Cosmic Rays 2
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Vacuum Ultraviolet (VUV) and Infrared (IR) Photo-Absorption Spectroscopy of Space-Related Ice: Ethanolamine under 1 keV Electron Irradiation

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Background

2 atoms	H_2	AlF	AlCl	C_2**	CH	CH+	CN	CO	CO+	CP	SiC	HCl	KCl	NH	NO	NS	NaCl	OH	PN	SO	SO^+	SiN	SiO	SiS	CS	HF	HD	FeO ?	O2	CF+	SiH?	PO	AlO	OH+	CN-	SH+	SH	HCl+	TiO	ArH+	N2	NO+ ?	NS+	HeH+	PO+ (2022)
3 atoms	C3*	C2H	C2O	C2S	CH2	HCN	HCO	HCO+	HCS+	HOC+	H2O	H2S	HNC	HNO	MgCN	MgNC	N_2H^+	N_2O	NaCN	OCS	SO_2	c-SiC2	CO_2*	NH2	H3+(*)	SiCN	AlNC	SiNC	HCP	CCP	AlOH	H2O+	H2Cl+	KCN	FeCN	HO2	TiO2	C2N	Si2C	HS2	HCS	HSC	NCO	CaNC	NCS (2021)
4 atoms	c-C3H	l-C3H	C_3N	C3O	C3S	C2H2*	NH3	HCCN	HCNH+	HNCO	HNCS	HOCO+	H2CO	H2CN	H2CS	H3O+	c-SiC3	CH_3*	C3N-	PH3	HCNO	HOCN	HSCN	H2O2	C3H+	HMgNC	HCCO	CNCN	HONO	MgC2H	HCCS (2021)	HNCN (2021)	H2NC (2021)	HCCS+ (2022)
5 atoms	C5*	C4H	C4Si	l-C3H2	c-C3H2	H2CCN	CH_4*	HC_3N	HCCNC	HCOOH	H2CNH	H2C2O	H2NCN	HNC3	SiH4*	H2COH+	C4H-	HC(O)CN	HNCNH	CH3O	NH4+	H2NCO+	NCCNH+	CH3Cl	MgC3N	NH2OH	HC3O+	HC3S+ (2021)	H2C2S (2021)	C4S (2021)	HC(O)SH (2021)	HC(S)CN (2021)	HCCCO (2021)
6 atoms	C5H	l-H2C4	C_2H_4*	CH3CN	CH3NC	CH3OH	CH3SH	HC3NH+	HCCCHO	NH2CHO	C5N	l-HC4H*	l-HC4N	c-H2C3O	H2CCNH	C5N-	HNCHCN	SiH3CN	C5S	MgC4H	CH3CO+ (2021)	C3H3 (2021)	H2C3S (2021)	HCCCHS (2021)	C5O (2021)	C5H+ (2022)	HCCNCH+ (2022)	c-C3C2H (2022)
7 atoms	C6H	CH2CHCN	CH3C2H	HC5N	CH3CHO	CH3NH2	c-C2H4O	H2CCHOH	C6H-	CH3NCO	HC5O	HOCH2CN	HCCCHNH	HC4NC	c-C3HCCH (2021)	l-H2C5 (2021)	MgC5N (2021)	CH2C3N (2021)
8 atoms	CH3C3N	HC(O)OCH3	CH3COOH	C7H	C6H2	CH2OHCHO	l-HC6H*	CH2CHCHO	CH2CCHCN	H2NCH2CN	CH3CHNH	CH3SiH3	H2NC(O)NH2	HCCCH2CN	HC5NH+	CH2CHCCH (2021)	MgC6H (2021)	C2H3NH2 (2021)	(CH3OH)2 (2022)
9 atoms	CH3C4H	CH3CH2CN	(CH3)2O	CH3CH2OH	HC7N	C8H	CH3C(O)NH2	C8H-	C3H6	CH3CH2SH	CH3NHCHO	HC7O	HCCCHCHCN (2021)	H2CCHC3N (2021)	H2CCCHCCH (2021)	HOCHCHCHO (?) (2022)
10 atoms	CH3C5N	(CH3)2CO	(CH2OH)2	CH3CH2CHO	CH3CHCH2O	CH3OCH2OH	c-C6H4 (2021)	H2CCCHC3N (2021)	C2H5NCO (2021)	C2H5NH2 (?) (2021)	HC7NH+ (2022)	CH3CHCHCN (2022)	CH3C(CN)CH2 (2022)	CH2CHCH2CN (2022)
11 atoms	HC9N	CH3C6H	C2H5OCHO	CH3OC(O)CH3	CH3C(O)CH2OH	c-C5H6 (2021)	HOCH2CH2NH2 (2021)	H2CCCHC4H (2022)
12 atoms	c-C6H6*	n-C3H7CN	i-C3H7CN	C2H5OCH3	1-c-C5H5CN (2022)	2-c-C5H5CN (2021)	CH3C7N (?) (2022)	n-C3H7OH (2022)	i-C3H7OH (2022)
>12 atoms	C60*	C70*	C60+*	c-C6H5CN	HC11N	1-C10H7CN (2021)	2-C10H7CN (2021)	c-C9H8 (2021)	1-c-C5H5CCH (2021)	2-c-C5H5CCH (2021)	c-C5H4CCH2 (2022)	2-C9H7CN (2022)

