Electron and photon impact on organic molecules: Astrochemical implications.

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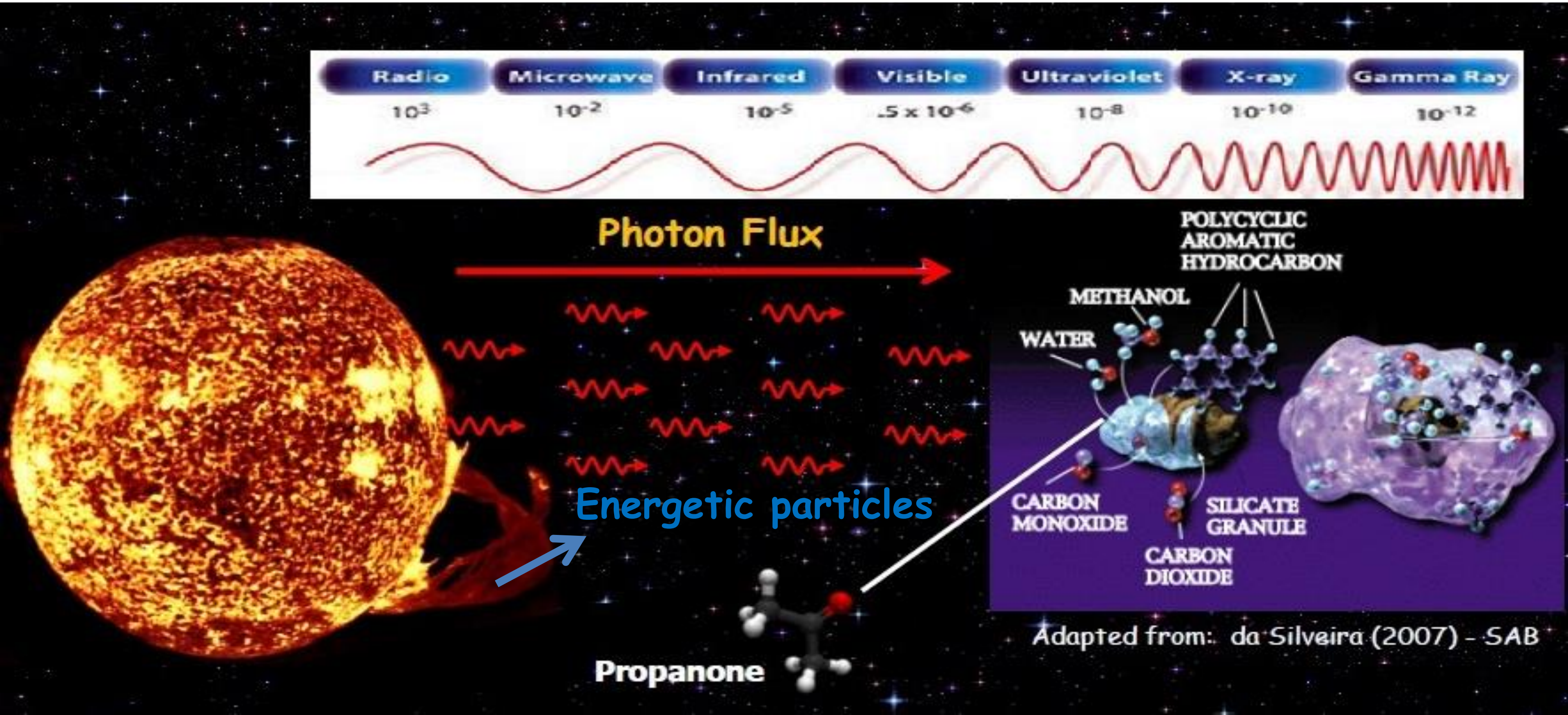
Motivation

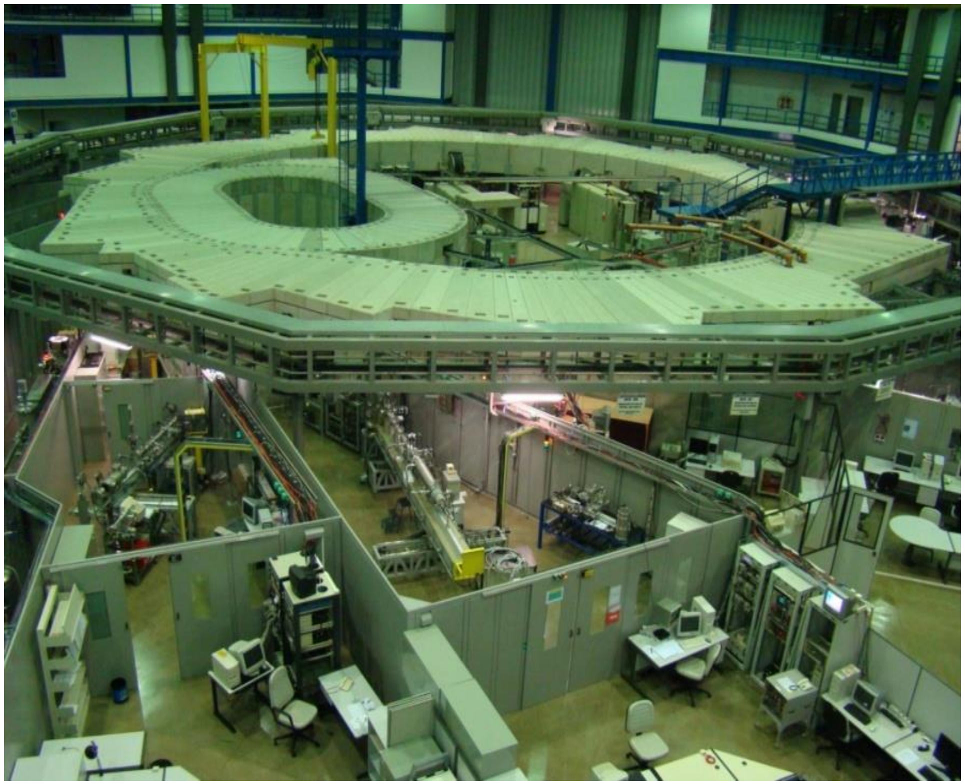
The aim of this work is to experimentally study the ionization, dissociation and ion desorption processes induced by photons and electrons on alcohols as part of a systematic experimental study of condensed (ice phase) molecules of astrophysical interest.

Going On Outside Earth.....



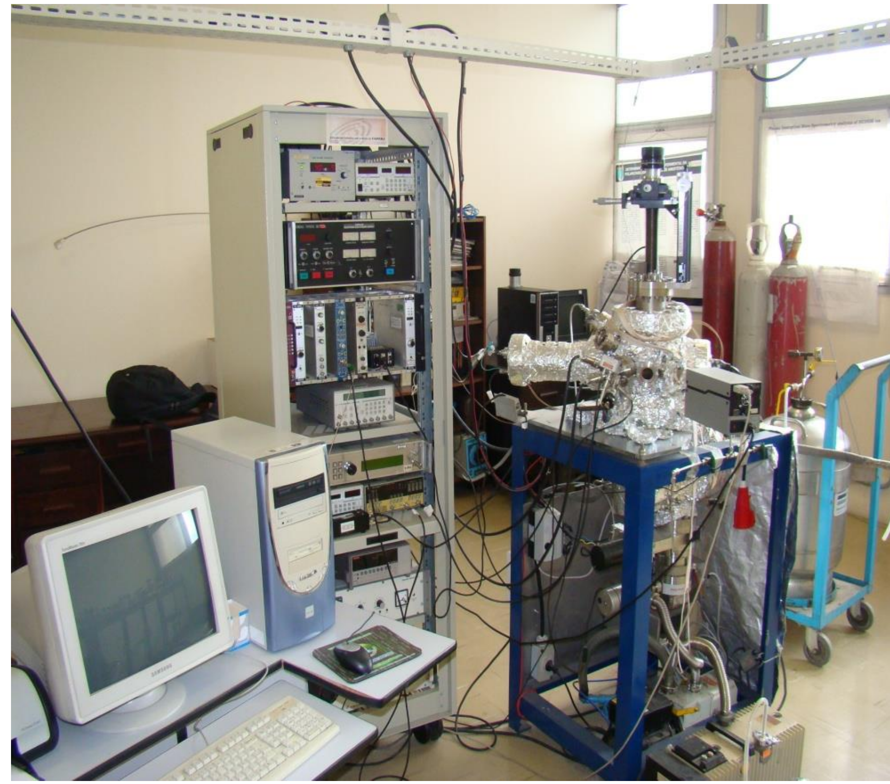
How do we simulate it in laboratory?

