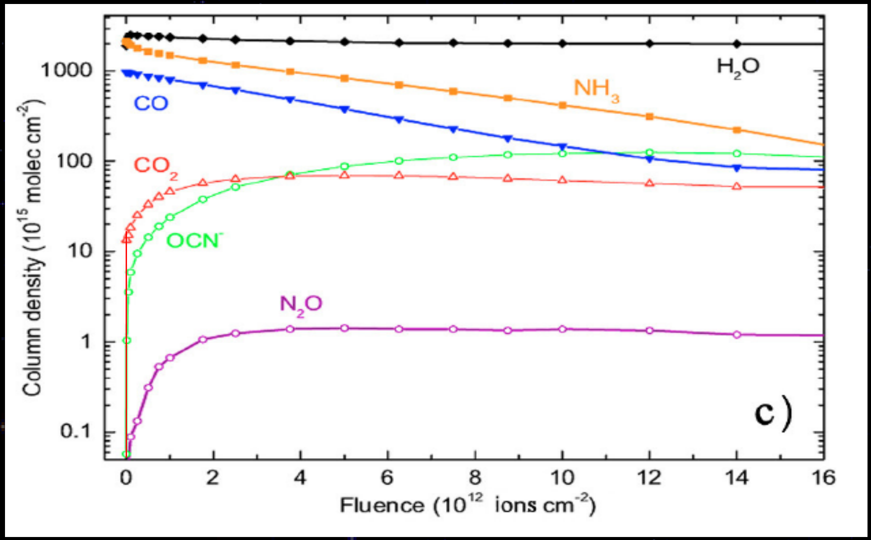
1) IR bands (molecular vibration modes)
Band area + Band strength A (typical from each molecule and each vibration mode) → Molecular column density N

$$N = \frac{1}{A}\int \tau_\nu \mathrm{d}\nu = \frac{2.3}{A}\int a_\nu \mathrm{d}\nu \quad (\text{molecules cm}^{-2}),$$

where $a_\nu = \ln(I_0/I)/\ln(10) = \tau_\nu/2.3$.

OBS. Good baseline correction is needed!!
OBS2. For good N calculation good band strengths is needed!!
OBS3. The IR spectrum of mixed ices is not equal to the sum of the individual IR spectra of ices (environment affects molecular band strengths)
OBS4. Temperaure also affect the band strenghts

e.g. irradiation of $H_2O:NH_3:CO$ (~1:1:1) at 12K (pilling etal. 2010)



2) The evolution of N with the fluence or exposure time allows the determination of cross sections.

$$N = N_0 \exp(-\sigma_d F),$$ parents

$$N_k \approx N_0 \sigma_{f,k}\left(F - \frac{\sigma_d + \sigma_{d,k}}{2}F^2\right),$$ daughters

OBS. If the band strength A is not known we still can determine de cross section by measuring the relative band area (or subtracted band area) depencenswith fluence.

3) cross section → rates → half-life (parents)