MOLECULAR UNIVERSE

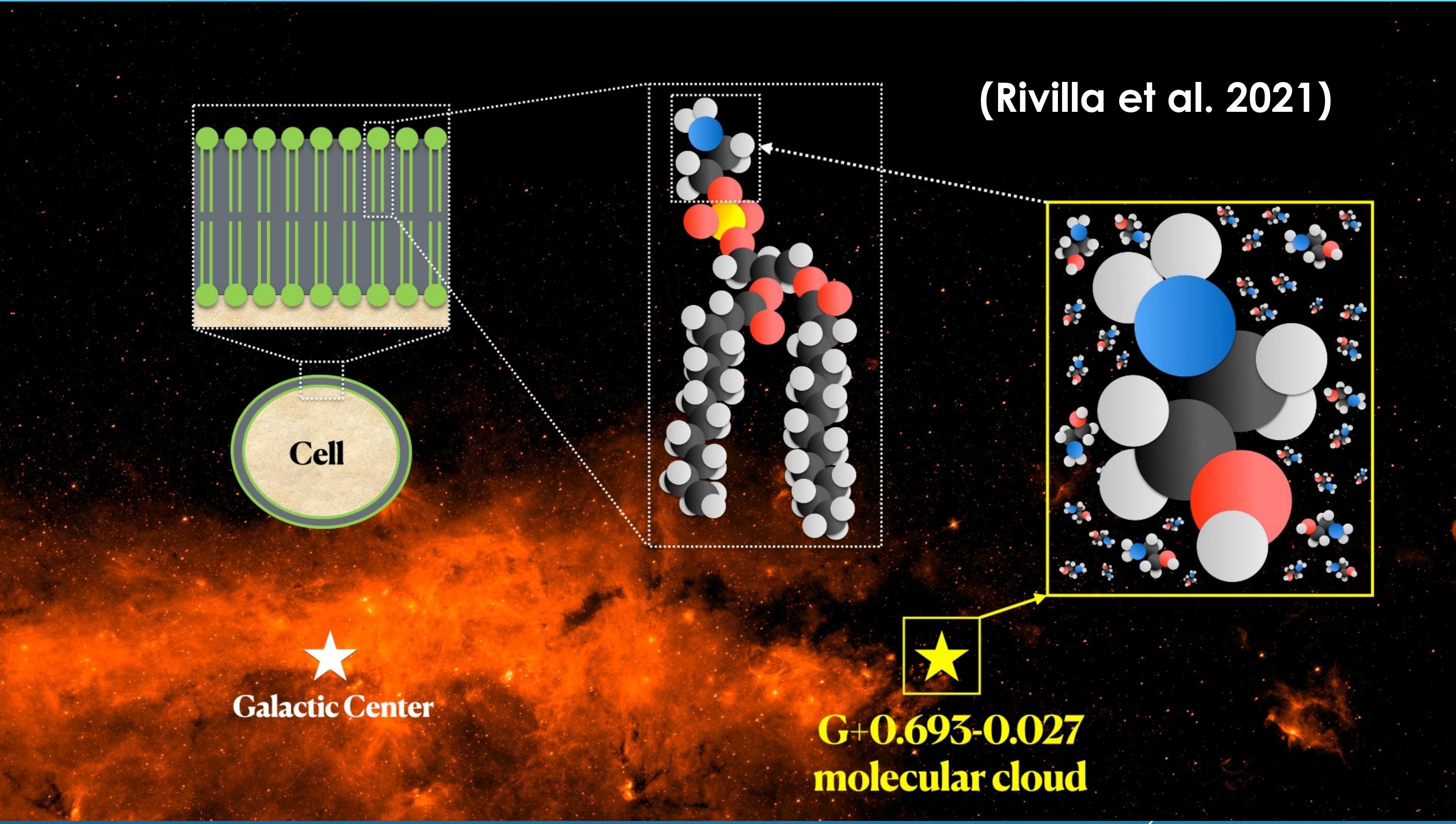
~ 270 molecules have been detected in the interstellar medium (ISM) or circumstellar shells as of Oct. 2022

One third being complex organic molecules (COMs)

→ **Ingredients of life in space!**

https://cdms.astro.uni-koeln.de/classic/molecules

Detection of Ethanolamine (EtA)



https://www.iram-institute.org/EN/news/2021/206.html

Origin of Earth life

Delivery of prebiotic COMs from Space to Earth

Existence of EtA in ISM and on the Almahata Sitta meteorite (in our Solar system),

+

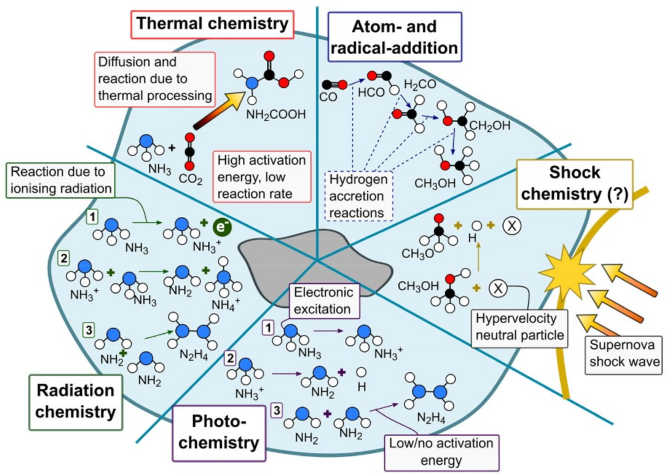
Efficient synthesis and stability under astrophysical conditions

EtA in the ISM could be seeded to planetesimals during the formation of the Solar System and subsequently transferred to the early Earth.

?

Stability of EtA in ISM

Ice Grain Chemistry



Arumainayagam et al., *Chem. Soc. Rev.* (2019)

Cold clouds: molecules are in the solid phase on interstellar grains.

Chemical processes:

- Photochemistry
- Radiation chemistry
- Thermal chemistry
- Shock chemistry
- Dark chemistry (surface atom addition reactions)

} Energetic processing (Photochemistry, Radiation chemistry, Thermal chemistry, Shock chemistry)

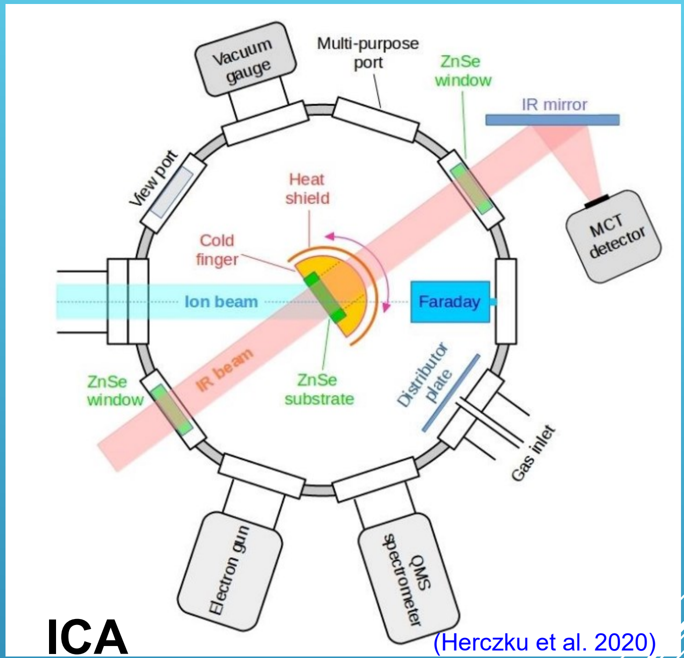
} Non-energetic processing (Dark chemistry)

- 1-keV electron beam irradiation to simulate the interaction of electron irradiation with interstellar icy mantles.