Photon Impact: Synchrotron Radiation



Brazilian Synchrotron Light Source (LNLS)
Campinas-SP, Brazil

Energetic Electrons: Electron beam

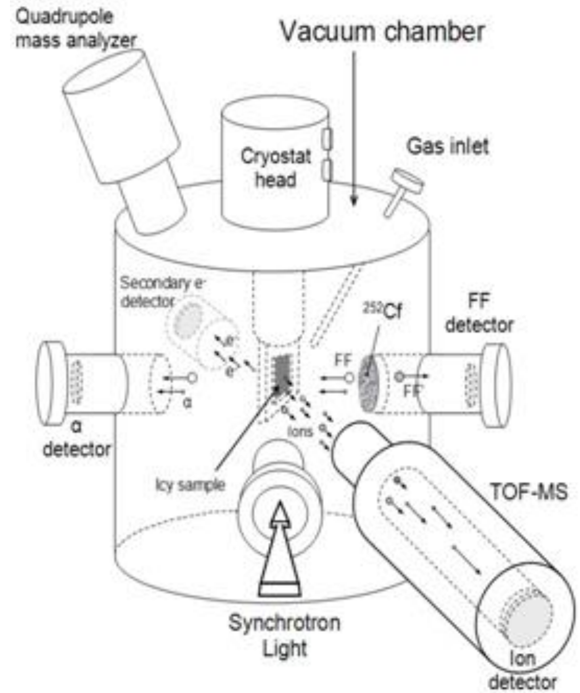


Surface Chemistry Laboratory (LAQUIS)
Federal University of Rio de Janeiro-RJ, Brazil

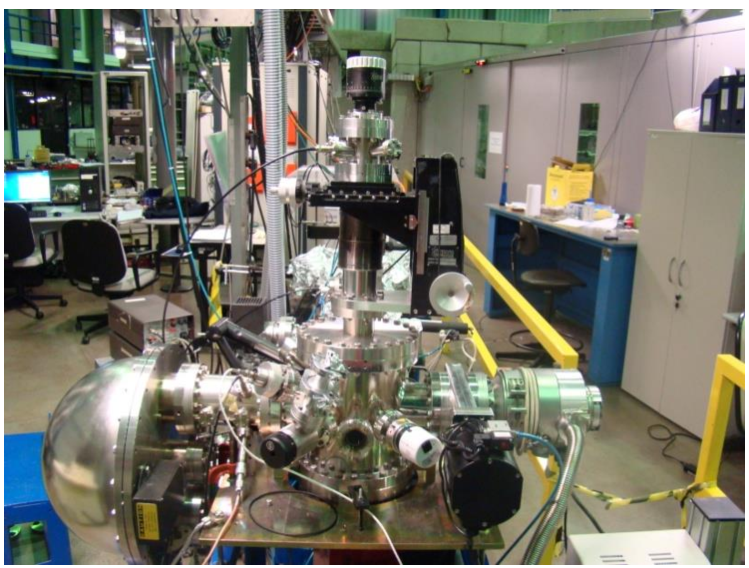
Experimental Setup

Spherical Grating Monochromator (SGM) beam line, operated in the single-bunch (SB) mode of the storage ring, with a period of 311 ns and bunch width of 60 ps.

Photon Stimulated Ion Desorption (PSID)

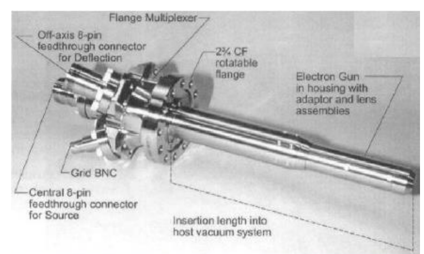


PDMS Chamber – PUC-RJ



(LNLS)

Electron Stimulated Ion Dessorption (ESID)

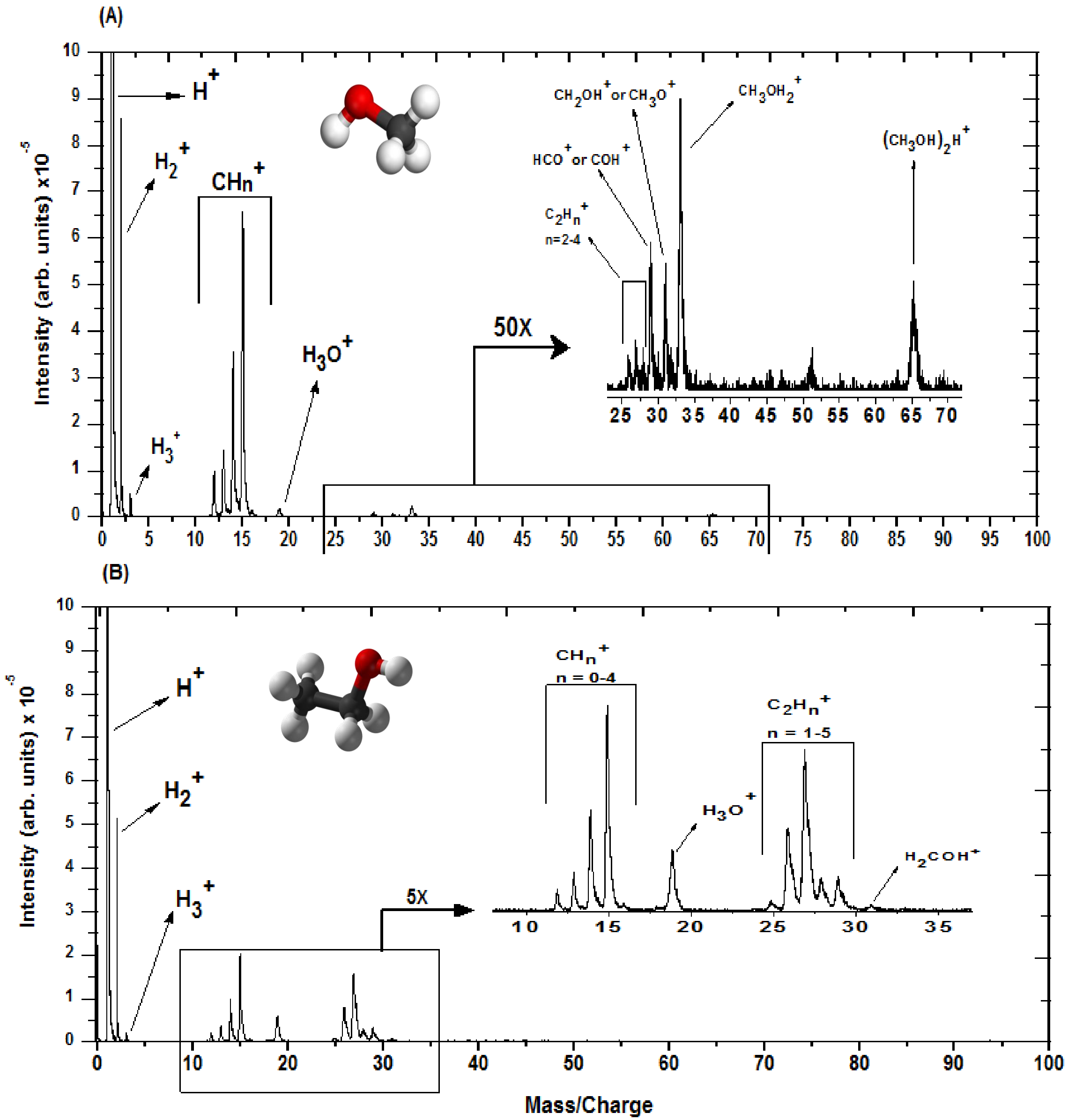


Electron Gun

(100-1000eV)

