



ION IRRADIATION OF ETHANE AND WATER MIXTURE ICE AT 15 K: IMPLICATIONS FOR THE SOLAR SYSTEM AND THE ISM

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ABSTRACT

Solid water has been observed on the surface of many different astronomical objects and is the dominant ice present in the universe, from the solar system (detected on the surface of some asteroids, planets and their satellites, trans-Neptunian objects [TNOs], comets, etc.) to dense cold interstellar clouds (where interstellar dust grains are covered with water-rich ices). Ethane has been detected across the solar system, from the atmosphere of the giant planets and the surface of Saturn's satellite Titan to various comets and TNOs. To date, there were no experiments focused on icy mixtures of C_2H_6 and H_2O exposed to ion irradiation simulating cosmic rays, a case study for many astronomical environments in which C_2H_6 has been detected. In this work, the radiolysis of a $C_2H_6:H_2O$ (2:3) ice mixture bombarded by a 40 MeV $^{58}Ni^{11+}$ ion beam is studied. The chemical evolution of the molecular species existing in the sample is monitored by a Fourier transform infrared spectrometer. The analysis of ethane, water, and molecular products in solid phase was performed. Induced chemical reactions in $C_2H_6:H_2O$ ice produce 13 daughter molecular species. Their formation and dissociation cross sections are determined. Furthermore, atomic carbon, oxygen, and hydrogen budgets are determined and used to verify the stoichiometry of the most abundantly formed molecular species. The results are discussed in the view of solar system and interstellar medium chemistry. The study presented here should be regarded as a first step in laboratory works dedicated to simulate the effect of cosmic radiation on multicomponent mixtures involving C_2H_6 and H_2O .

Key words: methods: laboratory: solid state – molecular data – molecular processes – techniques: spectroscopic

1. INTRODUCTION

Solid water (H_2O) ice has been observed on the surface of many different astronomical objects and is the dominant ice present in the universe. In the solar system water ice has been found as a constituent of the surface of some asteroids, planets and their satellites, Centaurs, comets, and trans-Neptunian objects (TNOs). In dense, cold interstellar clouds, infrared observations show that interstellar dust grains are covered with water-rich ices. Ethane (C_2H_6), the second species considered in our study, has been detected across the solar system, from the atmosphere of the giant planets and the surface of Saturn's satellite Titan to various comets and TNOs. Observations of Titan with *Infrared Space Observatory* by Coustenis et al. (2003) revealed the presence of traces of ethane and other hydrocarbons (ethylene, acetylene, and propane) besides the main species, methane. Moreover, Griffith et al. (2006) and Brown et al. (2008) reported that ethane aerosol with drops in sizes of 1–3 μm in diameter is an effective element of a massive cloud capping the northern hemisphere of Titan. Johnson (2011) and Tielens (2013) have reviewed the radiolysis and observation of astrophysical water.

Ethane was also discovered on the surface of Titan in the organic lake, Ontario Lacus, where it was identified to be a liquid component (Brown et al. 2008). In comets, C_2H_6 has been detected by means of spectroscopic surveys after sublimation from their interior and, with methane (CH_4) and acetylene (C_2H_2), is regarded as a primary cometary volatile (Mumma et al. 2003; Bockele-Morvan et al. 2004; DiSanti & Mumma 2008). Ethane has been already observed in more than 10 comets, including 1P/Halley, C/1996 B2 Hyakutake, and

C1995 O1 Hale–Bopp, and its abundance ranges from 0.1% to 2% relative to water (see Mumma & Charnley 2011 and references therein). Among the TNOs, C_2H_6 has already been observed on Pluto (see, e.g., Cruikshank et al. 2015 and references therein), Quaoar (Schaller & Brown 2007), Make-make (Sasaki et al. 2005; Brown et al. 2007), and has been suggested for Orcus (Delsanti et al. 2010).

The formation of ethane in our solar system has been discussed for a long time (see, e.g., Mumma et al. 1996), and it has been commonly advocated for the radiation processing of methane-rich ices. Experiments studying the effects of ultraviolet (UV) photolysis and ion and electron irradiation on ices of astrophysical interest have been carried out and supported the proposed view of ethane being a processing product of pure methane ices (Gerakines et al. 1996; Kaiser & Roessler 1998; Baratta et al. 2002; Bennett et al. 2006) or icy mixtures of methane and water (Moore & Hudson 1998; Wada et al. 2006). On the contrary, to our best knowledge, few laboratory experiments have been conducted that investigate the interaction of ionizing radiation with pure ethane ices (Strazzulla et al. 2002; Hudson et al. 2009; Kim et al. 2010), but there are no experiments focused on icy mixtures of ethane and water (in the keV–GeV regime) at lower temperatures. Khare et al. (1993) have considered the same mixture, but they used plasma interaction (eV range), and the icy mixture was at 77 K. Therefore, it is clear that studying the role of C_2H_6 in icy mixtures with H_2O is of particular interest and is necessary to understand the genesis and evolution of organics in comets, TNOs, planets, and their satellites. In this context, the current paper presents the results of a laboratory study focused on the reaction products of C_2H_6 and H_2O in an icy mixture at 15 K

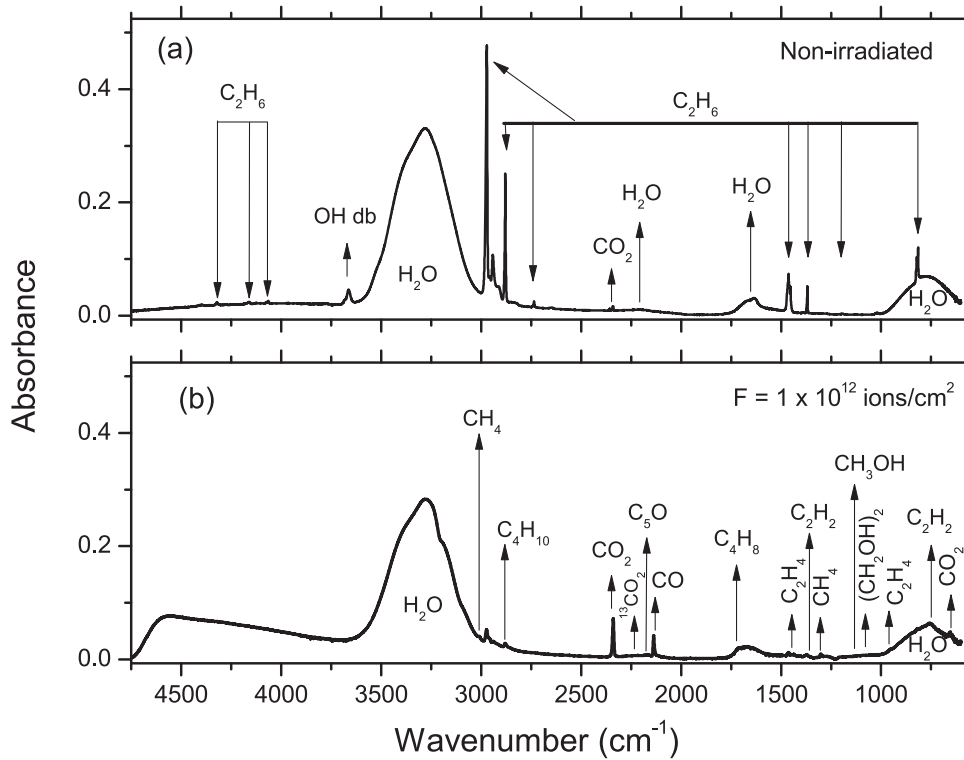


Figure 1. FTIR spectrum (4750–600 cm⁻¹) of the C₂H₆:H₂O (2:3) ice at 15 K: (a) before irradiation and (b) at 1.0×10^{12} ions cm⁻² fluence.

and relative ratio 2:3, when irradiating the mixture with fast heavy ions used to simulate cosmic rays.