❖ **FTIR+VUV Spectroscopy**

Experimental methodology

Mid-Infrared Spectroscopy Experiments at ATOMKI, Hungary



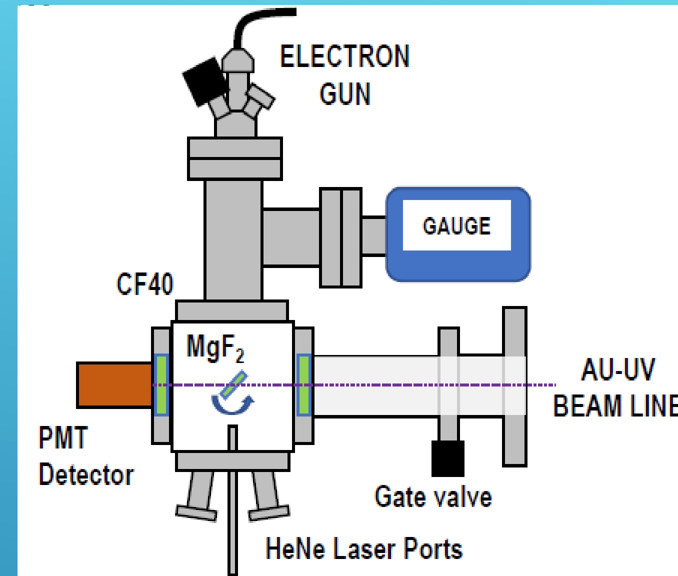
(Herczku et al. 2020)

Ice Chamber for Astrophysics-Astrochemistry (ICA):

- **UHV-compatible chamber with a base pressure of 10^{-9} mbar.**
- **ZnSe substrates cooled to 20 K.**
- **EtA ice was deposited at 20 K, and a mid-infrared absorption spectrum was acquired.**
- **Ice irradiated with 1 keV electrons.**
- **Mid-infrared absorption spectra were acquired throughout irradiation.**

(spectral resolution = 0.5 cm^{-1}; spectral range = 4000-650 cm^{-1}; number of co-added scans = 256 per spectrum).

Vacuum-Ultraviolet (VUV) Spectroscopy at ASTRID-2 synchrotron, Aarhus University, Denmark



PAC (Ioppolo et al. 2020)

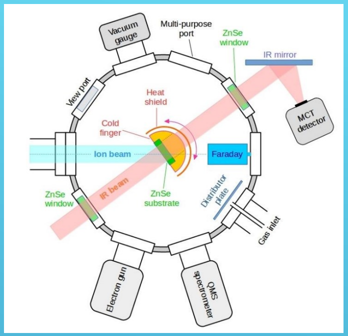
- The PAC was adjoined to the AU-UV beamline at the ASTRID-2 synchrotron light source (115-700 nm). A photomultiplier tube was connected to the PAC to detect the incident synchrotron radiation of the VUV spectroscopic beam.
- Degassed EtA was deposited, after which a VUV absorption spectrum was acquired.
- The EtA ice was then irradiated using 1 keV. Additional vacuum-ultraviolet absorption spectra were acquired throughout irradiation.

Open University Portable Astrochemistry Chamber (PAC): base pressure of 10^{-9} mbar, MgF_2 substrate, which may be cooled to 20 K.

Electron irradiation with a flux of 2×10^{13} electrons^{-1} cm^{-2}, corresponding to an overall delivered fluence of 7.2×10^{16} electrons cm^{-2}