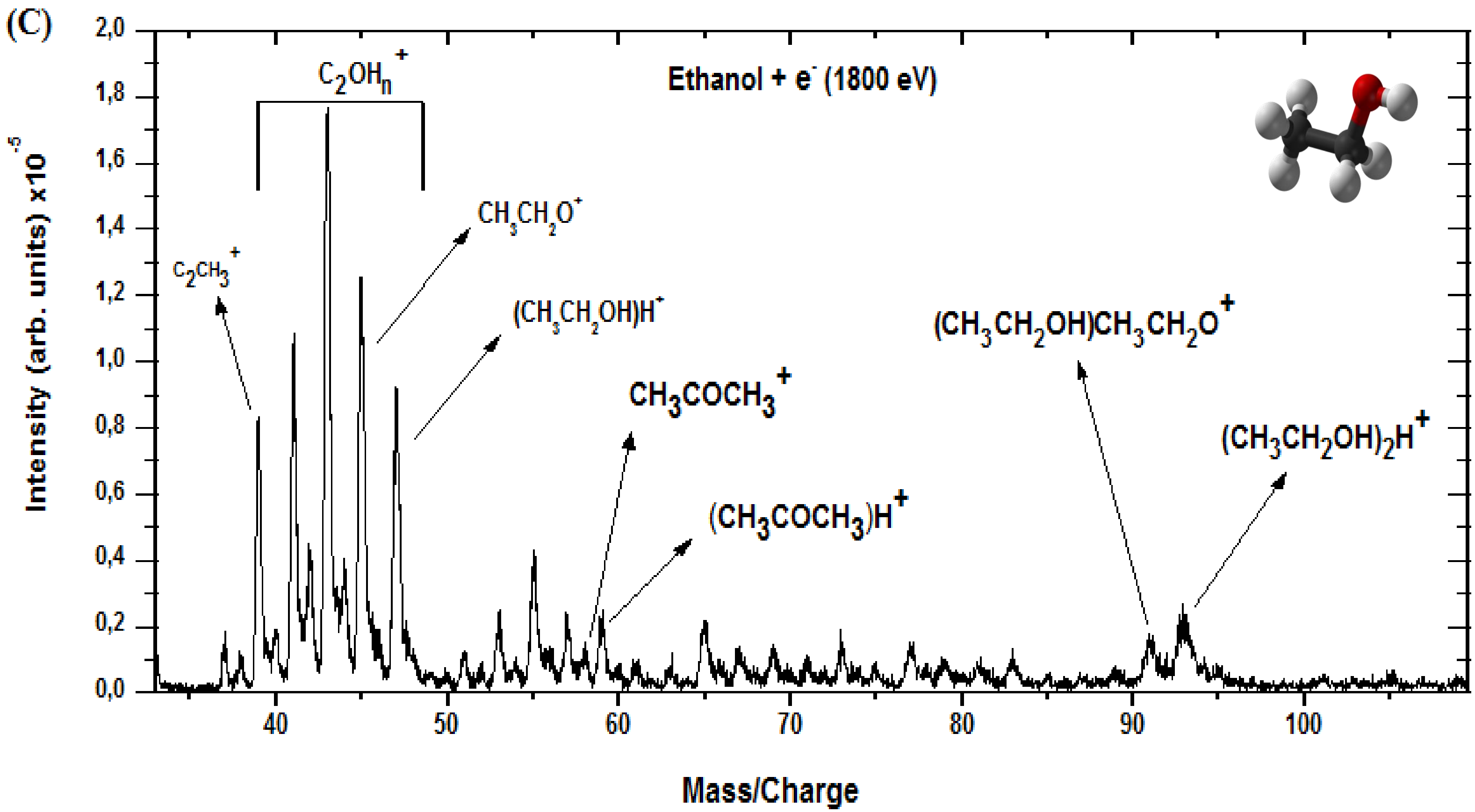
(LAQUIS)

ESID mass spectra of condensed alcohols



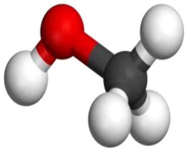
(a) Methanol at 900 eV electron impact energy. (b) Ethanol at 900 eV electron impact energy.

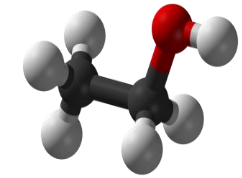
ESID mass spectra of condensed alcohols

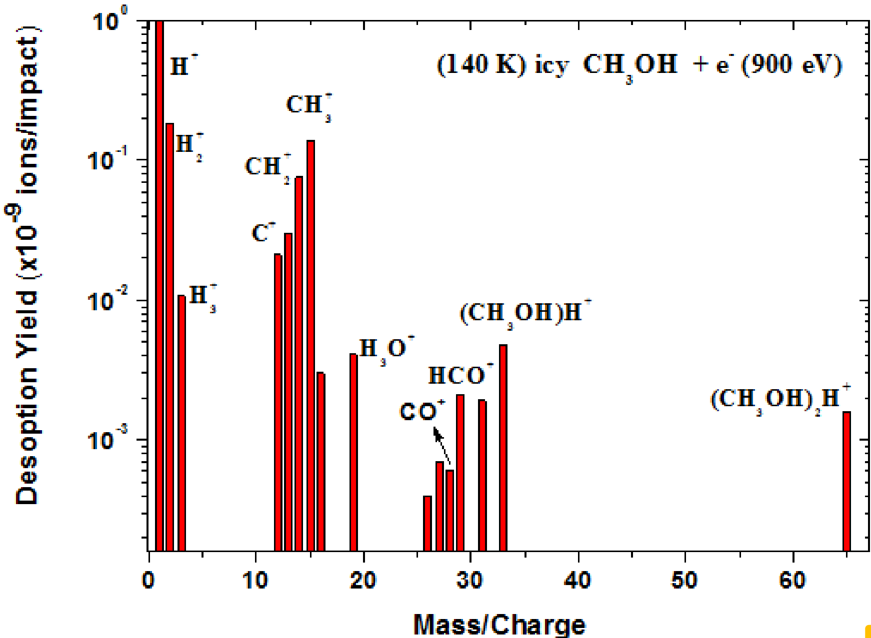


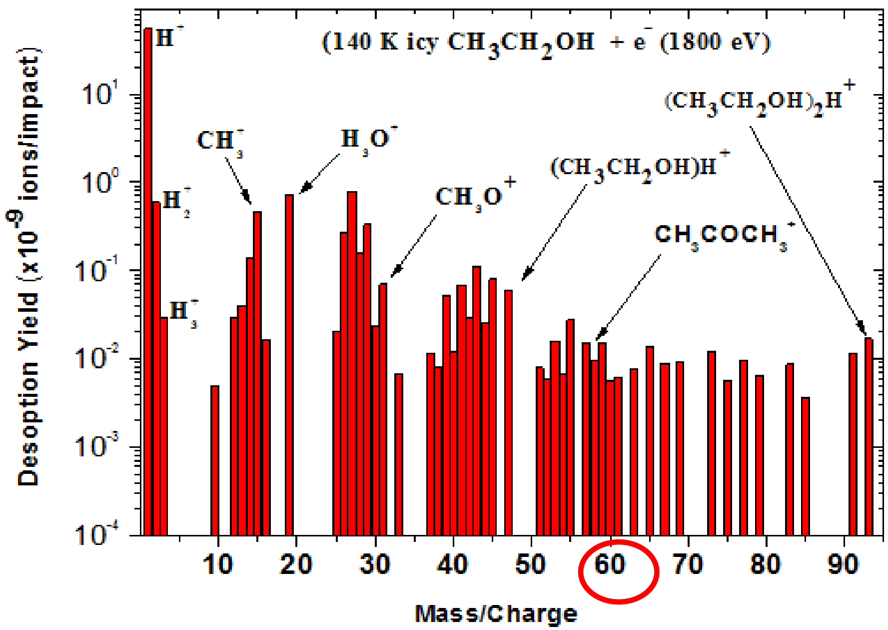
(c) Ethanol at 1800 eV electron impact energy.