The study presented here should be regarded as a first step into laboratory works dedicated to simulate the effect of cosmic radiation on multicomponent mixtures involving C₂H₆ and H₂O. Such studies are required for a deeper understanding of the chemical evolution of the solar system and the interstellar medium (ISM).

2. EXPERIMENTAL

The experimental setup has been described previously (Seperuelo Duarte et al. 2009). In the center of a high vacuum chamber, which is evacuated down to 3×10^{-8} mbar, a closed cycle helium cryostat keeps the CsI substrate at 15 K. To analyze the ice sample, a Nicolet Magna 550 Fourier transform infrared (FTIR) spectrometer, running in transmission mode with the IR beam perpendicular to the sample surface, was used. Each spectrum was acquired by 256 scans from 5000 to 600 cm⁻¹ (2–16.7 μm) with a wavenumber resolution of 1 cm⁻¹. The ice target was prepared by depositing a homogenous vapor mixture of carrier argon, ethane (99.999%), and triply distilled water on the 15 K substrate. The liquid water had an electric resistance greater than $10^7 \Omega$ cm. The deposition occurred for 2 minutes and 10 seconds, through a 4 mm diameter tube placed perpendicularly to the substrate, whose extremity was held 10 mm away. After that, the ice mixture was warmed up to 50 K, in order to obtain sublimation of the argon atoms, and then cooled down to 15 K. A typical virgin C₂H₆:H₂O (2:3) FTIR spectrum is shown in Figure 1(a).

The sample was irradiated by 40 MeV ⁵⁸Ni¹¹⁺ ions ($E/m \sim 0.7$ MeV/u) in a chamber at the IRRSUD beam line of the heavy ion accelerator Grand Accélérateur National d'Ions

Lourds (GANIL). The ion beam impinged perpendicularly to the sample at a constant beam flux of 1×10^9 ions cm⁻² s⁻¹ up to a final fluence of 3.0×10^{13} ions cm⁻². A sweeping device assured a homogeneous irradiation of the sample volume. As an example of the spectral changes induced by irradiation, Figure 1(b) presents the FTIR spectrum collected at $F = 1.0 \times 10^{12}$ ions cm⁻², which is about 3% of the final fluence.

Figure 2 depicts selected segments of four mid-infrared spectra of the 2:3 ethane water ice prepared as described above. The vibrational assignments, extracted from the literature, and their A-values are presented in Table 1 (Hepp & Herman 1999).

The column density (molecules cm⁻²) of the molecular species is determined by using the Beer–Lambert law: the band absorbance S is equal to the column density N multiplied by the absorbance coefficient (A-value) and divided by $\ln 10$. The used A-values are those from the literature, assuming that they have been measured for (usually porous) ices produced by deposition, that is, non-irradiated pristine ices. For C₂H₆, the used coefficient is $A_{\nu_{10}}^p = 14.8 \times 10^{-18}$ cm molecule⁻¹ for the ν_{10} band at 2971 cm⁻¹ (Moore & Hudson 1998; Kim et al. 2010; de Barros et al. 2011a), which leads to an initial column density value of $(15.4 \pm 0.6) \times 10^{17}$ molecules cm⁻² and a thickness of ~ 1.09 μm. For water, the column density was estimated taking its integrated absorption coefficient as 12×10^{-18} cm molecule⁻¹ for the ν_2 band at 1655 cm⁻¹ (de Barros et al. 2014b), leading to a column density of $(23.6 \pm 0.7) \times 10^{17}$ molecules cm⁻² and a thickness of ~ 0.73 μm. The total ice thickness is therefore 1.82 μm, which was determined after taking into account that the densities of solid ethane are 0.701 g cm⁻³ (Donnay & Ondik 1972) and 0.94 g cm⁻³ for water (Hama & Watanabe 2013). The stopping power of 40 MeV nickel projectiles in C₂H₆:H₂O is 1.41×10^{-13} eV/molecule cm⁻² (Stopping and Range of Ions in Matter, SRIM; Ziegler et al. 2010).

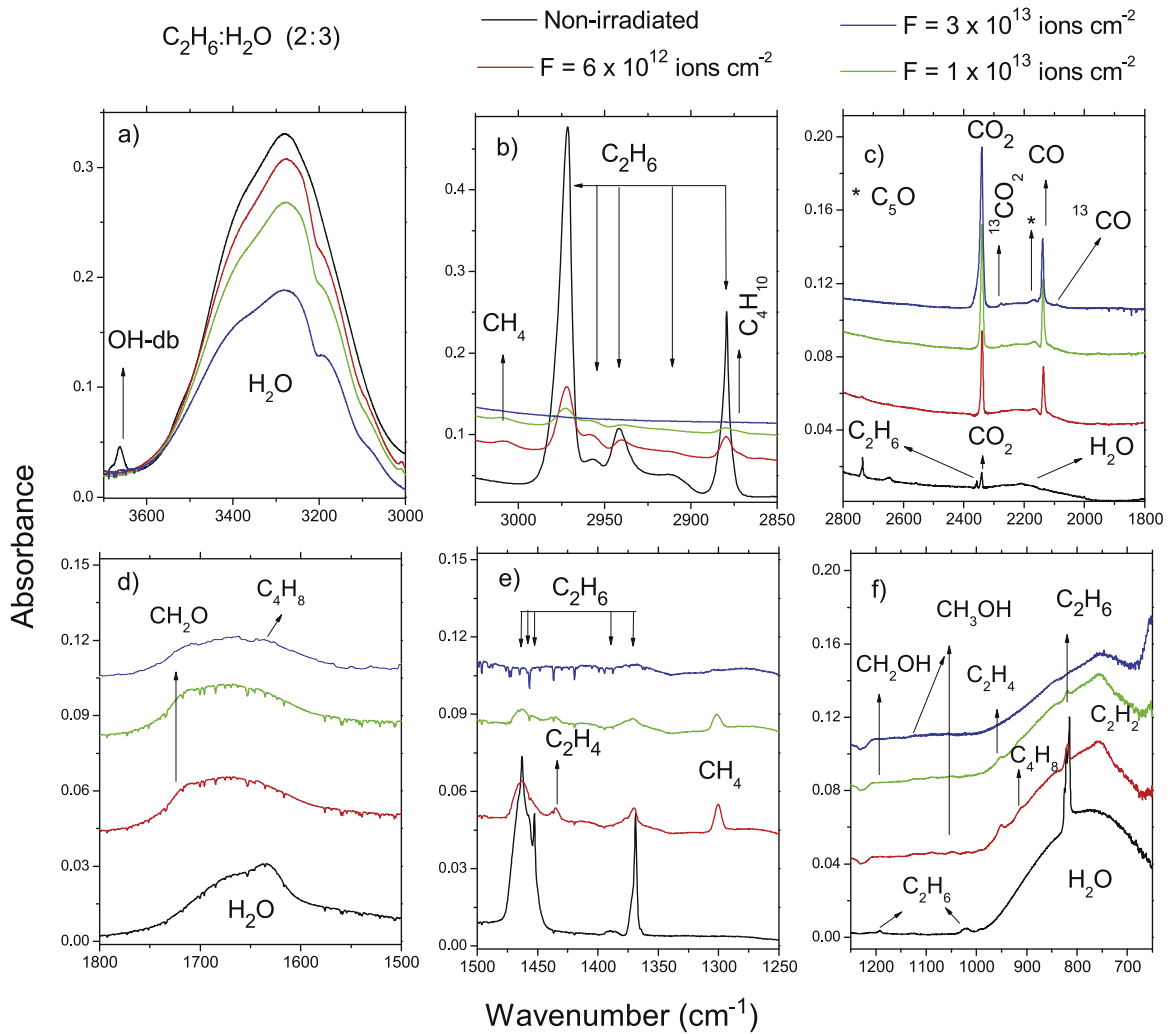


Figure 2. Segments of infrared spectra measured for the ice mixture at 15 K, before and after irradiation, for three fluences: 0.6, 1.0, and 3.0×10^{13} ions cm^{-2} . Six spectral regions are shown for peak shape analysis: (a) 3700–3000 cm^{-1} , (b) 3100–2850 cm^{-1} , (c) 2800–1800 cm^{-1} , (d) 1800–1500 cm^{-1} , (e) 1500–1250 cm^{-1} , and (f) 1250–650 cm^{-1} .