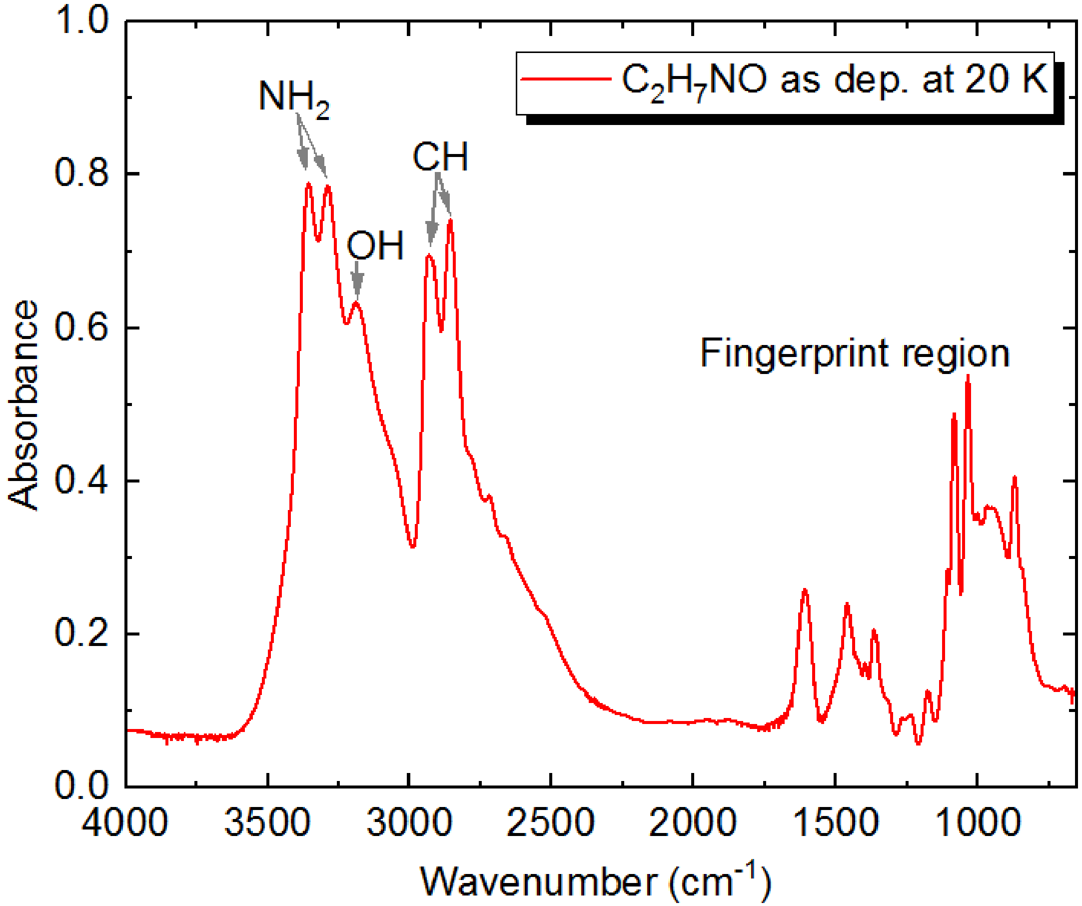
Results & Discussion

Atomki



IR Absorption Spectrum of Deposited EtA ice

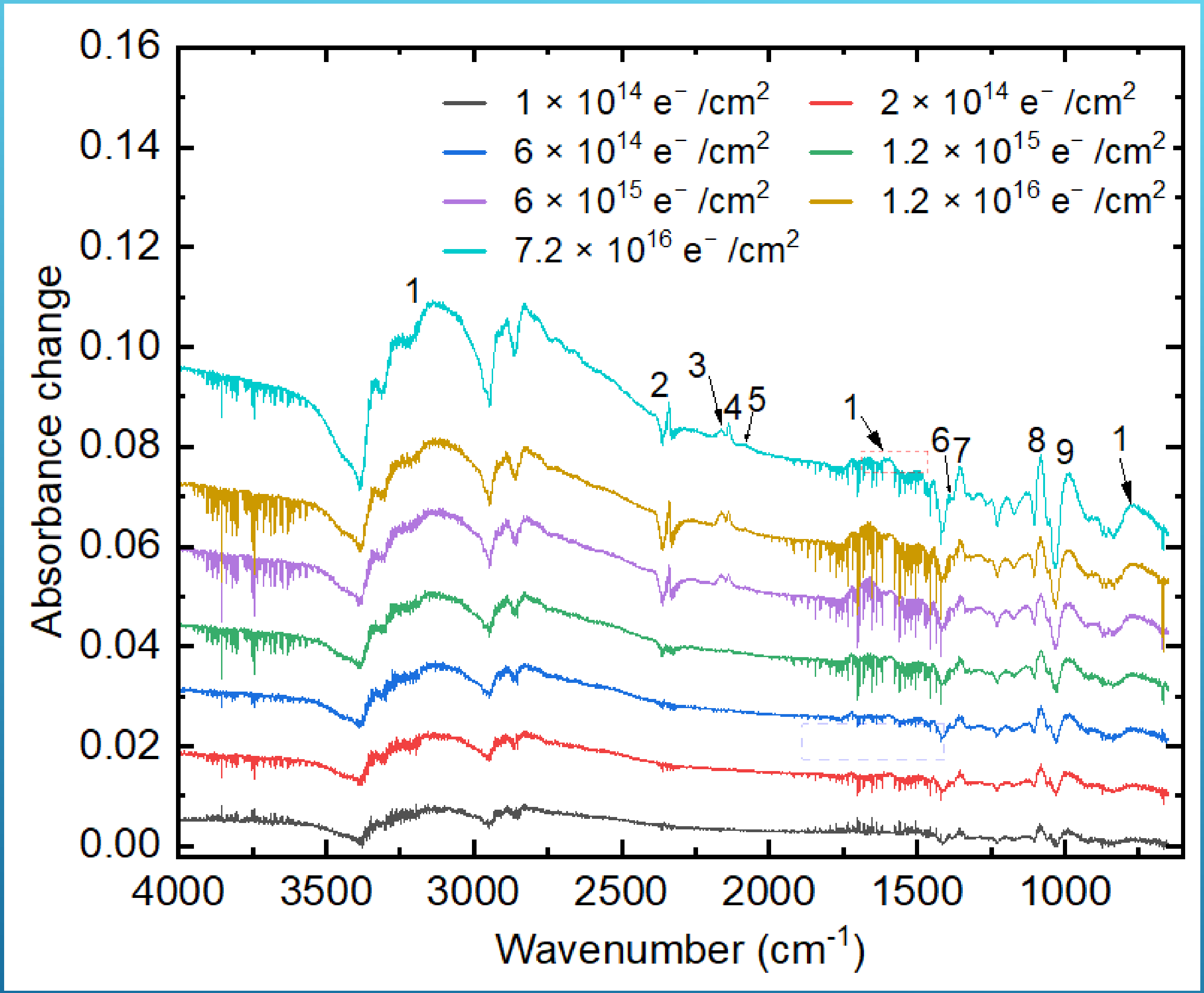
Spectral resolution: 0.5 cm^{-1}



- Intensive peaks around 3300 cm^{-1} are assigned to the -NH_2, (symmetric and antisymmetric NH_2 stretching fundamentals at 3287 and 3353 cm^{-1}).
- OH stretching fundamentals at 3187 cm^{-1},
- CH stretching bands at 2857 and 2933 cm^{-1}.
- Fingerprint region (from about 1500 to 650 cm^{-1}).

Electron Irradiation: 1 keV e^- on pure EtA

---To simulate secondary electrons emitted from ice mantles upon cosmic ray irradiation in cold clouds



Spectra change during electron irradiation

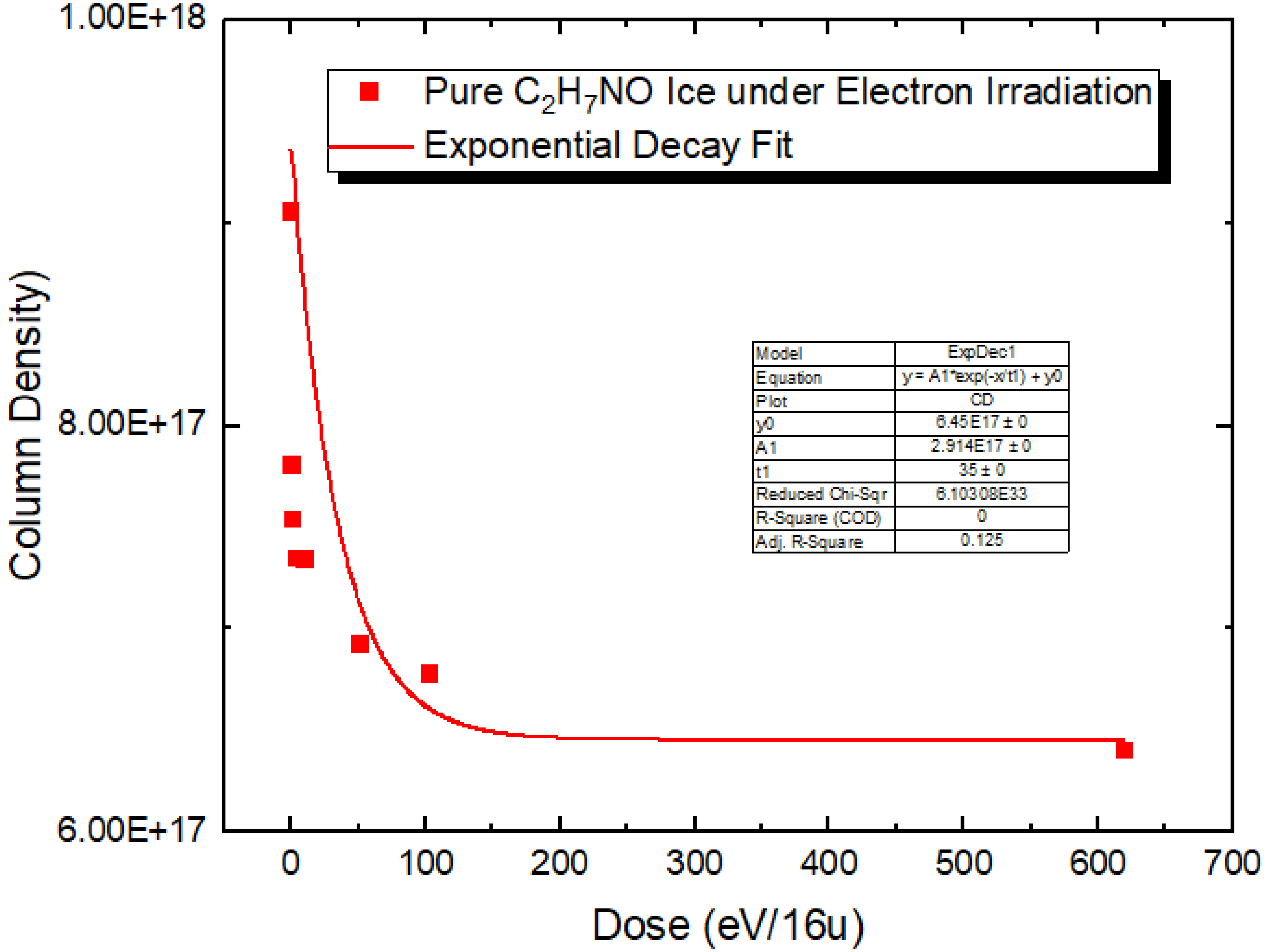
Products formation from Destructed EtA ice