$$k = \sigma \times \phi \quad [\mathrm{s}^{-1}]$$

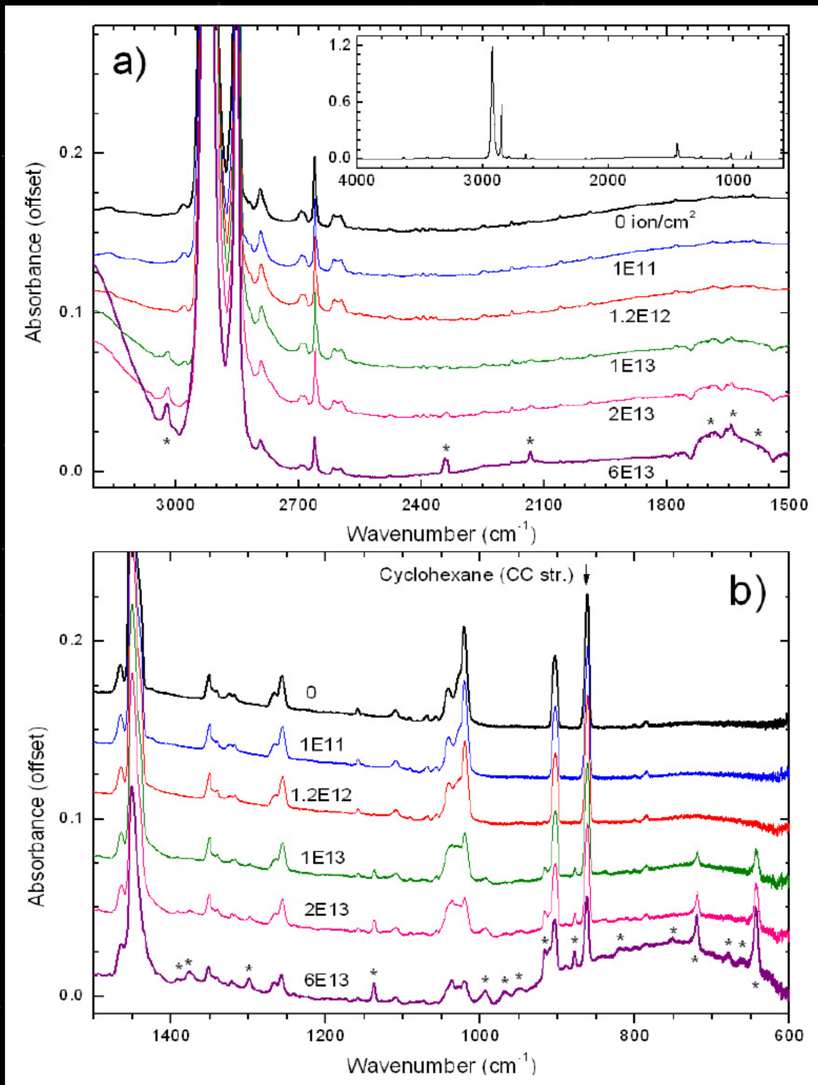
$$t_{1/2}(\text{lab}) = \ln(2)/k \quad [\mathrm{s}]$$