Results and Discussion









$$H_2COH^+ + CH_3CH_2OH \rightarrow CH_2OCH_2CH_3^+ + H_2O$$

$$CH_2OCH_2CH_3^+ + H_2 \rightarrow CH_3OCH_2CH_3 + H^+$$

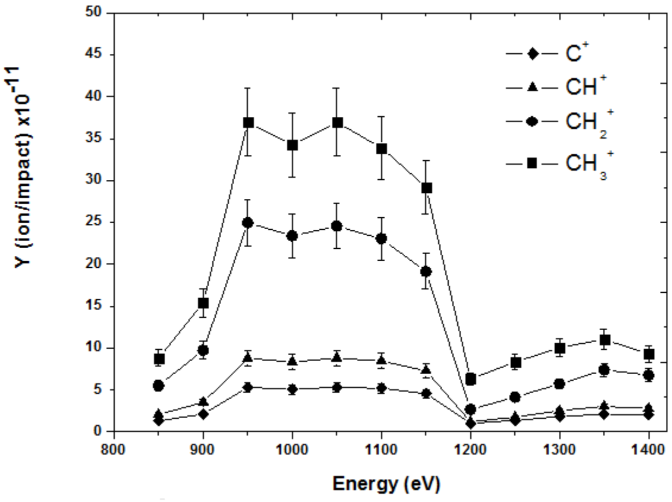
m/z=60

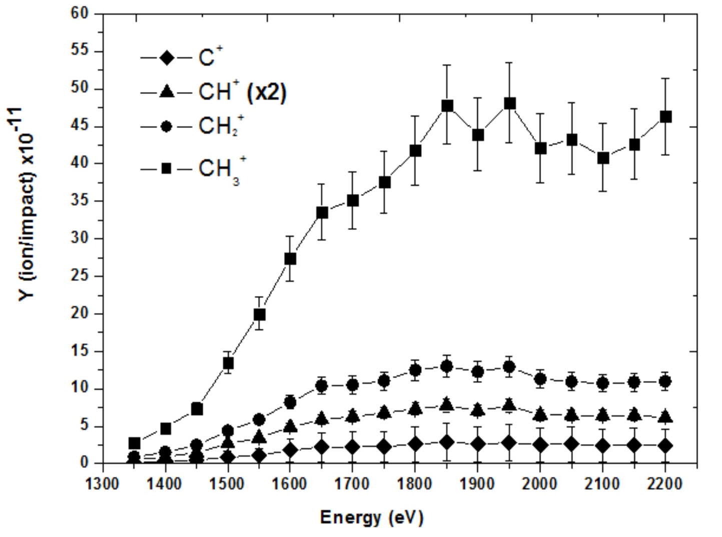
Metil Formate	**$HCOOCH_3$**
Glicoaldehyde	**$HOCH_2CHO$**
n-propyl alcohol	**$CH_3CH_2CH_2OH$**
Methyl-ethyl éther	**$CH_3OCH_2CH_3$**

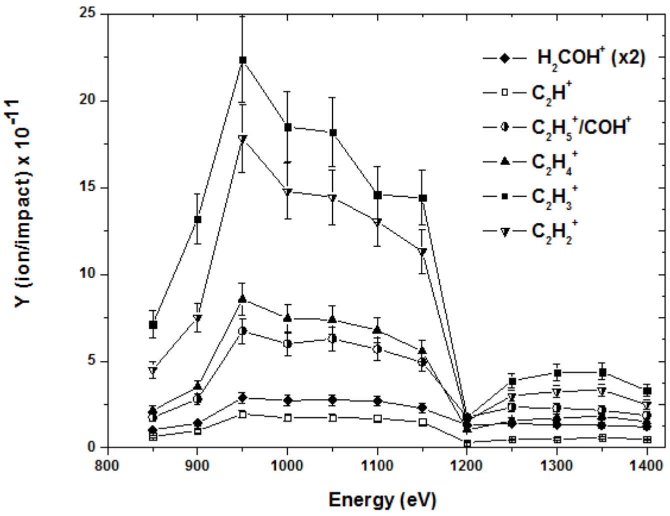
Millar, T. J.; Herbst, E.; Charnley, S. B. Astrophys. J. 1991, 369, 147–156
Fuchs, G. W.; Fuchs, U.; Giesen, T. F.; Wyrowski, F. *Astron. Astrophys.* 2005, *444*,521–530

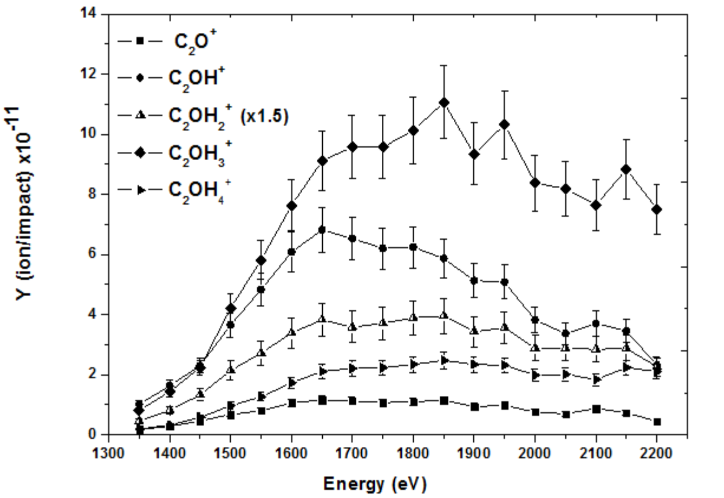
Results and Discussion

$$Y_i = \frac{A_i}{N_{pulses} \cdot \frac{electrons}{pulse}}$$









THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Desorption from Methanol and Ethanol Ices by High Energy Electrons: Relevance to Astrochemical Models

Guilherme C. Almeida,*[†] Diana P. P. Andrade,[‡] C. Arantes,[†] Andressa M. Nazareth,[†] Heloisa M. Boechat-Roberty,[§] and Maria Luiza M. Rocco[†]

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[‡]Instituto de Pesquisa e Desenvolvimento, Universidade do Vale do Paraíba, 12244-000, São José dos Campos, SP, Brazil

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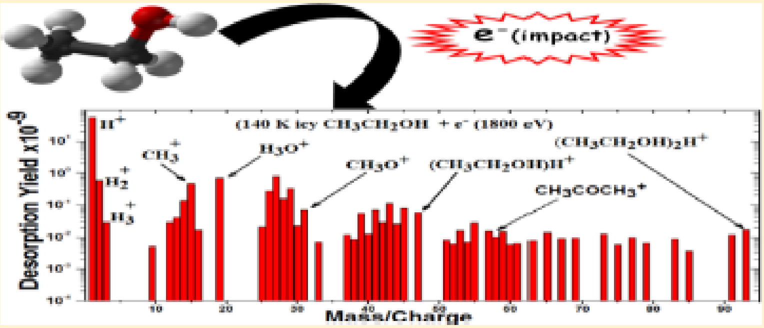
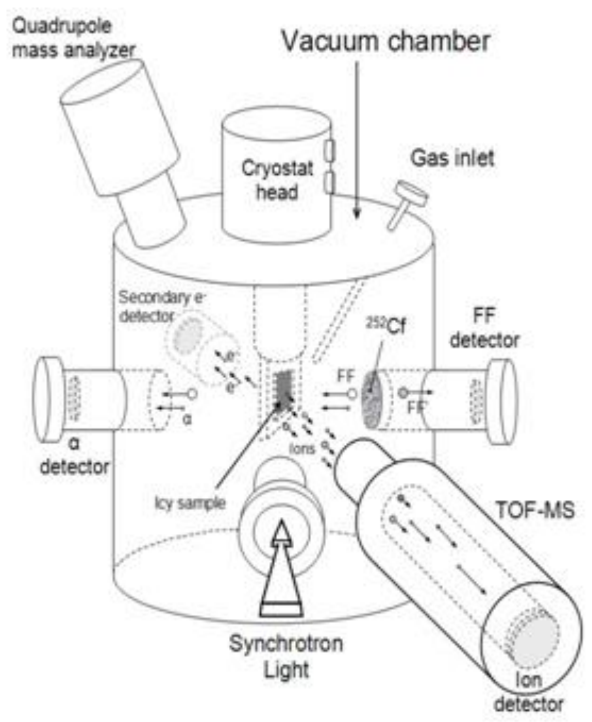
ABSTRACT: Methanol and ethanol, precursors of prebiotic molecules, are found in interstellar and circumstellar environments. At low temperatures, electrons may interact with these frozen molecules on dust grain surfaces stimulating desorption of atomic and molecular ions and charged clusters. These heavy fragments released from the icy mantles could contribute to the abundance in the gas phase of organic molecules in such environments. In this work, we investigate the ionic fragments desorbed from methanol and ethanol pure ices due to high energy electron impact. Absolute desorption yields (ions/impact) for each fragment desorbed from the ice surface were determined. Several clusters and heavier molecular ions were observed at higher electron energies. Two mechanisms seem to be involved in the desorption process, namely, the Auger stimulated ion desorption and that of secondary electrons. These data may provide support to establish more accurate astrochemical models and contribute to explain the influence of solar wind on condensed alcohols.



Almeida, G. C. *et al.* J. Phys. Chem. C 2012, 116, 25388–25394.