Band no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Product	H_2O	CO_2	OCN^-	CO	O_3	C_2H_5OH	CH_3CHO	NH_3	C_2H_4

Electron Irradiation: 1 keV e^- on pure EtA

Destruction of pure EtA ice under electron irradiation

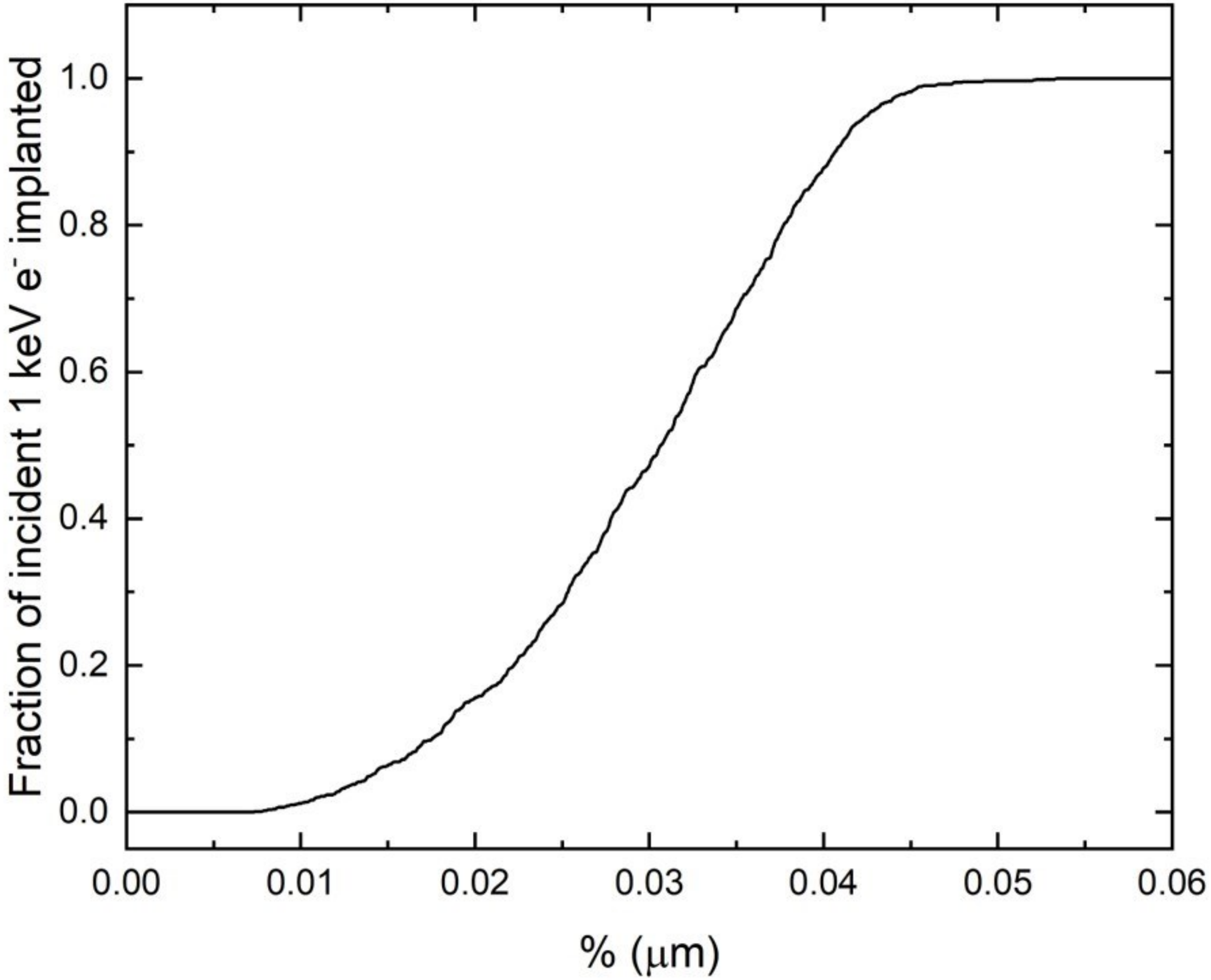
Deposition Thickness: 885 nm



- **29.3% EtA Destroyed**
- **Half-life dose: 1.7 eV/16u**

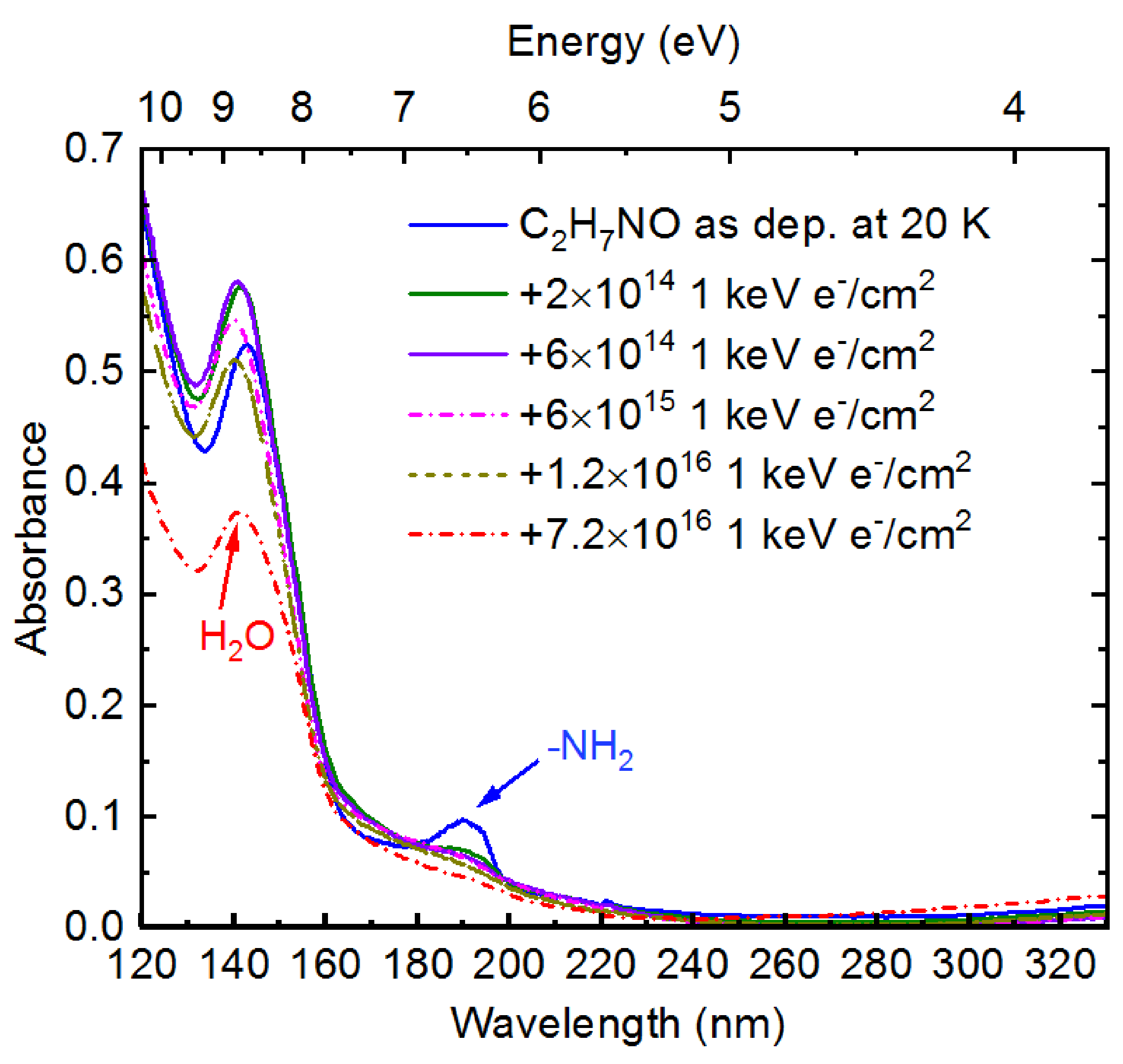
Electron Irradiation: 1 keV e^- on pure EtA

CASINO simulation on electron implantation



Penetration depth: 45 nm