$$t_{1/2_s} \approx \frac{\ln 2}{\phi_s \times \sigma_d} \quad [\mathrm{s}]$$

Selected results

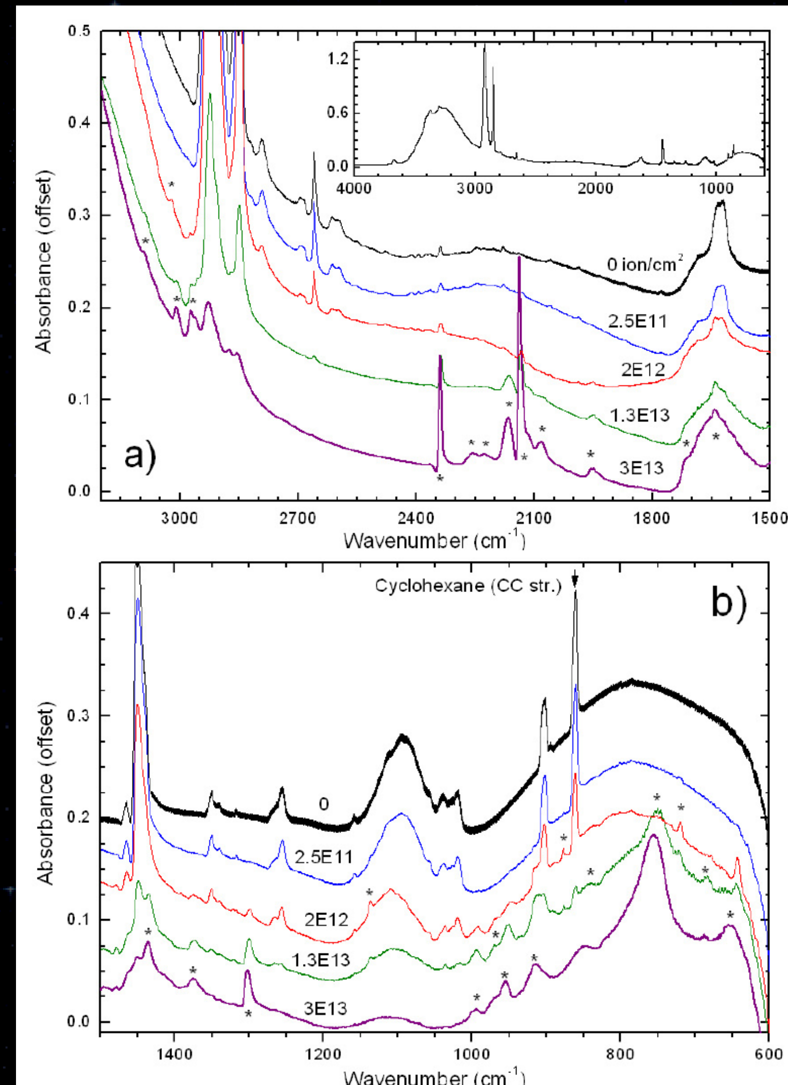
c-C_6H_{12} ice

Bombarded with 219 MeV O ions



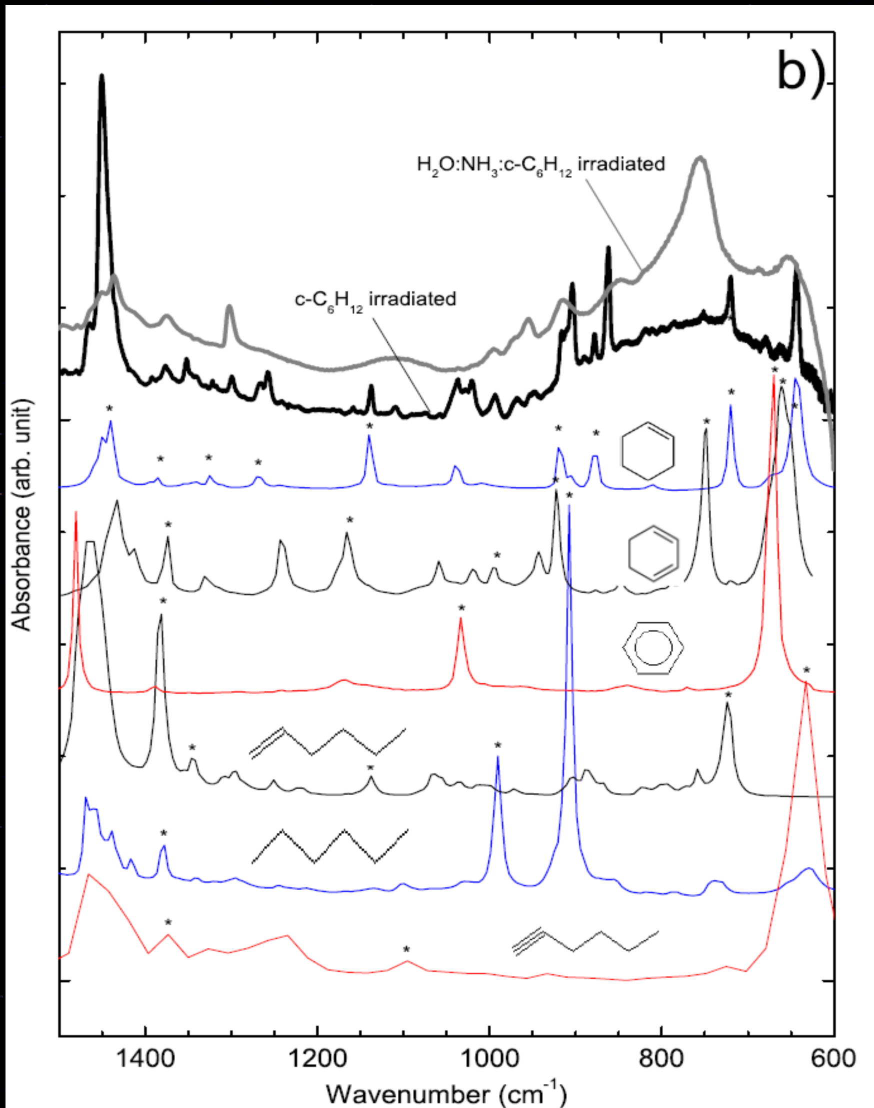
H_2O:NH_3:c-C_6H_{12} ice (1:0.3:0.7)