Impacting Photons

- ✓ **Photon Estimulated Ion Desorption (PSID): Acetone Ice (CH_3COCH_3)**
- ✓ **Photostability studies with a white beam of synchrotron radiantion fallowed by NEXAFS (XAS) spectroscopy: Acetone and Acetonitrile (CH_3CN) Ices**

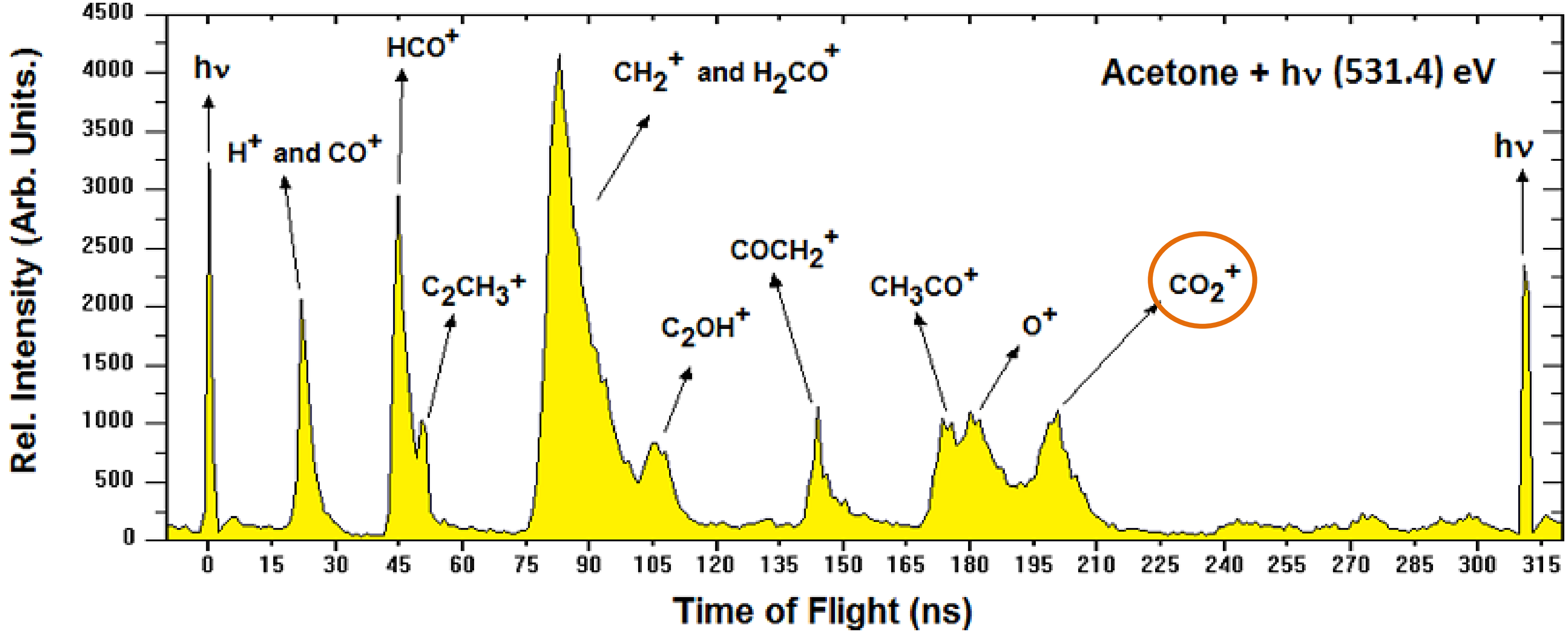


UHV Chamber at SGM Beamline

Pressures of order of 10^{-9} mbar

PSID spectrum of Condensated Acetone

➢ Simulations were carried out with the program SIMION 3D 7.0 in order to obtain the experimental time of flight of all desorbed fragments.



$$R\text{-}CH_3 + h\nu_{(O1s)} \rightarrow R^+ + CH_3^{\cdot}$$

$$CO^+ + CO \rightarrow CO_2^+ + C$$

$$CO + O^+ \rightarrow CO_2^+$$

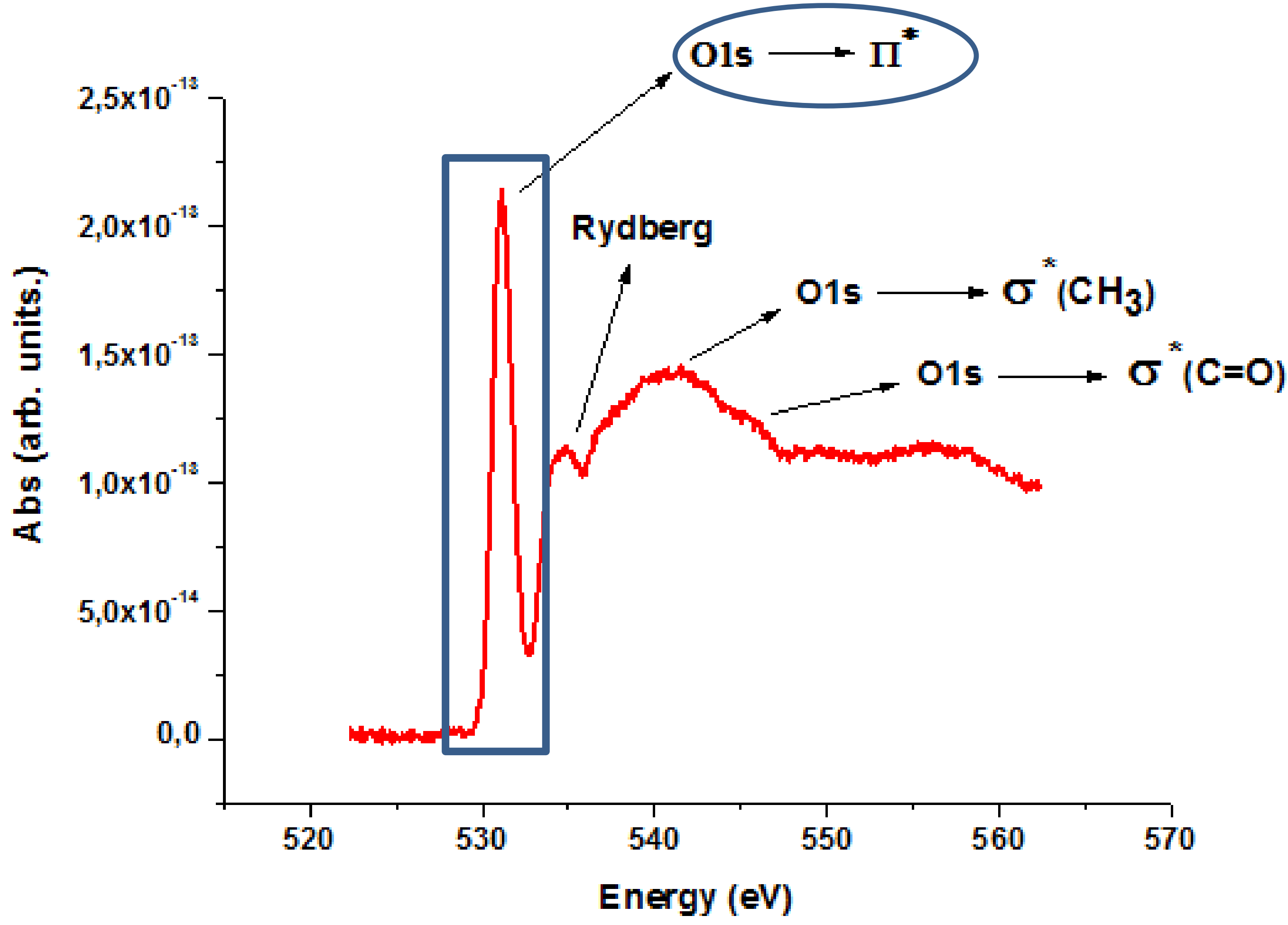
Ponciano et al. J. Am. Soc. Mass. Spectrom. 2006, *17*, 1120 –1128.

TOF (SB) = [(TOF (Simion 3D)/311 – n) x 311]