VUV Absorption Spectra of Deposited pure EtA ice



Absorption features of deposited EtA ice

- A broad absorption peak centred at 143 nm.
- A minor band centred at 190 nm (amine, $-NH_2$), assigned to the $n\rightarrow\sigma^*$ transition of the lone pair of electrons in N atom.

During irradiation

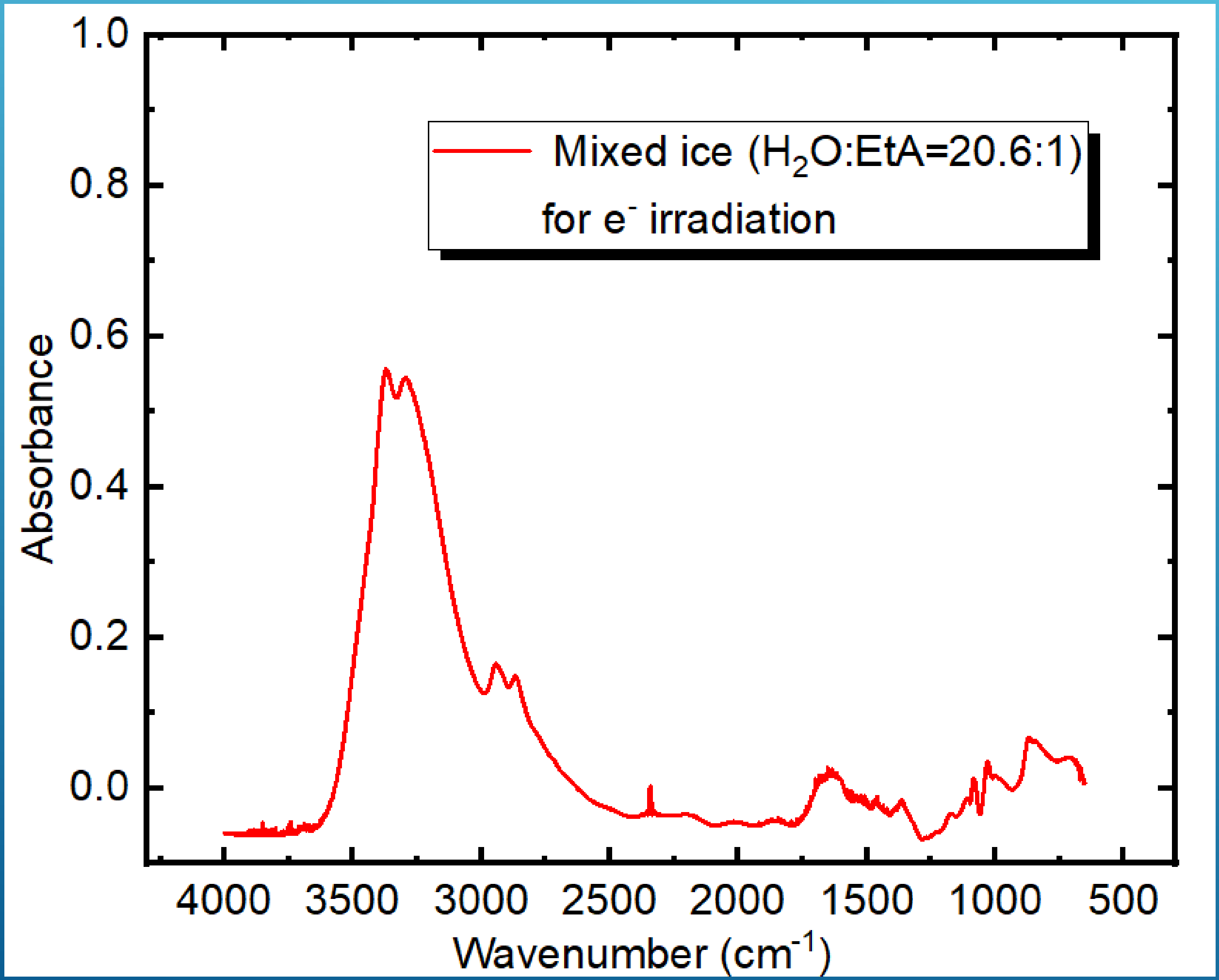
- The $-NH_2$ peak disappears as irradiation dose grows, showing EtA was destroyed by the electrons, and almost all of the EtA was destroyed eventually.
- H_2O was formed, with absorption peak at 142 nm (8.83 eV).