The most suitable ice layer thickness of the sample is determined by three conditions: (i) thickness much smaller than the ion penetration depth in order to keep the energy loss small and minimize the kinetic energy variation of the projectile inside the ice, which assures that the cross section remains constant in good approximation (Figure 10, Mejía et al. 2013); (ii) thickness thin enough to avoid IR absorption saturation (Figure 2 of de Barros et al. 2011a); and (iii) thickness large enough to allow a reliable signal-to-noise ratio for weak FTIR peaks corresponding to low abundant daughter species. All of these conditions are indeed fulfilled by the $1.82 \mu\text{m}$ ice layer prepared for the present experiment.

Finally, it should be mentioned that C_2H_6 is a nonpolar molecule while H_2O is a polar one. During the vapor mixture deposition, segregation of the two species may occur. However, we do not think that the segregation happened in the present experiment: the substrate temperature was permanently very low (~ 15 K) and the deposition rate also low ($1840 \text{ nm}/130 \text{ s} = 14 \text{ nm s}^{-1} \sim 44 \text{ monolayers s}^{-1}$), and therefore the sticking coefficient should be close to unity; the carrier argon should also contribute to the homogeneous dispersion of the species. In accordance, the extra argument is that the $N_0(\text{C}_2\text{H}_6)/N_0(\text{H}_2\text{O})$ ratio was found to be $15.4/23.6 \sim 2/3$,

which is the nominal ratio of the partial pressures of the two vapors before entering the deposition chamber.

3. RESULTS

3.1. Infrared Spectroscopy

Figure 2 shows six infrared spectral regions of an ice layer consisting of C_2H_6 and H_2O condensed at 15 K, before and after irradiation. Spectra for the irradiated ice are shown for three fluences: 0.6, 1.0, and 3.0×10^{13} ions cm^{-2} . Thirteen C_2H_6 bands and five H_2O bands are identified, including the water dangling bond (OH-db) commonly seen for amorphous water. They are listed in Table 1, and their evolutions with increasing projectile fluence F are presented in Figure 3. The A -values for the C_2H_6 bands are displayed in the last column of Table 1. The 2971 cm^{-1} band has been chosen as a reference for the cross section determinations. From Figure 3(a), it can be seen that the column density evolutions for all the vibration modes agree quite well with each other. For the precursor H_2O , out of the five peaks observed in the spectrum, data of the band at 1655 cm^{-1} have been chosen as reference for the cross section calculations. Once again, as shown in Figure 3(b), the abundance evolutions based on three water bands agree quite

Table 1

Wavenumbers, Vibrational Assignments, and Absorbance Coefficients (A -values) in 10^{-18} cm molecule $^{-1}$ for Pure Compounds of $C_2H_6:H_2O$ (2:3) at 15 K^a

Observed Frequency (cm $^{-1}$)	Assignment	Carrier	A -value ^a
C_2H_6			
815/821/825	ν_9/ν_{12}	CH $_3$ rock	1.9 ^{b,c}
1024	...	...	0.3 ^d
1190	ν_{11}	CH $_3$ rock	- ^e
1389	ν_{10}	CH $_3$ s-deform	2.9 ^e
1373	ν_6	CH $_3$ s-deform	0.33 ^{e,f}
1452/1457/1463	ν_8/ν_{11}	CH $_3$ deform	2.5 ^c
2357	...	...	0.07 ^d
2736	$\nu_2 + \nu_6$	Combination	0.2 ^{c,g,h}
2880	ν_5	CH $_3$ stretch	3.2 ^{c,g,h}
2915	$\nu_8 + \nu_{11}$	CH $_3$ rock	0.5 ^{c,g}
2940	$\nu_8 + \nu_{11}$	Combination	3.5 ^{c,g,h}
2954	ν_9	CH $_3$ s-stretch	2.1 ^{e,f}
2971^a	ν_{10}	CH $_3$ stretch	14.8 ^{c,g,h}
4068	$\sum(\nu_i)$	Overt./combinat.	0.2 ^{c,h,i}
4164	$\sum(\nu_i)$	Overt./combinat.	0.16 ^{i,j}
4326	$\sum(\nu_i)$	Overt./combinat.	0.096 ^k
H_2O			
3660	ν_3	OH-db stretching	7.8 ^{i,l,m}
3250	ν_1	O-H stretching	200 ^{c,l}
2220	$\nu_L + \nu_2/3\nu_L$	Combinat./libration	... ⁿ
1655^a	ν_2	H-O-H bending	12 ^{i,l}
765	ν_L	OH-libration	26 ^k

Notes. These A -values (A_i^p) are considered valid for the ice as deposited, therefore porous ices.

^a In bold are the C_2H_6 and H_2O reference bands used in the cross section calculations.

^b Kaiser & Roessler (1998).

^c de Barros et al. (2011a).

^d Bennett et al. (2011).

^e Bohn et al. (1994).

^f Shimanouchi (1972, p. 1).

^g Moore & Hudson (1998).

^h Kim et al. (2010).

ⁱ Ehrenfreund et al. (1996).

^j Palumbo et al. (1999).

^k Bennett et al. (2007).

^l Öberg et al. (2007).

^m This work.

ⁿ Zheng et al. (2006).

well with each other. The inset in Figure 3(b) shows the ν_3 monomer of the dangling bond (OH-db) at 3660 cm $^{-1}$ with an A -value of 7.8×10^{-18} cm molecule $^{-1}$ adopted (Ehrenfreund et al. 1996). The observation of the OH-db peak indicates that the ice mixture was porous at the beginning of irradiation; its disappearance at $F \sim 0.3 \times 10^{13}$ ions cm $^{-2}$ shows that ice was compact after that.