Bombarded with 632 MeV Ni ions



* New species

IR bands



Tentative identificaitons

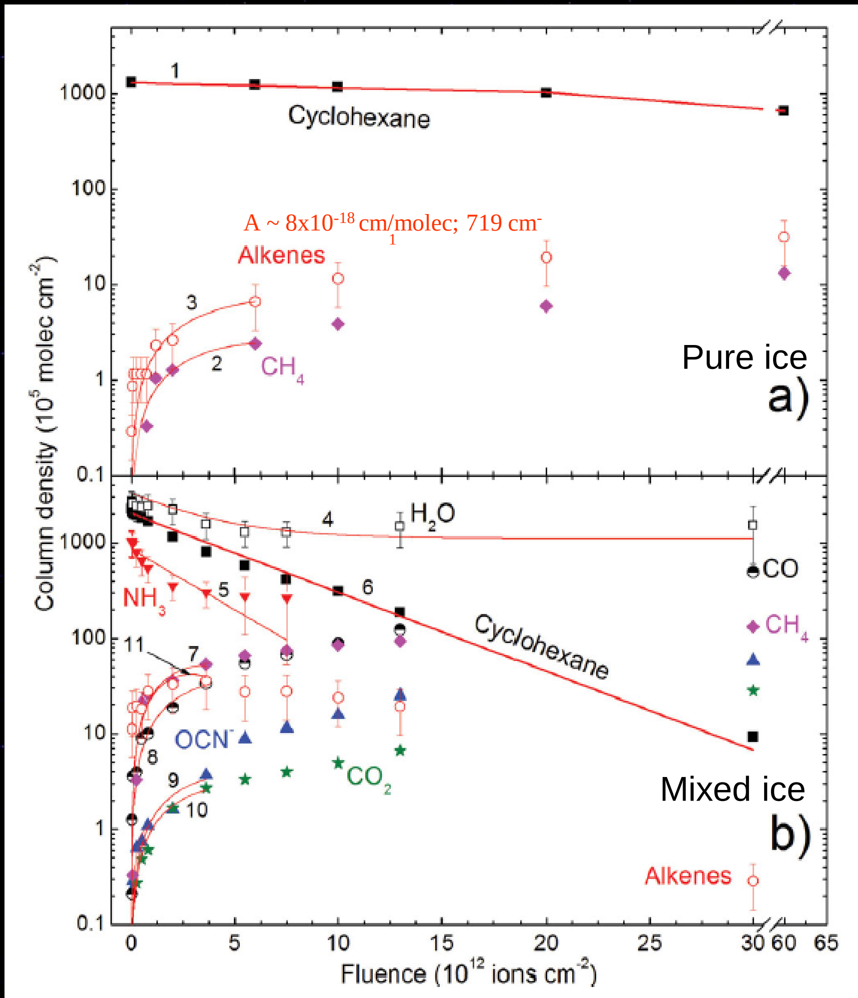
Frequency (cm^{-1})		Attribution and comments
c-C_6H_{12}	H_2O:NH_3:c-C_6H_{12}	
-	3091	=C-H (sp2) str. benzene; cyclohexene; alkenes
3021	3021[a]	=C-H (sp2) str. benzene; aromatic ?
-	3008	=C-H (sp2) str. alkenes
-	2971	?
2341	2337	CO_2
2334	-	-C≡C- str. alkynes?
-	2258	?
-	2225	-C≡C-H (CC str. of internal alkynes at 2220 cm^{-1})?
-	2166	OCN-
2133	2137	CO; -C≡C-H (CC str. of terminal alkynes at 2120 cm^{-1})?
-	2081	?
-	1951	?
-	1713	?
1688	-	broad. C=C str. aromatic?, ring?
1642	1641	broad. C=C str. aromatic?, ring?
1584	1584	broad. $NH_3CH_2COO^-$?
-	1436	$NH_3CH_2COO^-$?
1392	-	t-butyl; benzene?
1376	1375	-CH_3 bending sym. t-butyl or dimethyl
1300	1302	CH_4 (C-H ν_4 deformation mode) Boogert et al. 1997
1137	1136[a]	?
993	994	${}^{R}_{H}C{=}C^{H}_{H}$ (C-H bending out plane); cyclohexene; aromatic?
967	-	?
-	954	?
948	-	?
916	916	${}^{R}_{H}C{=}C^{H}_{H}$ (C-H bending out plane); terminal vinyl at 910 cm^{-1}?
877	877[a]	?
-	845	${}^{R}_{R}C{=}C^{R}_{H}$ (C-H bending out plane)
818	-	? weak
810	-	? weak
751	754	? broad and strong; aromatic C-H bending out plane; CH_2 rocking aliphatic alkanes (present in molecules with less then 4 carbon and very strong in molecules with less then 3 carbon)
720	719[a]	${}^{R}_{H}C{=}C^{R}_{H}$ bending out of plane aliphatic alkenes; cyclohexene
680	683	benzene? (CH bending in plane)
661	-	CO_2 bending?
643	644	${}^{R}_{H}C{=}C^{R}_{H}$ (CH bending out of plane); cyclohexene

Sample of spectra comparison: irradiated ices with non irradiated sample from literature - NIST (e.g. cyclohexene, 1-3 cyclohexadiene, benzene, hexane,1-hexene, 1-hexyne).