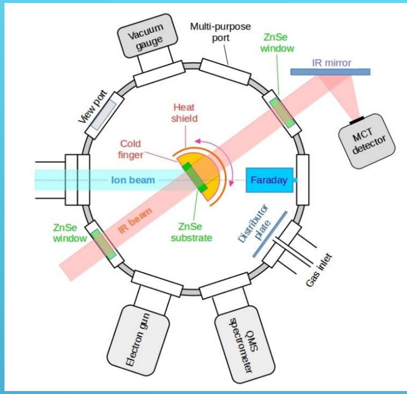
Deposition Thickness: 40 nm

Electron Irradiation: 1 keV e^- on mixed ice (H_2O:EtA=20.6:1)

---To simulate EtA diluted in water under secondary electron irradiation in cold clouds

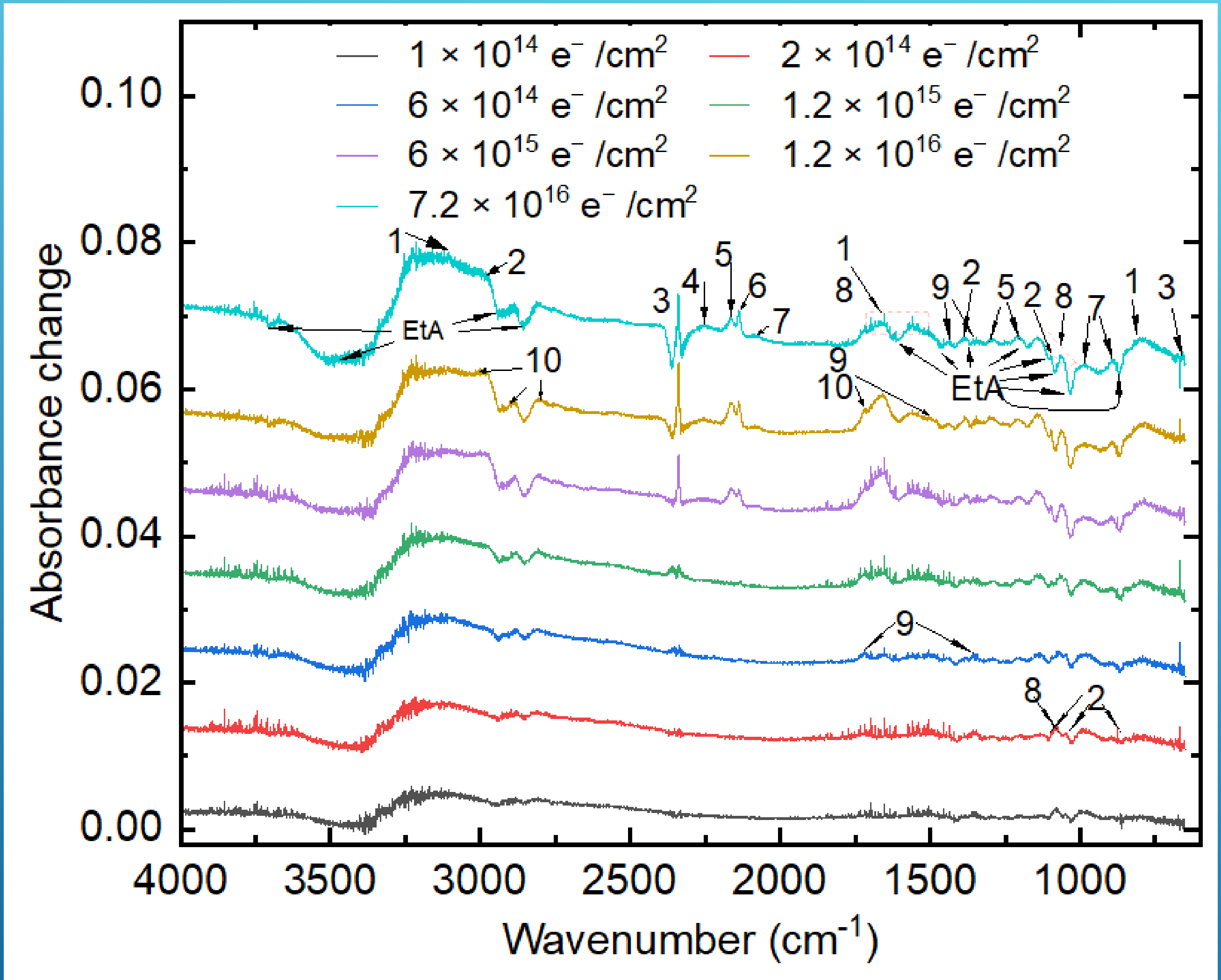
IR absorption spectrum of deposited mixted ice





ICA (Herczku et al. 2020)