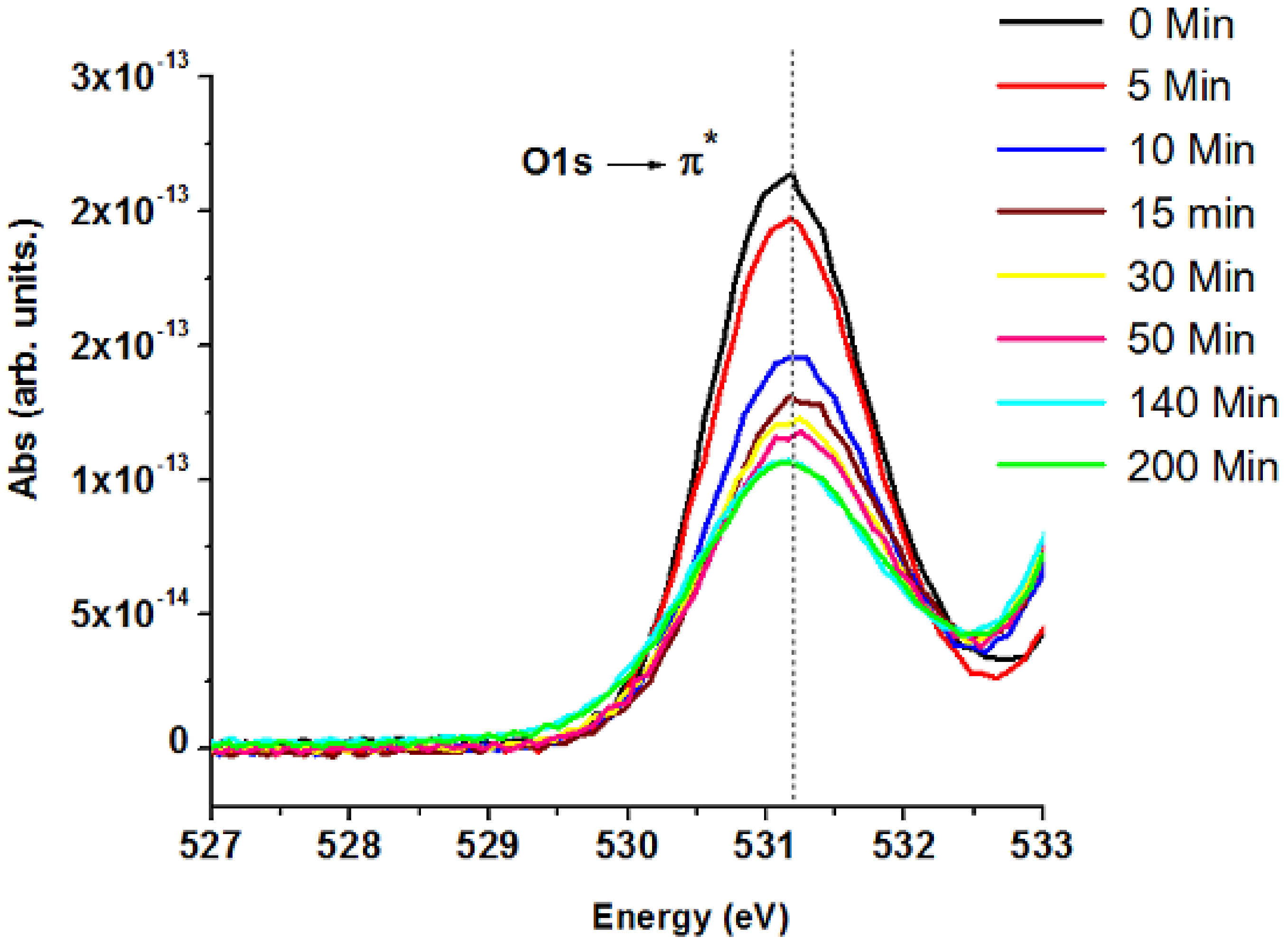
The SAI Photostability Experiment

****SAI – Simulated Astrophysical Ice***

Acetone NEXAFS Spectra (10K) at T=0



The Ice Matrix Degradation



Fitting Experimental Data

$$A_{(t)} = A_{s(o)}\, e^{-\sigma\phi(t)} + A_b$$

Acetone

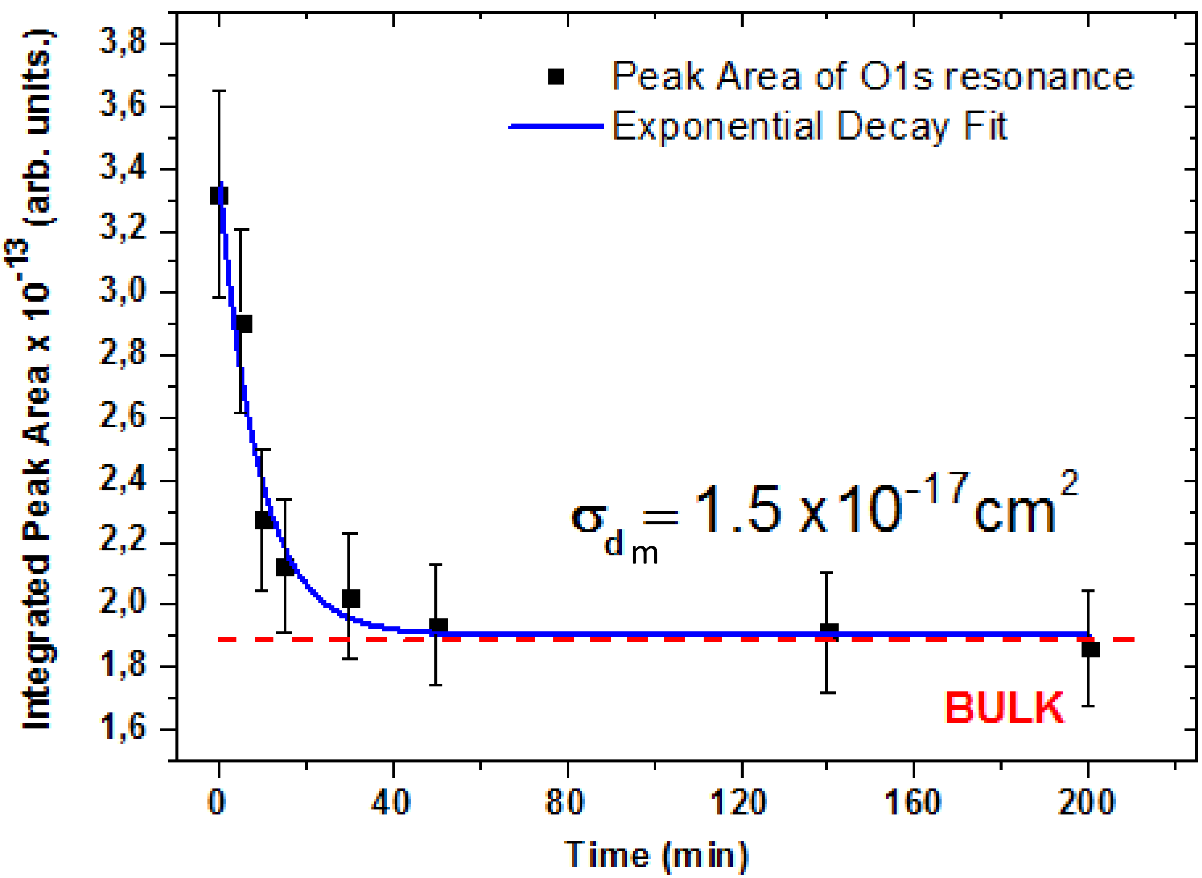
$A_{(t)}$ = Peak Surface Area after irradiation time (t)

A_0 = Peak Surface Area before irradiation

$\phi_{(t)}$ = Photon Fluence (Photons/cm^2)

σ_d = Soft X-Ray Destruction Cross Section

A_b = Ice Bulk Area



Fitting Experimental Data

$$A_{(t)} = A_{s(o)}\, e^{-\sigma\phi_{(t)}} + A_b$$

$A_{(t)}$ = Peak Surface Area after irradiation time (t)