The appearance of infrared lines of many newly formed molecular species can be seen in Figures 1(b) and 2. A list of the formed species is displayed along with the vibrational assignments in Table 2. Six daughter hydrocarbons were observed: methane (CH $_4$), acetylene (C $_2$ H $_2$), ethylene (C $_2$ H $_4$), and propane (C $_3$ H $_8$), together with butane (C $_4$ H $_{10}$) and isobutene (C $_4$ H $_8$). The evolutions of their abundance with fluence are presented in Figures 5 and 6. Because of the water presence in the mixture, the formation of carbon monoxide (CO), carbon dioxide (CO $_2$), hydroxymethyl radical (CH $_2$ OH),

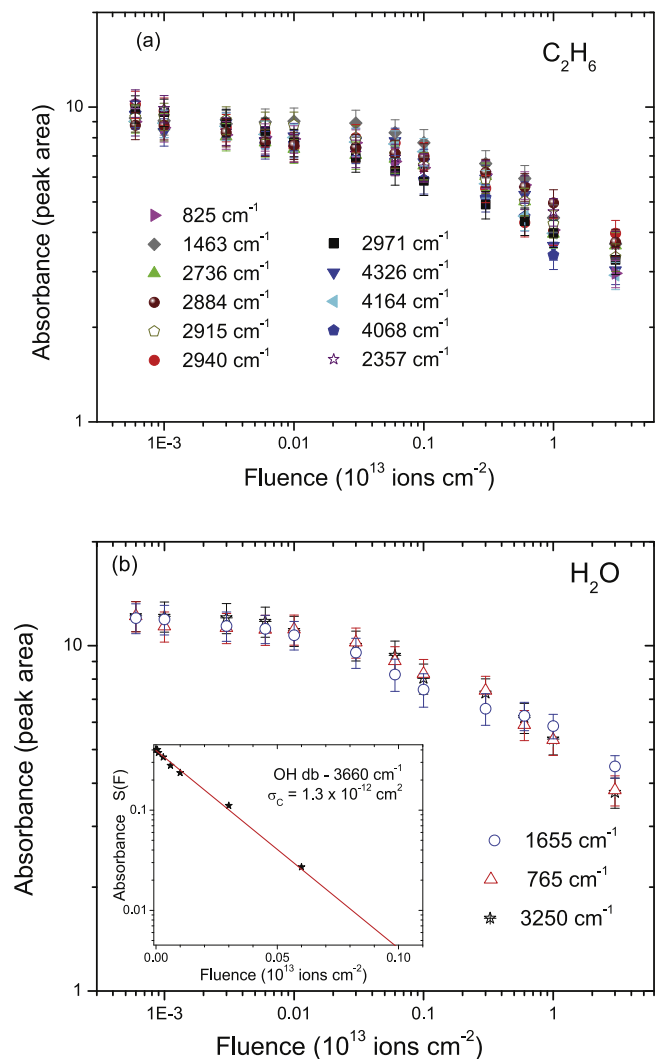


Figure 3. Dependence of band absorption on beam fluence for (a) 11 C_2H_6 bands and (b) three H_2O bands and, in the inset, one OH-db band whose points are fitted by a single exponential (with an error bar of 5%).

methanol (CH $_3$ OH), ethylene glycol ((CH $_2$ OH) $_2$ or HOCH $_2$ CH $_2$ OH), formaldehyde (CH $_2$ O), and pentacarbon monoxide (C $_5$ O) was also observed; their evolutions are also presented in Figures 5 and 6.

The abundance of methane is monitored via the fundamental bands at 1300 (ν_4) and 3009 cm $^{-1}$ (ν_3) (de Barros et al. 2011a). The ethylene fundamental modes were detected in three vibration modes at 951 cm $^{-1}$ (ν_7), 3092 cm $^{-1}$ (ν_9) (Kaiser & Roessler 1998; de Barros et al. 2011a), and 1436 cm $^{-1}$ (ν_{12}) (Mejía et al. 2013), in full agreement with literature values. Note that ν_7 of ethylene appeared quite blended with a group of absorption bands near the 950 cm $^{-1}$ region. Two acetylene bands were identified at about 746 cm $^{-1}$ (ν_5) and 1360 cm $^{-1}$ ($\nu_4 + \nu_5$), in good agreement with Coustenis et al. (1999), Bohn et al. (1994), and Kaiser & Roessler (1998). The band at 2865 cm $^{-1}$ is identified for butane (ν_3 in agreement with Bohn et al. 1994). The main band of C $_3$ H $_8$ (propane) at 2962 cm $^{-1}$ could not be confirmed since a C_2H_6 band at 2971 cm $^{-1}$ is very close to it. Two additional bands are identified as butene at 910 and 1645 cm $^{-1}$ (ν_{25} and ν_7 ; Gallinella & Cadioli 1997; Kim et al. 2010). All the above molecules were formed basically by

Table 2
Infrared Absorption Features, Assignments, and A-values
(10^{-18} cm molecule $^{-1}$) of the Formed Species during
the Irradiation of the Ethane + Water Mixture Ices

Molecules	Wavenumbers (cm $^{-1}$)	Absorption Mode	Carrier	A-value
CH ₄	3009^a	ν_3	stretching	10.5 ^b
	1300	ν_4	deform	7.76 ^b
C ₂ H ₂	1360	$\nu_4 + \nu_5$	CCH	3 ^{c,d}
	746^a	ν_5	CCH bend	30 ^{b,c,d}
C ₂ H ₄	3092	ν_6	CH ₂ asym str.	1.0 ^{b,d}
	1436^a	ν_{12}	CH ₂ scissor	1.6 ^{b,d}
	951	ν_7	CH ₂ wag	15 ^{b,d}
C ₃ H ₈	2962	ν_2	CH ₃ deform	15.8 ^{b,e}
C ₄ H ₈	1645	ν_7	C = C stretching	1.3 ^{f,g,h}
	910^a	ν_{25}	CH ₂ twist	6 ^{f,g,h}
C ₄ H ₁₀	2865	ν_3	CH ₂ stretching	3.6 ^b
CO	2136^a	ν_1	stretching	11 ^{i,j}
	4247	$2\nu_1$	overtone	... ^{i,j,k,l}
¹³ CO	2091	ν_1	stretching	13 ^{i,m}
CO ₂	2342	ν_3	CO-stretching	76 ^{m,n}
¹³ CO ₂	2280	ν_3	CO-stretching	78 ^{m,n}
(C ₅ O)	2165	ν_2	stretching	110 ^m
CH ₂ O	1726	ν_2	CO-stretching	6.9 ^{b,e,n}
CH ₂ OH	1193	ν_4	CO-stretching	16 ^{j,o}
CH ₃ OH	1129^a	ν_7, ν_{11}	CH ₂ , CH ₃ rocking	1.3 ^{j,p}
	1020	ν_2, ν_8	CO stretch	1.8 ^{b,e,j,p}
(CH ₂ OH) ₂	1090	ν_9	CO-stretching	3.65 ^{b,n}

Notes.

^a In bold are the reference bands used in the cross section calculations.

^b de Barros et al. (2011a).

^c Bohn et al. (1994).

^d Kaiser & Roessler (1998).

^e Moore & Hudson (1998).

^f Gallinella & Cadioli (1997).

^g Kim et al. (2010).

^h Mejía et al. (2013).

ⁱ Gerakines et al. (1995).

^j de Barros et al. (2014b).

^k Bennett et al. (2005).

^l Bennett & Kaiser (2007).

^m Jamieson et al. (2006).

ⁿ Bennett et al. (2007).

^o Gerakines et al. (1996).

^p Sandford & Allamandola (1993).

the C₂H₆ precursor (some hydrogen atoms may be furnished by the radiolysis of water).

Molecules with oxygen and carbon are identified as follows: CO band at 2136 cm $^{-1}$ (ν_1) and a very small peak at 4247 cm $^{-1}$ ($2\nu_1$), ¹³CO at 2091 cm $^{-1}$ (ν_1), CO₂ at 2342 cm $^{-1}$ (ν_3), and ¹³CO₂ at 2280 cm $^{-1}$ (ν_3) (Jamieson et al. 2006). Figure 2(c) shows that CO₂ was detected in the non-irradiated ice and its column density increased with irradiation; for the cross section calculations, the initial column density was considered background and subtracted from the ones measured during irradiation.