Asterisks indicates the location of possible identification in the spectra of irradiated ices.

Models

Alkene production!!!



Cross sections and Radiolysis yield

Pure c-C_6H_{12} ice irradiated with 219-MeV O^{7+}

Species[a]	σ_f ($\times 10^{-13}$ cm^2)	σ_d ($\times 10^{-13}$ cm^2)	G_f (molecules per 100 eV)	G_d (molecules per 100 eV)	Model
c-C_6H_{12}	0^a	0.1	0^a	2.9	1
CH_4	0.006	1.4	0.17	40	2
Alkenes[b]	~0.01	~1.2	~0.3	~34	3

Mixed H_2O:NH_3:c-C_6H_{12} (1:0.3:0.7) ice irradiated with 632-MeV Ni^{24+}

Species[a]	σ_f ($\times 10^{-13}$ cm^2)	σ_d ($\times 10^{-13}$ cm^2)	G_f (molecules per 100 eV)	G_d (molecules per 100 eV)	Model
H_2O	0^a	~3	0^c	~24	4
NH_3	0^a	~3	0^c	~24	5
c-C_6H_{12}	0^a	~2	0^c	~16	6
CH_4	0.14	0.9	1.1	7.1	7
CO	0.07	<0.01	0.55	<0.08	8
OCN$^-$	0.007	<0.01	0.06	<0.08	9
CO_2	0.006	<0.1	0.05	<0.8	10
Alkenes[b]	~0.1	~1.5	~0.8	~12	11

Column density

$$N = \left(N_0 + \frac{Y}{\sigma_d}\right)\exp(-\sigma_d F) - \frac{Y}{\sigma_d}$$

$$N_k \approx N_0 \sigma_{f,k}\left[F - \frac{\sigma_d + \sigma_{d,k}}{2} F^2 \exp(-\sigma_d F)\right]$$