A_0 = Peak Surface Area before irradiation

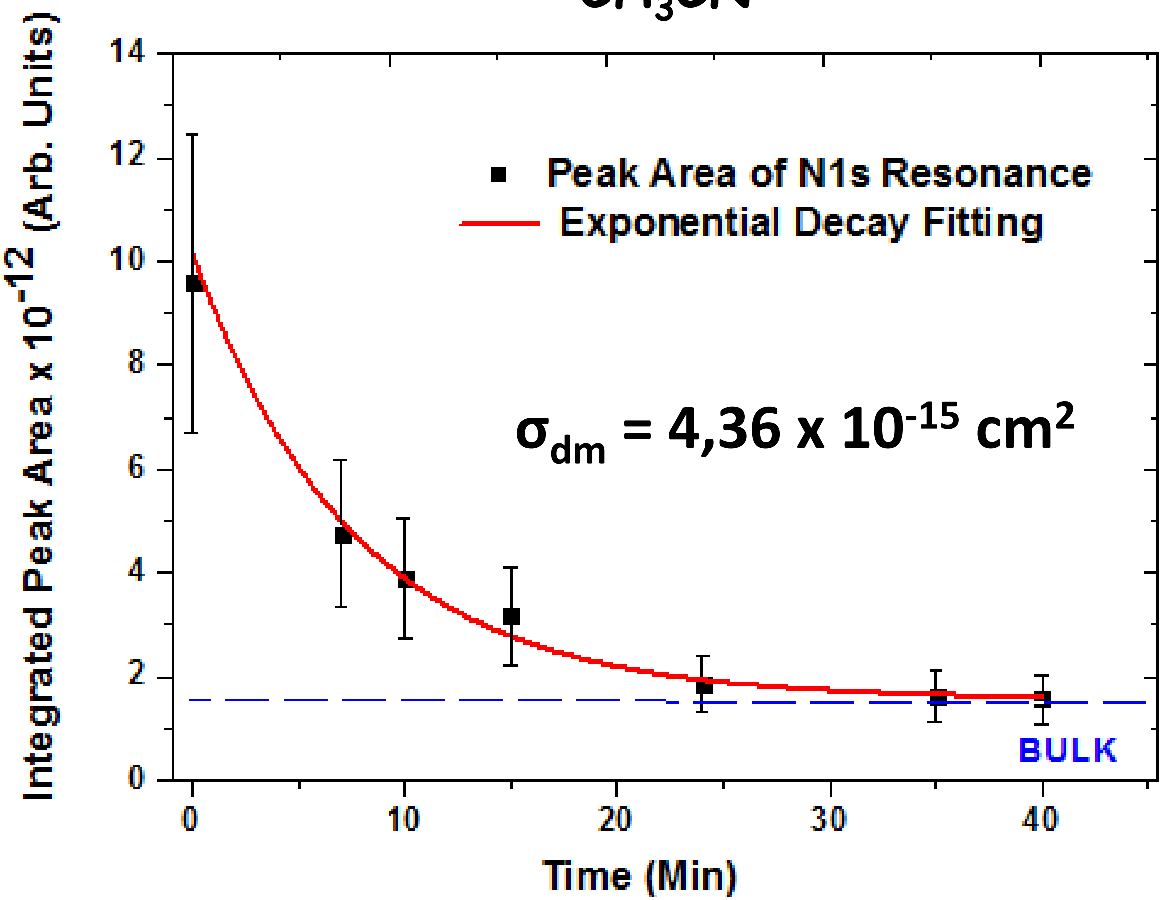
$\phi_{(t)}$ = Photon Fluence (Photons/cm^2)

σ_d = Soft X-Ray Destruction Cross Section

A_b = Ice Bulk Area

ACETONITRILE

CH_3CN



An Astrophysical Implication

$$t_{\frac{1}{2}} = \frac{\ln 2}{\sigma_d . \varphi}$$

φ *(Soft X-Rays)* *(Photons/s.cm^2)*			
	SGM (LNLS) MB Mode $\varphi = 1.7x10^{13}$	SGM (LNLS) SB Mode $\varphi = 5.0x10^{11}$	Oort Cloud* $\varphi = 2,5x10^{-3}$
Molecule	$t_{1/2}$	$t_{1/2}$	$t_{1/2}$
CH_3COCH_3	47 Min	26h	$5,9x10^{11}$ years
CH_3CN	10 s	5min	$2,0x10^{9}$ years

*** Rosat and Chandra Data. Kastner *et al.* Astrophys. J. 2002, 567, 434–440**

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

pubs.acs.org/JPCC

Photodesorption and Photostability of Acetone Ices: Relevance to Solid Phase Astrochemistry

Guilherme C. Almeida,*,† Sérgio Pilling,‡ Diana P. P. Andrade,‡ Nathany Lisbôa S. Castro,† Edgar Mendoza,§ Heloísa M. Boechat-Roberty,§ and Maria Luiza M. Rocco†

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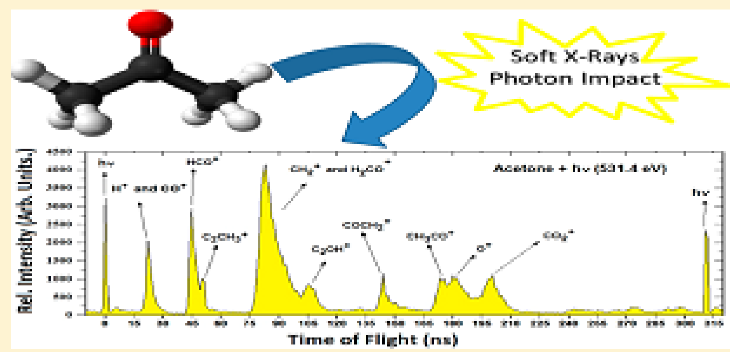
§Observatório do Valongo, Universidade Federal do Rio de Janeiro, 20080-090 Rio de Janeiro, RJ, Brazil

Supporting Information

ABSTRACT: Acetone, one of the most important molecules in organic chemistry, also a precursor of prebiotic species, was found in the interstellar medium associated with star-forming environments. The mechanisms proposed to explain the gas phase abundance of interstellar acetone are based on grain mantle chemistry. High energy photons coming from the stellar radiation field of the nearby stars interact with the ice mantles on dust grains leading to photoionization, photodissociation, and photodesorption processes. In this work we investigate the photodesorption and the photostability of pure acetone ices due to soft X-ray impact. Absolute desorption yields per photon impact for the main positive ionic fragments were determined at the O 1s resonance energy (531.4 eV). The photostability of acetone ice was studied by exposure to different irradiation doses with a white beam of synchrotron radiation. The degradation of the ice was monitored by NEXAFS around the O 1s threshold. From this study we determine the photodissociation cross-section to be about 1.5×10^{-17} cm^2 which allowed us to estimate the half-life for acetone ice in astrophysical environments where soft X-rays play an important role in chemical processes.

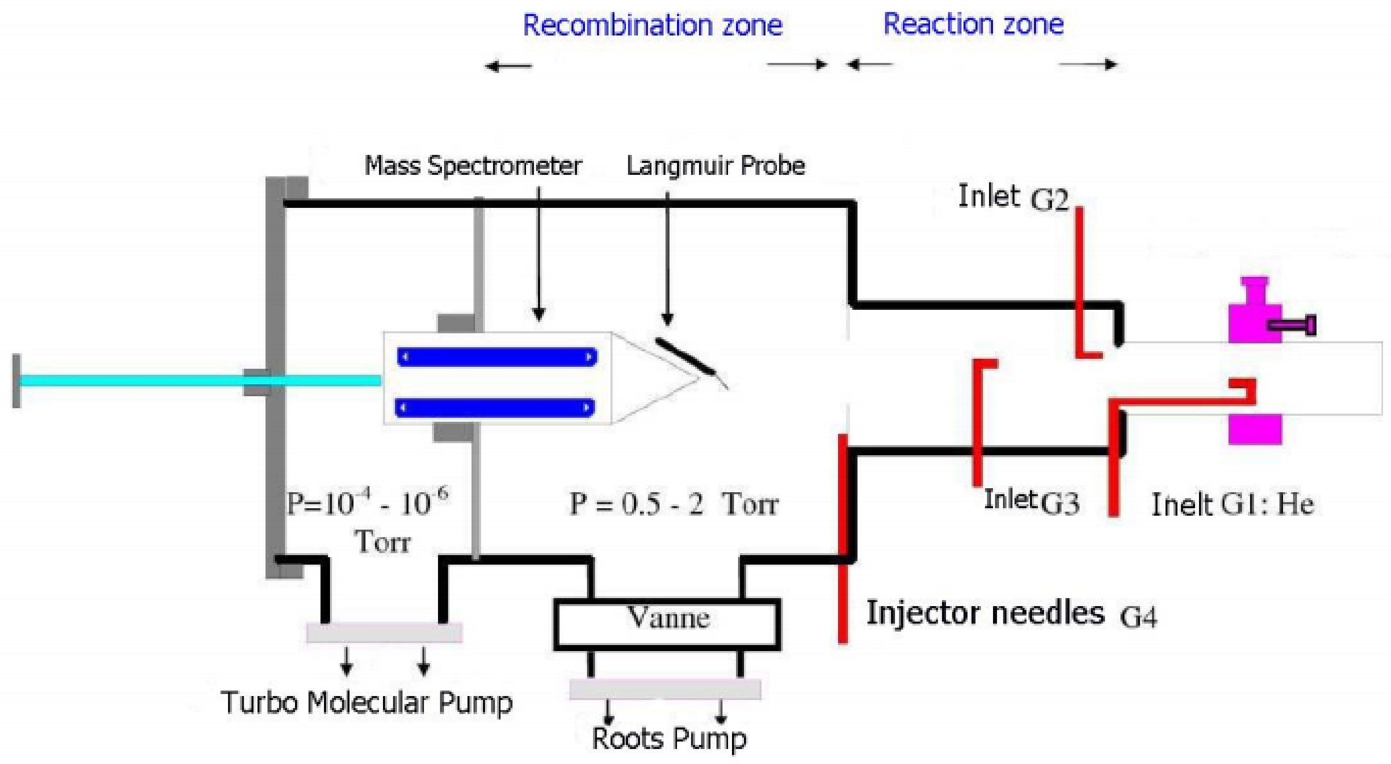


Almeida, G. C. et al. J. Phys. Chem. C 2014, 118, 6193–6200.