Destruction of EtA and formation of products

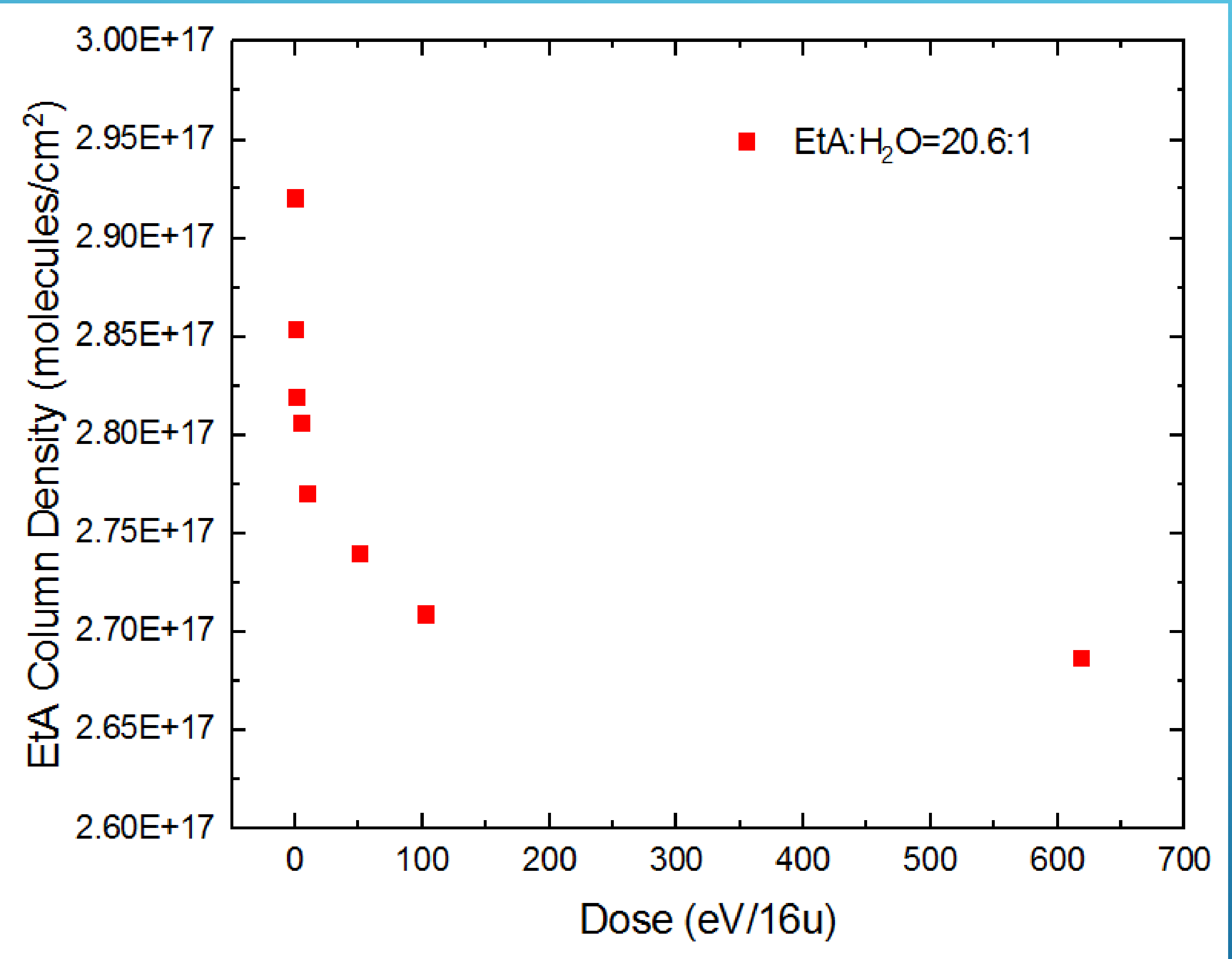


Spectra change during electron irradiation

Band no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Product	H_2O	C_2H_5OH	CO_2	HNCO	OCN^-	CO	CH_2CNH	NH_3	CH_3CHO	HCHO

Destruction of EtA in mixed water/EtA ice under electron irradiation

Deposition Thickness: 1.9 μm



- **7.98 % EtA** Destroyed **$2.92\times10^{17} \rightarrow 2.687\times10^{17}$**
- Half-life dose: **5.1 eV/16u**

Astrochemical Implications

Estimated half life of EtA ice in dense clouds and cometary ices

(only for order-of-magnitude estimates)

Location	Lifetime of ices (yr)	Depth (cm)	Dose rate (eV molecule^{-1} yr^{-1})	Half-life (yr)	Half-life diluted in water (yr)
KBO	4.6×10^{9}	...	5.6×10^{-3}	3×10^{2}	9.1×10^{2}
(40 au beneath H_2O ice)	...	10^{-3}	1.6×10^{-8}	1.06×10^{8}	3.2×10^{8}
Cold dense cloud	10^{7}	...	3×10^{-7}	5.7×10^{6}	1.7×10^{7}

- **EtA ice in cold dense clouds has half life of 5.7×10^{6} years; if diluted in water, it is 1.7×10^{7} years.**
- **EtA ice on the Kuyper Belt Objects (KBOs) has only a half-life of 300 years. However, if it is buried below the water ice with a depth of 10^{-3} cm , its half life could be1.06×10^{8} years; if it is diluted in water, its half life could be 3.2×10^{8} years.**

SUMMARY

- The **IR spectra** of pure EtA, water-EtA mixtures under electron irradiation processes were obtained. CD changes show that it underwent an exponential decay with a half-life dose of 1.7 eV/16u, 5.1 eV/16u, respectively. The formation products include H_2O, CO, CO_2, OCN^-, HNCO, NH_3, C_2H_5OH, CH_3CHO, etc.
- **VUV spectra** of the EtA ice under irradiation show the thin ice was destroyed, and water was formed.
- The survivability of EtA in ISM and the Solar system is analysed. The EtA ice on the Kuyper Belt Objects (KBOs) has only a half-life of 300 years, showing that it is destructed easily. However, if it is buried below the water ice with a depth of 10^{-3} cm , its half life could be1.06×10^8 years; if it is diluted in water, its half life could be 3.2×10^8 years. .

ACKNOWLEDGMENTS

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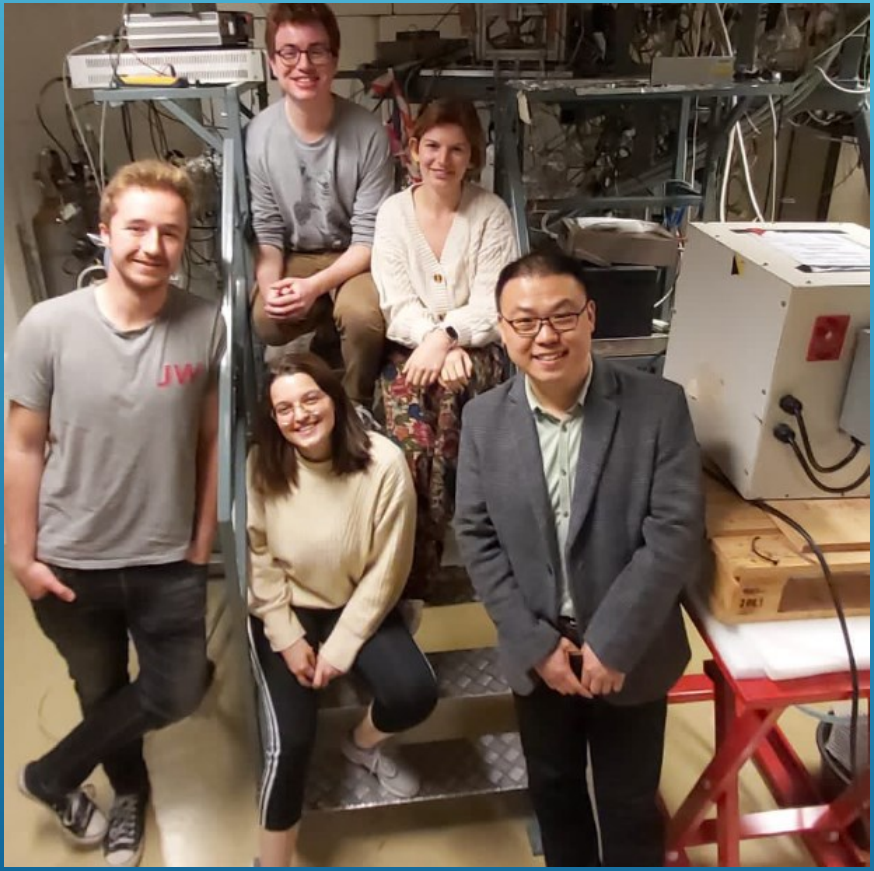
OUR GROUP



THANKS!

Any questions?

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