Half-life

$$\tau_{1/2} \simeq 3.2 \times 10^{-8} \frac{F}{\phi} \quad \text{[year]}$$

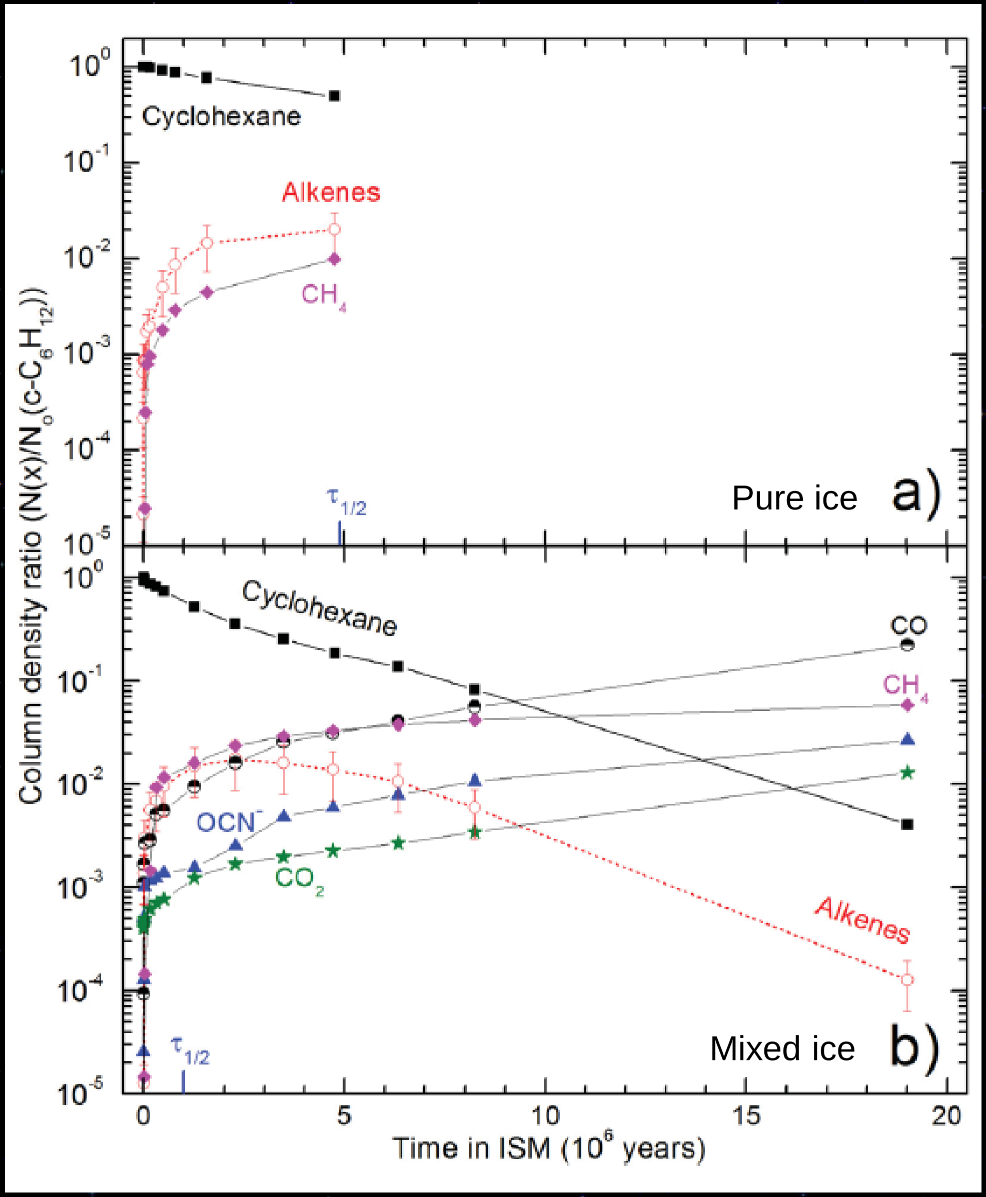
$$\phi_{MCR} \sim 4 \times 10^{-1}\ \text{cm}^{-2}\ \text{s}^{-1}$$

$$\phi_{HCR} \sim 5 \times 10^{-2}\ \text{cm}^{-2}\ \text{s}^{-1}$$

Radiochemical yield

$$G_f = 100 \frac{\sigma_f}{S}$$

Extrapolation to interstellar medium



The estimated $t_{1/2}$ (cyclohexane) in the ISM as a result of cosmic ray bombardment for pure c-C_6H_{12} ice is about 5 × 10^6 yr (considering only medium-mass cosmic rays), and for mixed ice is about 1 × 10^6 yr (considering only heavy-ion cosmic rays).

For the mixed ice, after 20 × 10^6 yr in ISM, almost 20% of the initial cyclohexane was converted into CO by heavy cosmic rays, 3% was transformed into OCN^- and 1% into CO_2. This suggests that highly hydrogenated hydrocarbons in water-rich grain mantles can be largely converted into CO during the lifetime of the cloud.

Some daughter species such as CH_4 and OCN^- can be used to estimate the integrated dose of incoming radiation and, assuming a constant cosmic ray flux over the time, the exposure time of interstellar ices to cosmic rays. At ion fluences higher than 3 × 10^{12} ions cm^{-2} (~1×10^{16} yr in ISM), the abundance of these species increases almost linearly with the fluence.

3.4 µm band

(Comparison with two temperatures and two diferrent mixtures)