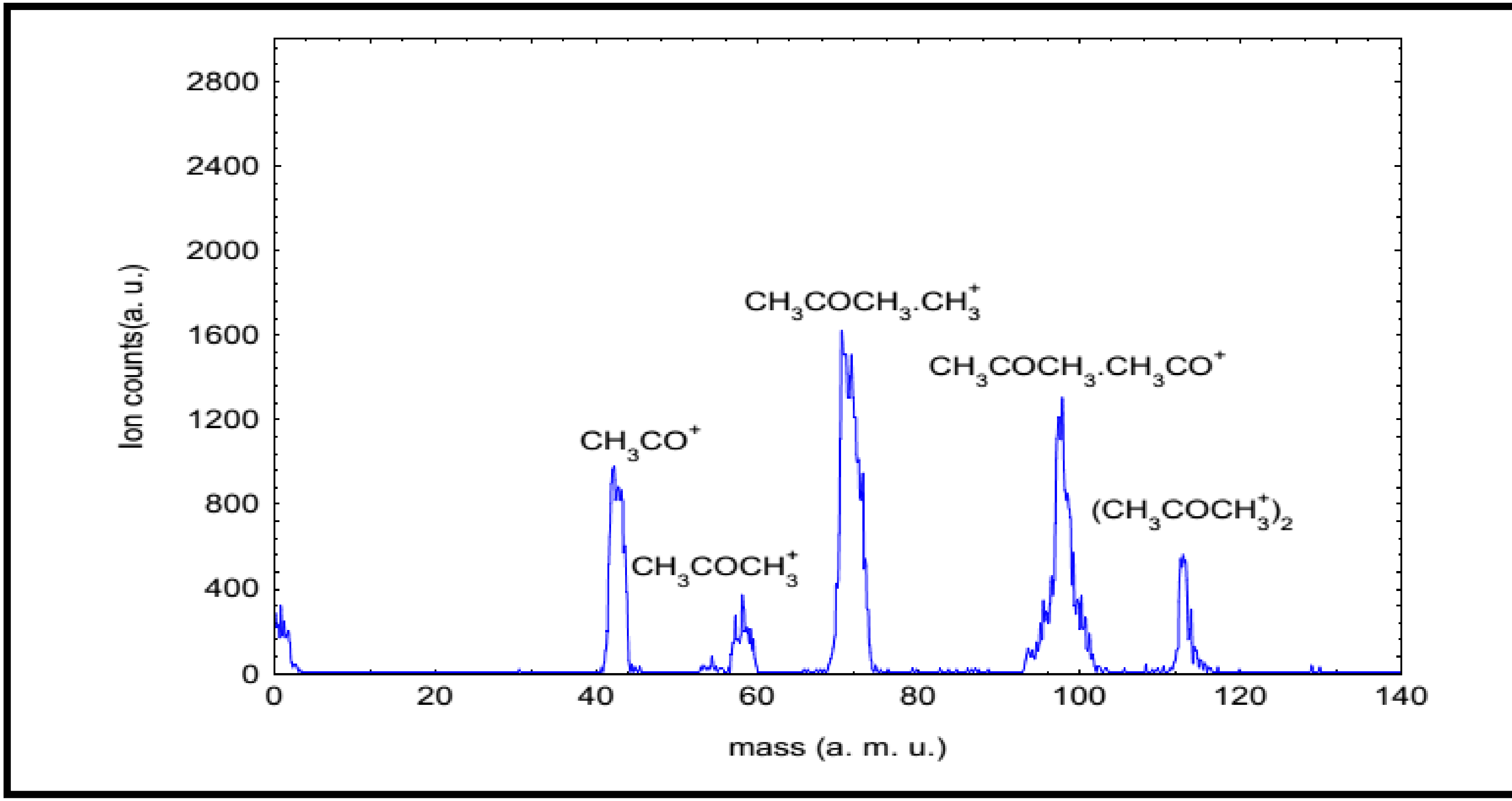
Dissociative Recombination on He/Ar Plasma

UNIVERSITÉ DE RENNES 1

Le FALP-MS



Acetone Ions Produced on Plasma

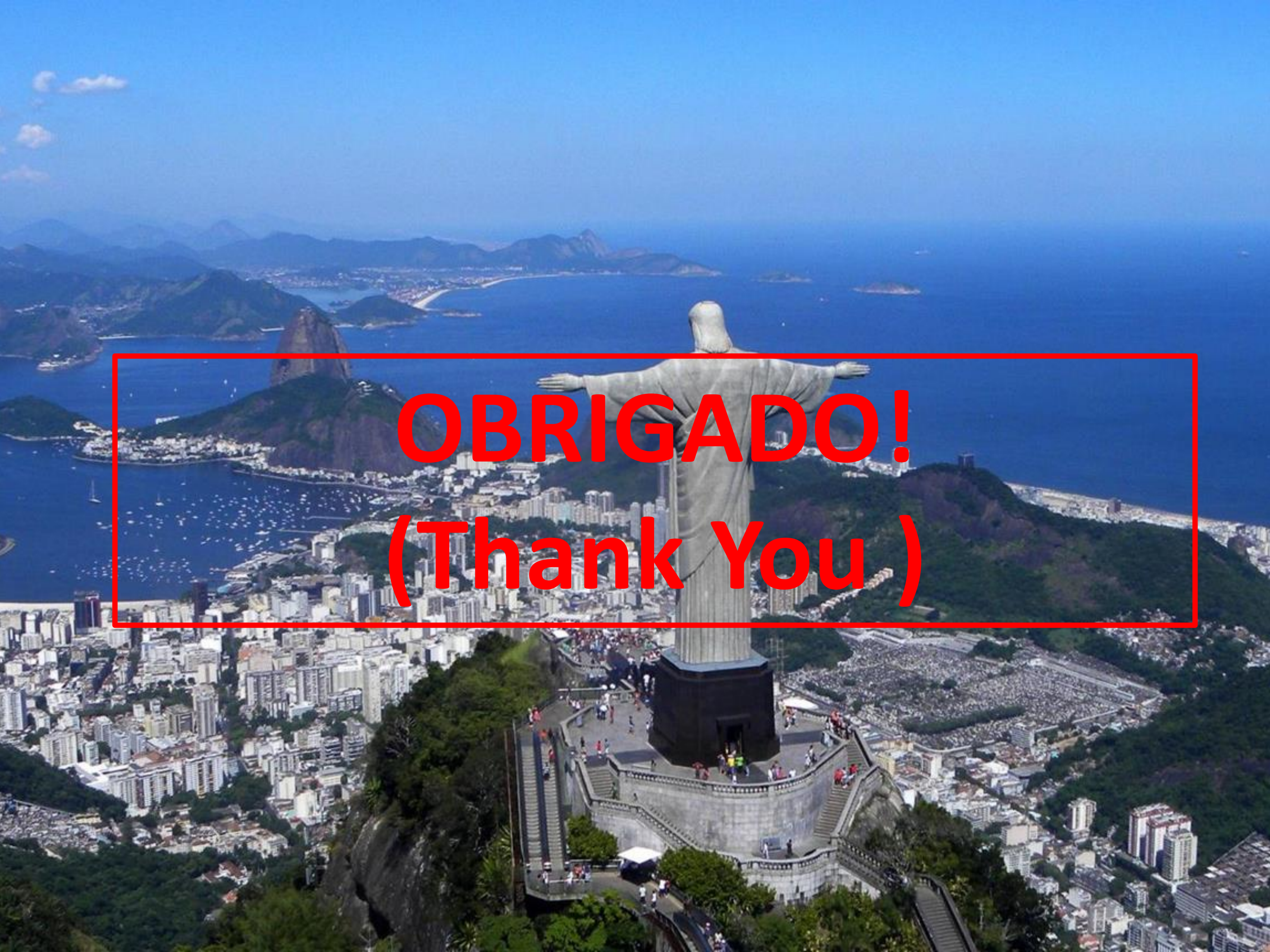


Measured Recombination Rates for Acetone ions

Ion	Rate coefficient ($\times 10^{-6}\, cm^3\, s^{-1}$)
CH_3CO^+	4.92 ± 2.03
$CH_3COCH_3^+$	3.00 ± 1.50
$(CH_3COCH_3).CH_3^+$	2.13 ± 0.55
$(CH_3COCH_3).CH_3CO^+$	2.87 ± 0.55

To Reflect About....

- ✓ **Does adduct ions could be the source for the production of complex organic molecules in hot cores like Sgr B2?**


OBRIGADO!
(Thank You)