CHO-bearing molecules, such as the hydroxymethyl radical (CH₂OH) at 1193 cm $^{-1}$, formaldehyde (CH₂O) at 1726 cm $^{-1}$, and two methanol bands at 1129 and 1020 cm $^{-1}$, were formed during irradiation. We also observed the formation of more complex molecules such as ethylene glycol at 1090 cm $^{-1}$ (ν_9 ; Bennett et al. 2007; de Barros et al. 2011a). Another possible attribution for this band is HCO ν_1 , seen at 1096 cm $^{-1}$ by

Moore & Hudson (2003), Bennett et al. (2007), and de Barros et al. (2011a). The C₂H₅ transition at band 534 cm $^{-1}$ is out of range of the current FTIR spectrometer, so it could not be observed. We stress that neither the methyl (CH₃) radical nor vinyl radical C₂H₃ peak at 893 cm $^{-1}$ nor propylene (C₃H₆) was detected in the current irradiation of ethane and water mixture.

In Table 2, the band positions, assignments, A-values, and characterization of all the observed vibration modes of formed species from the irradiated C₂H₆:H₂O mixture are compared with those of the literature. The knowledge of the A-value is crucial for determining the correct column density that should be used in the cross section calculations, as discussed in the next section.

3.1.1. Contaminants

In high vacuum analyzing systems (residual pressures higher than 10 $^{-9}$ mbar), the usual contaminants are H₂, H₂O, N₂, O₂, CO₂, CO, and possibly oil vapors from the vacuum pumps. Presence of oil vapors was possible since fore pumping was not provided by scroll pumps; however, contamination was minimized by using turbo molecular pumps all along the beam line and by installing a cryostat pump close to the beam port of the analyzing chamber. The IR spectrum acquired before irradiation (Figure 1(a)), in which the background was subtracted, shows the presence of CO₂ but not of N₂, O₂, or CO.

H₂: A very small peak (whose area decreases with fluence) was observed in the pristine ice at 4128 cm $^{-1}$ and may be due to trapped H₂ carried during deposition. Similar observations were reported by Loeffler & Baragiola (2010) and by Bordalo et al. (2013) for peaks at 4131 and 4130 cm $^{-1}$, respectively.

N₂: Relatively large column densities of N₂ can be monitored through the peaks at 4657, 2347 (the stronger one), and 2328 cm $^{-1}$ (de Barros et al. 2015). Inspection of Figures 1(b) and 2(c) indicates that these bands are absent (within the sensitivity and resolution of our experimental setup). Another criterion that gives us confidence about the absence of this contaminant is looking for nitrogen compounds: e.g., N₂O₂ (1766 cm $^{-1}$), NO₂ (1613), N₂O (2236 cm $^{-1}$), NH₃ (3459 and 1074 cm $^{-1}$), and HCN (2386 cm $^{-1}$); none of these peaks are seen in the current IR spectra.

O₂: In gas phase, like the H₂ and N₂ diatomic homonuclear molecules, O₂ is not IR active (Cairns & Pimentel 1965). As an ice, relatively high column densities may be observed as two small lines at 2139 and 1549 cm $^{-1}$ (e.g., de Barros et al. 2014b). It is not the case here. Anyway, the absence of O₂ contamination is expected as a consequence of what is said for N₂ (the main constituent of air).

CO₂: FTIR analysis of CO₂ in gas phase shows the 2334–2362 cm $^{-1}$ peak groups, while solid CO₂ produces a single, asymmetric peak around 2344 cm $^{-1}$ (Isokoski et al. 2013). Figures 1(a) and 2(c) display a peak at 2341 cm $^{-1}$ observed for the pristine ice. It was observed that the 2341 cm $^{-1}$ absorbance increases with the beam fluence and reaches saturation, a typical behavior shown by species produced under irradiation. The small amount of CO₂ observed in the virgin spectrum is thought to come from impurities in the lecture bottle. Its column density is measured as 1.43×10^{14} molecules cm $^{-2}$, and this quantity is negligible when compared with the deposited quantities (about 10 18 molecules cm $^{-2}$) of C₂H₆ and H₂O.

CO: Besides H_2O and H_2 , CO molecules desorb from stainless steel chambers particularly during the backout; Rezaie-Serej & Outlaw (1994). We should not expect a significant contribution of CO in cryogenic systems. The most intense CO band occurs at $2136\text{--}2139\text{ cm}^{-1}$. Using the same experimental setup, de Barros et al. (2011a) analyzed the CH_4 radiolysis and did not notice any peak at this position; Bordalo et al. (2013), studying the bombardment of pure NH_4 , did report the CO band, but its origin was attributed to the radiolysis of residual CO_2 . In the current data, no peak is seen at this position before irradiation; but once the radiation was started, its area increased linearly with fluence, a typical behavior of daughter species.

In the virgin spectrum we also observed two small bands at 1024 and 2357 cm^{-1} , decreasing as irradiation proceeds. Those peaks are not identified in previous works; we think they could be C_2H_6 minor bands.

Back-side deposition: Another kind of contaminant that needs to be investigated concerns the molecular deposition onto the back side of the substrate, which is never touched by the ion beam but is analyzed by the FTIR spectrometer in transmission mode. If contaminant deposition occurs at the front side, the condensed molecules are preferentially and severely sputtered by the heavy ion beam: this fact may be not a real concern except if the deposition rate exceeds the sputtering rate. If contaminant deposition occurs at the back side, its column density remains constant after the end of deposition, or, for a residual gas that may condense at the substrate temperature, increases linearly with time up to the end of the irradiation. Inspection on the highest fluence spectrum shows no trace of N_2 . The column density of H_2O deposited at the back side is expected to be negligible compared to the column density variation of that at the front side. As discussed in Section 3.1, the CO_2 column density evolution can be fitted by the function $a(1-\exp(-bF))$, suggesting that a possible linear contribution with the fluence F is not relevant. As a conclusion, we estimate that none of the expected contaminants alter the essential results of this work.

3.1.2. Astrophysics Timescales

Aiming to apply in astrophysics the fundamental aspects treated in the current work, it is useful to remind how to estimate destruction rates or half-lives of molecules exposed to cosmic radiation. These calculations have already been performed for some ices, in particular, CH_3OH (de Barros et al. 2011b), $\text{H}_2\text{O}:\text{C}^{18}\text{O}_2$ (Pilling et al. 2011), and HCOOH (Andrade et al. 2013). For a given kinetic energy of the projectile and for a given molecular species, the two ingredients for this analysis are (i) $\Phi_j(E)$, the flux density of the radiation (e.g., solar wind or galactic cosmic rays) corresponding to the constituent j , and (ii) $\sigma_d(E)$, the destruction cross section of that molecule by that radiation as a function of the projectile kinetic energy. The destruction rate of the ice for each radiation constituent, R_j , is obtained by integrating the product $\Phi_j(E) \times \sigma_d(E)$ over the energy range. It is predicted in this way that $R_{\text{Fe}} > R_{\text{H}}$ in the ISM, and vice versa for the solar system. The timescale is given by the ISM (10^{-5} to 10^{-6} ions $\text{cm}^{-2}\text{ s}^{-1}$) and laboratory (10^9 ions $\text{cm}^{-2}\text{ s}^{-1}$) heavy ion beam fluxes, that is, around 10^{14} orders of magnitude: as far as radiolysis is concerned, 1 s of the employed GANIL beam simulates about 10 million yr of ISM radiation.

3.2. Cross Section Determination

Several particular processes occur when fast ions traverse ices: structure modifications, sputtering, and chemical reactions following molecule fragmentation.