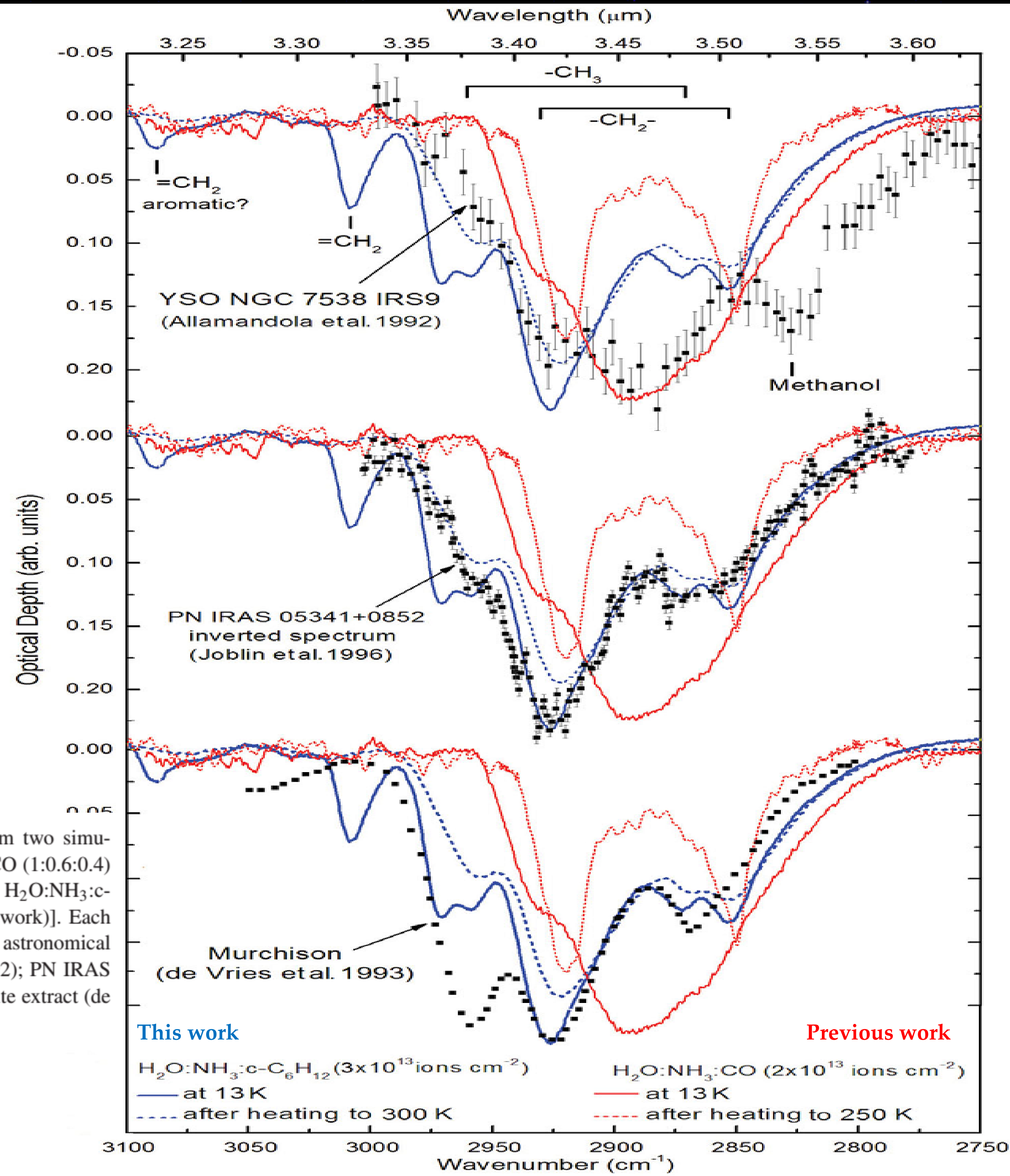


Figure 9. Comparison between the radiolysis products from two simulated interstellar ices at 13 K and after warming [H_2O:NH_3:CO (1:0.6:0.4) bombarded with 46-MeV $^{46}Ni^{13+}$ (Pilling et al. 2010a) and H_2O:NH_3:c-C_6H_{12} (1:0.3:0.7) bombarded with 632-MeV $^{58}Ni^{24+}$ (this work)]. Each set in this figure also compares the laboratory spectra with one astronomical IR spectrum (YSO NGC 7538 IRS9 (Allamandola et al. 1992); PN IRAS 05341+0852 (Joblin et al. 1996)) and the Murchison meteorite extract (de Vries et al. 1993).

5-10 μm range

(Comparison involving different irradiated ices)

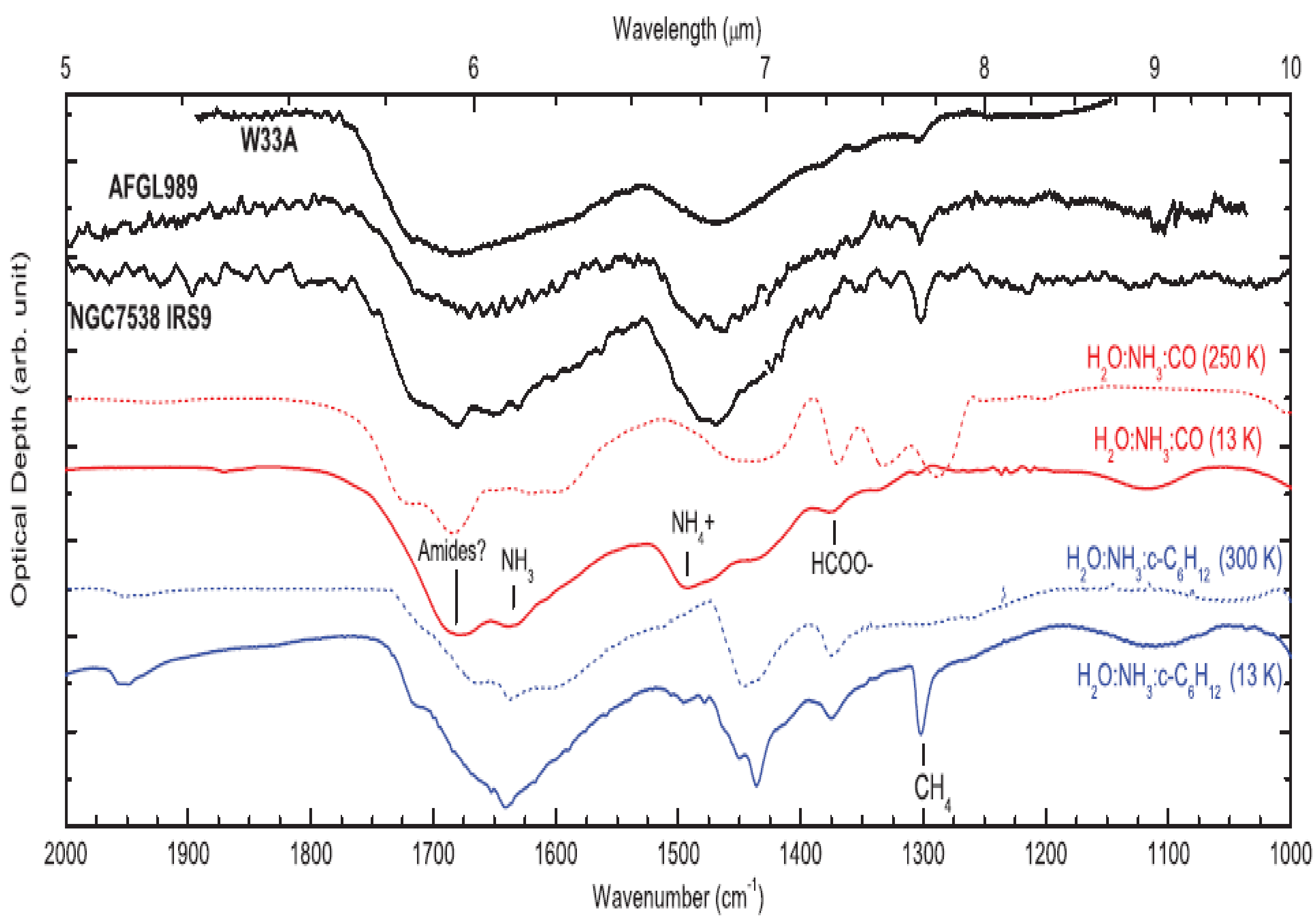


Figure 10. Comparison between IR spectra in the 2000 to 1000 cm^{-1} range (6–10 μm), of ices observed in the interstellar medium and produced in the laboratory. The top three curves are IR spectra of young stellar sources obtained by the *ISO*. Lower traces indicate different laboratory spectra of two ammonia-containing ices irradiated by heavy-ions at 13 K [$H_2O:NH_3:CO$ (1:0.6:0.4) bombarded with 46-MeV $^{46}Ni^{13+}$ (Pilling et al. 2010a) and $H_2O:NH_3:c\text{-}C_6H_{12}$ (1:0.3:0.7) bombarded with 632-MeV $^{58}Ni^{24+}$ (this work)].

Conclusion: The results suggest an alternative scenario for the production of unsaturated carbon chain species (and dehydrogenation) in interstellar ices induced by cosmic rays bombardment!

Thank you for your attention

Acknowledgments: FAPESP (JP 2009-18304-0) , CNPq, UNIVAP, LNLS and INCT-A