3.2.1. Ice Compaction

Ion beams are able to decrease the crystallinity of ices (amorphization). They are also able to partially organize highly disorganized systems through a process called compaction. As a consequence, after a long enough irradiation time (or fluence), the equilibrium state is not expected to depend on the structure of the starting ices. Such transformations do not modify the column density of the irradiated target molecular constituents, but may alter progressively the sample diffraction index, which in turn changes the band integrated absorbance (A -values or band strengths). Then, at the beginning of irradiation, the compaction in the sample induced by the beam interaction may give the false impression in FTIR spectroscopy that the destruction rates of the sample molecules are either negative or higher than the actual ones (Strazzulla et al. 1992; Pilling et al. 2010; Dartois et al. 2015). For porous ices irradiated by MeV ions, it has been reported that the compaction process is accomplished at fluences (deposited doses) orders of magnitude smaller than complete radiolysis. Following the procedure described by Mejía et al. (2015), the area $S(F)$ of a given IR peak evolves as a function of the beam fluence, F , as

$$\begin{aligned} S(F) &= S_0 \exp(-\sigma_d^{\text{ap}} F) - (S_0 - S_p) \exp(-(\sigma_c + \sigma_d^{\text{ap}}) F) \\ &= S_p \exp(-\sigma_d^{\text{ap}} F) \frac{1 - \zeta \exp(-\sigma_c F)}{1 - \zeta}, \end{aligned} \quad (1)$$

where S_p is the peak area of the porous ice as deposited, S_0 is a parameter interpreted as the initial peak area of a compacted ice, $\zeta = (S_0 - S_p)/S_0$ is the relative porosity, σ_c is the compaction cross section, $\sigma_d^{\text{ap}} = \sigma_d + Y_0/N_0$ is the apparent destruction cross section, σ_d is the usual destruction cross section, Y_0 is the initial sputtering yield, and N_0 is the initial column density given by the Lambert–Beer law: $N_0 = \ln 10 S_0/A_v^{\text{eq}}$. The band strength A_v^{eq} is the A -value for the compacted ice at equilibrium ($F \rightarrow \infty$); the relationship between A_v^{eq} and the usual A -value for the non-irradiated porous ice is $A_v^p = A_v^{\text{eq}}(1 - \zeta)$, where ζ may be positive or negative (Andrade et al. 2013).

Of course, $S_0/A_v^{\text{eq}} = S_p/A_v^p$ must hold, both ratios being equal to the actual number of molecules in the virgin ice divided by $\ln 10$.

In fact, Equation (1) explicitly considers that the A -value in the Lambert–Beer law varies exponentially with fluence: $A_v(F) = A_v^{\text{eq}} [1 - \zeta \exp(-\sigma_c F)]$.

The derivative of $S(F)$ at the very beginning of the irradiation is $dS(0)/dF = -S_0 \sigma_d^{\text{ap}} + S_0 \zeta(\sigma_c + \sigma_d^{\text{ap}})$. If ζ is positive ($S_0 > S_p$) and if $\zeta \sigma_c \gg \sigma_d^{\text{ap}}$, the peak area rate at the beginning of irradiation becomes positive: $dS(0)/dF \sim \zeta \sigma_c S_0$. For the current data, ζ is negative and $\sigma_c \gg \sigma_d^{\text{ap}}$, so that the $S(F)$ decrease is steeper:

$$dS(0)/dF \sim -(\sigma_d^{\text{ap}} - \zeta \sigma_c) S_0.$$

The fitting of the C_2H_6 and H_2O data (Figure 4(a)) by Equation (1) yields the cross sections presented in Table 3. The evolution of the dangling bond peak, shown in the inset of Figure 3(b), is perfectly fitted by one very fast decreasing

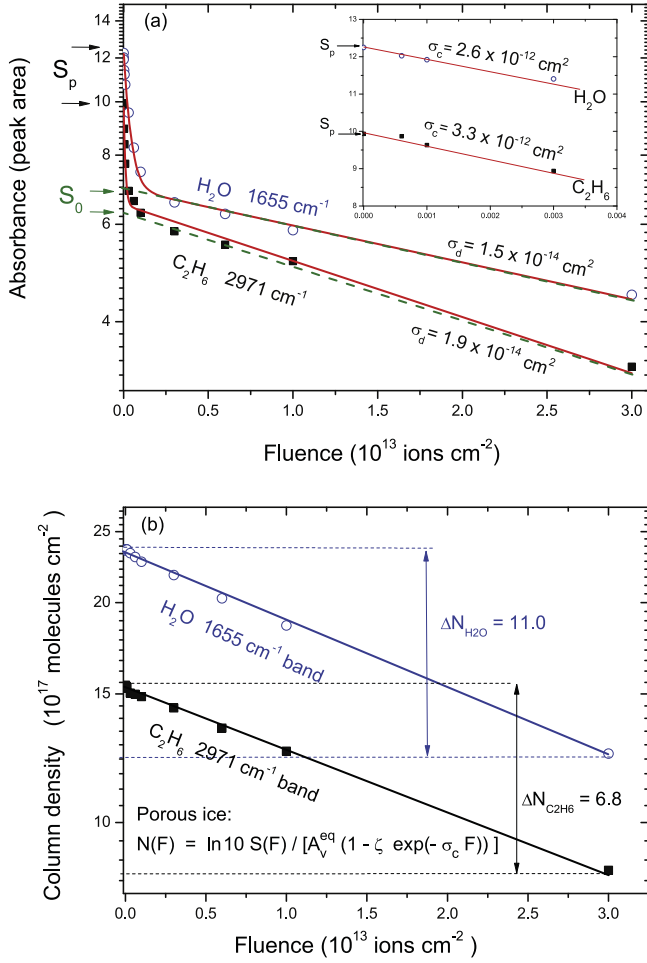


Figure 4. (a) Dependence of H₂O and C₂H₆ band absorbance, $S(F)$, on beam fluence. The solid lines are fittings with Equation (1), where the free parameters are S_p , σ_d^{ap} , ζ , and σ_c . The inset is a zoom-in of the low-fluence regime. (b) Dependence of H₂O and C₂H₆ column densities, $N(F)$, on beam fluence. Data are obtained from panel (a) through $N(F) = (\ln 10) S(F) / A_v^{\text{eq}}(F) = N_0 \exp(-\sigma_d^{\text{ap}} F)$.

Table 3

Parameters Used in Equation (1) for Fitting the Peak Area Evolution of the Precursor Molecules Bombarded by 40 MeV Ni Ions

Parameter	H ₂ O	OH-db	C ₂ H ₆
Reference band (cm ⁻¹)	1655	3660	2971
S_p	12.3	...	9.93
S_0	6.96	...	6.21
$\zeta = (S_0 - S_p) / S_0$	-0.77	...	-0.59
σ_c (10 ⁻¹² cm ²)	2.6	1.3	3.3
σ_d^{ap} (10 ⁻¹⁴ cm ²)	1.5	...	1.9
A_v^p (10 ⁻¹⁸ cm molecule ⁻¹)	12.0	...	14.8
$A_v^{\text{eq}} = A_v^p (1 - \zeta)^{-1}$	6.7	...	9.3
N_0 (10 ¹⁷ molecules cm ⁻²)	23.6	...	15.4

Note. The dangling bond “destruction” cross section is included for comparison with the compaction cross section of water. $N_0 = \ln 10 S_p / A_v^p$.

exponential yielding the “destruction” cross section $\sigma_{c(\text{OH-db})} = 1.3 \times 10^{-12} \text{ cm}^2$. This value turns out to be close to the water compaction cross section ($2.6 \times 10^{-12} \text{ cm}^2$) obtained by fitting data presented in Figure 4(a), supporting the hypothesis that both parameters ($\sigma_{c(\text{OH-db})}$ and σ_c) concern the same phenomenon (Bordalo et al. 2013; Mejía et al. 2015).

In other words, the “destruction” of a dangling band may be regarded as part of the compaction process. The σ_c values for the 1655 and 3660 cm⁻¹ water bands are displayed in Table 3 to be compared with the C₂H₆ compaction cross section.

$N(F)$ data for the precursor molecules, presented in Figure 4(b), have been calculated from $S(F)$ divided by $A_v(F)$. The compaction effect has been removed, and both $N(F)$ functions exhibit an exponential decrease.

3.2.2. Sputtering and Molecular Dissociation

If the concentration of a given molecular species at the target surface would be constant during the bombardment, its sputtering yield Y would be also constant and its column density would decrease linearly with F . In general, however, the fragment concentrations increase in the sample and the precursor concentrations decrease exponentially with F , that is, $\exp(-\sigma_d F)$. As a consequence, the precursor sputtering yields also decrease exponentially with F . Under these conditions, the column density evolution due to sputtering becomes similar to that of the molecular dissociation, which means that the FTIR spectroscopy is only sensitive to the net effect of both processes (Mejía et al. 2013). Taking this into account, for each precursor species i , $N_i(F)$ is written as

$$N_i(F) = N_{i,0} \exp(-\sigma_{d,i}^{\text{ap}} F) \quad (2)$$

where the apparent destruction cross section has been defined in Section 3.2.1. The σ_d^{ap} values obtained from the actual precursor species are presented in Table 3. It is important to mention that if layering (particular of water molecules) occurs during the irradiation, Y_0 of the actual precursor species is progressively reduced (up to zero, after a certain time), so that the measured σ_d^{ap} is approximately σ_d .

3.2.3. Chemical Process: Formation of Products

The daughter species may be fragment or hybrid molecules, depending on whether they are formed from a single precursor or from more than one.

For fragment molecules, the variation rate of the species j is controlled by formation and destruction cross sections and by the sputtering yield, $Y_j(F) = Y_{j,0} (N_j(F) / N_0)$:

$$\frac{dN_j}{dF} = \sigma_{f,j} N_i(F) - \sigma_{d,j} N_j(F) - Y_j(F) = \sigma_{f,j} N_i - \sigma_{d,j}^{\text{ap}} N_j. \quad (3)$$

Repeating the description of precursors, the apparent destruction cross section, $\sigma_{d,j}^{\text{ap}} = \sigma_{d,j} + Y_{j,0} / N_0$, can be defined for the fragments j . If the daughter species j is a fragment of the molecular precursor i , then the substitution of Equation (2) into Equation (3) generates an equation with the solution

$$\frac{N_j(F)}{N_{i,0}} = \frac{\sigma_{f,j}}{\sigma_{d,i}^{\text{ap}} - \sigma_{d,j}^{\text{ap}}} [\exp(-\sigma_{d,i}^{\text{ap}} F) - \exp(\sigma_{d,j}^{\text{ap}} F)]. \quad (4)$$

For hybrid molecules, two or more precursors are involved and a given number of each precursor species i is necessary to form the daughter j . In this case, Equation (4) is still valid, but the precursor column density $N_{i,0}$ should be interpreted as the column density of the precursor group. For practical calculations, $N_{i,0}$ is considered to be proportional to $N_{<,0}$, the column density of the minority precursor; similarly, $\sigma_{d,i} = \sigma_{d,<}$ is taken as the destruction cross section of the minority precursor. It is expected that the lowest-concentration precursor plays the dominant role in the chemical reactions, in the sense that its

Table 4
Formation (σ_f) and Destruction (σ_d) Cross Sections of Daughter Molecules

Molecule	n_k	σ_f^* (10^{-15} cm^2)	σ_f (10^{-15} cm^2)	σ_d^{eff} (10^{-13} cm^2)	$\sigma_{d,j}$ (10^{-15} cm^2)	G_f (10^{15} molecules)	G_d (10^{15} molecules)
Hydrocarbons							
CH ₄	1	1.6	1.6 ± 0.3	36 ± 7	15 ± 4	0.035	0.32
C ₂ H ₂	1	1.5	1.5 ± 0.4	36 ± 5	14 ± 5	0.034	0.30
C ₂ H ₄	1	1.8	1.8 ± 0.2	38 ± 7	17 ± 6	0.038	0.37
C ₃ H ₈	3/2	1.9	1.3 ± 0.3	43 ± 8	22 ± 4	0.028	0.47
C ₄ H ₈	2	0.8	0.4 ± 0.2	47 ± 5	26 ± 1	0.008	0.56
C ₄ H ₁₀	2	3.4	1.7 ± 0.1	49 ± 7	28 ± 2	0.037	0.60
Hybrids							
CO	1/2	0.8	1.6 ± 0.2	36 ± 3	16 ± 5	0.035	0.35
CO ₂	2	1.8	0.9 ± 0.1	32 ± 3	11 ± 3	0.02	0.24
C ₅ O	5/2	1.3	0.5 ± 0.1	31 ± 5	10 ± 4	0.01	0.22
CH ₂ O	1	0.3	0.3 ± 0.3	29 ± 5	8 ± 4	0.006	0.17
CH ₂ OH	1	0.6	0.6 ± 0.1	30 ± 5	9 ± 3	0.012	0.19
CH ₃ OH	1	1.5	1.5 ± 0.2	37 ± 6	16 ± 3	0.032	0.35
(CH ₂ OH) ₂	2	0.2	0.1 ± 0.1	31 ± 6	10 ± 3	0.002	0.22

Note. $G = 100 \sigma / S_{n+e}$ molecules per 100 eV, where S_{n+e} (40 MeV nickel beam) = $4631 \times 10^{-15} \text{ eV molecule}^{-1} \text{ cm}^{-2}$ or $4.9 \times 10^4 \text{ eV } \text{\AA}^{-1}$.

N_k is the number of C₂H₆ molecules needed to form the given daughter molecules. The formation (G_f) and destruction (G_d) G -values of the precursors and their daughter species are also included: $\sigma_f^* = n_k \sigma$, see the text.

exhaustion stops the daughter production. Nevertheless, one should remember that the measured cross sections are only valid for those particular relative concentrations of all precursors. A detailed treatment requires an elaborated analysis of chemical kinetics, which is beyond the scope of this article.

If the data analysis concerns just low-fluence irradiation, the concept of effective destruction cross section is useful because the parameter $\sigma_d^{\text{eff}} = \sigma_{d,i}^{\text{ap}} + \sigma_{d,j}^{\text{ap}}$ is the one directly extracted from fittings. Indeed, for $\sigma_d F \ll 1$, Equation (4) may be expanded into

$$\frac{N_j(F)}{N_{<,0}} \sim (\sigma_{f,j} F) \left[1 - \frac{1}{2} \sigma_d^{\text{eff}} F \right]. \quad (5)$$

The $(\sigma_f F)$ factor describes the increase of the column density, while the latter one describes a tendency for its decrease. At the very beginning of the irradiation, only the first factor matters since the second factor is approximately constant (~ 1). Therefore, the low- F regime implies a linear evolution of $N(F)$ for both precursors (decrease) and products (increase): it corresponds to the situation in which the projectiles interact only with pristine sites, a convenient condition for measurement of the formation cross section. For high fluences, the second factor corresponds to track overlaps, which modifies progressively the linear dependence for precursors and products; data fitting in the high- F regime provides accurate destruction cross section determination. For the conditions in which Equation (5) is valid, the leveling off of the column density depends uniquely on the joint destruction of precursors and daughter molecules, that is, on σ_d^{eff} .

Inspection of Figure 4(a) shows that C₂H₆ is the minority precursor for the current experiment. Its initial column density and apparent destruction cross section were taken as its reference parameters: $N_{<,0}$ and $\sigma_{d,<}^{\text{ap}}$. The cross section $\sigma^* = n_k \sigma$ means that daughter cross sections were calculated for $N_{<,0}/n_k$ minority precursor species, where n_k is the number of precursor molecules needed to form the j daughter species. This

definition aims to obtain the relationship

$$\sigma_{d,i} = \sum_k n_k \sigma_{f,k} = \sum_k \sigma_{f,k}^*, \quad (6)$$

which helps the branching ratio analysis: the ratio $\sigma_{f,k}^*/\sigma_{d,i}$ appears as the probability of forming the species k from the radiolysis of the precursor i .

Note that the arbitrary decision of selecting σ_d of the minority precursor is not relevant for the current analysis, since the H₂O and C₂H₆ destruction cross sections are about the same. Table 4 presents the formation and destruction cross sections for the observed daughter products.

The G -values allow comparison among chemical reaction yields produced by electrons, photons, and ions in the literature. Figures 5 and 6 show the evolution of the column density of C₂H₆:H₂O produced species. The curves in Figure 6 are obtained from data fitting by Equation (5). Formation and destruction cross sections for the daughter species are presented in Table 4. The same data are also presented in Figures 6(c) and (d), but in log-log scale, in order to stress the proportionality on F observed for low fluence.

3.3. Carbon, Oxygen, and Hydrogen Budget

Since all the detected daughter species have at least one carbon, oxygen, or hydrogen atom, the atom budget procedure may be employed to test whether the column density of the ethane and water destroyed can account for the column densities of the products. Two points are relevant in this analysis:

(i) For each molecular species present (precursor or daughter), the consistency of the relative values of the absorbance factor (A -value) corresponding to its distinct bands can be checked by verifying whether the same column density is obtained from the respective absorbance bands. This procedure has been accomplished successfully for the precursor molecules, as shown in Figures 3(a) and (b): peak areas of 11

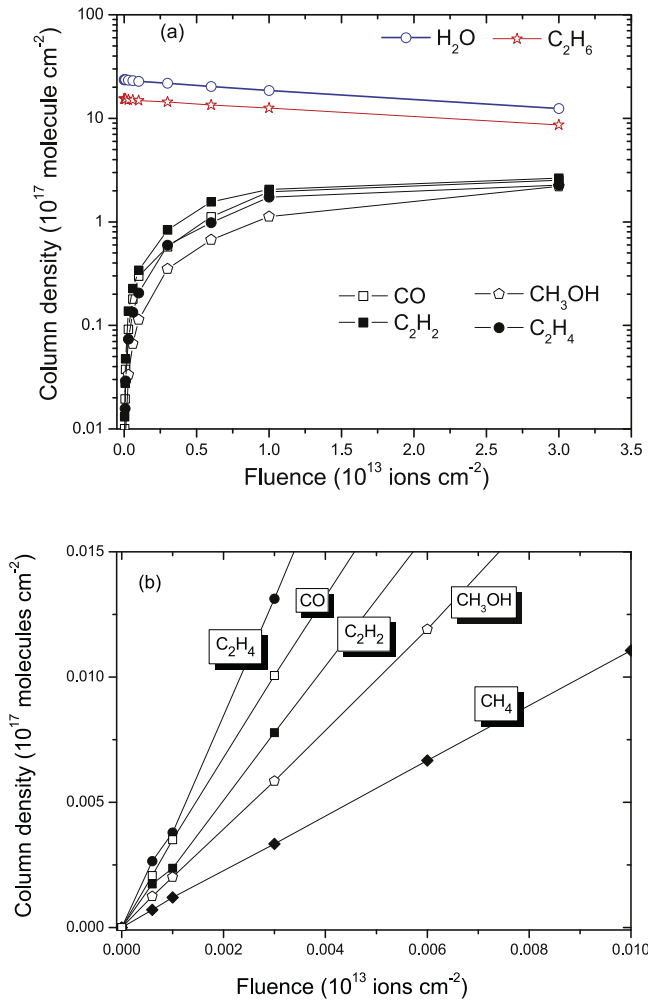


Figure 5. (a) Comparison of the column density evolutions of the two precursor species with those of the four most abundant daughter species containing C, H, and O at 3.0×10^{13} ions cm^{-2} . (b) Evolution of the column densities of the five most abundant daughter species produced by the C_2H_6 ; H_2O radiolysis (zoom-in at lower fluence, up to 1.0×10^{11} ions cm^{-2}).

C_2H_6 IR bands and three H_2O ones exhibit essentially the same behavior as the beam fluence increases.

(ii) The consistency of the relative A -values of precursors and their daughter species can be checked by the so-called atom budget analysis (Bennett et al. 2006). In the absence of sputtering, the total number of carbon, oxygen, or hydrogen atoms must stay constant during irradiation regardless of which chemical reactions are induced by the irradiation. Table 5 summarizes this situation comparing data obtained before the irradiation and at the end. The decrease of the column density of both precursor molecules is measured, and the numbers of hydrogen, carbon, and oxygen atoms delivered in the ice matrix by their radiolysis are determined. Note that the ratio of destroyed $\text{C}_2\text{H}_6/\text{H}_2\text{O}$ molecules at the end of irradiation is $\sim 6.8/11.0 \sim 2/3$, almost the same value of the $\text{C}_2\text{H}_6/\text{H}_2\text{O}$ concentration ratio in the sample; this means that both molecular species were destroyed with the same rate, that is, with about the same destruction cross section (see Table 3).

Determining by IR spectroscopy the column density decrease of precursor molecules (of a given molecular species) at the end of irradiation and dividing it by the corresponding fluence, the missing (sputtered plus dissociated)—called here

“destroyed”—molecular yield can be calculated. In average, during the whole irradiation, around 6.0×10^4 precursor molecules have been eliminated per Ni ion (3.7×10^4 water and 2.3×10^4 ethane), forming 2.8×10^4 observed molecules.

The average chemical reaction yield for each element of the formed molecules has also been performed at the fluence $F = 3 \times 10^{13}$ projectiles cm^{-2} (Table 5). Note that relative yields change with fluence: the CH_4 destruction cross section is one order of magnitude lower than that of C_2H_2 or C_2H_4 . For fluences higher than $F = 1 \times 10^{13}$ projectiles cm^{-2} , the concentrations of these three species surpass that of C_2H_6 , their formation rates decrease substantially, but only the destruction rates of C_2H_2 and C_2H_4 are high.

The consequence is that the destruction rate of C_2H_6 and H_2O must be at any time equal to or greater than the sum of formation rates of its daughter molecules (because some of the formed species cannot be observed by FTIR). From the data shown in Figure 7(a), and considering ethane and water as precursor species, it can be seen that, at the end of the irradiation, 6.0×10^4 $\text{C}_2\text{H}_6 + \text{H}_2\text{O}$ molecules were destroyed per square centimeter and per projectile (Table 5, “molecular yield” column). The total number of carbon atoms (per cm^2) required to account for the observed column densities of the products at the end of the irradiation is obtained by adding each column density multiplied by the number of carbon atoms in each species. Therefore, the total number of carbon atoms required by the observed number of products per projectile is 4.6×10^4 carbon atoms cm^{-2} , which corresponds to 90% produced by the destroyed ethane molecules. Figures 7 and 8 consolidate the budget analysis as a function of the fluence beam.

3.4. Discussion

Let us start with the reason for using an Ni beam of charge 11+. After many atomic collisions in the ISM or in a lab target, a projectile ion of a certain atomic number Z_p and having a velocity v_p tends to have the so-called “equilibrium” charge state distribution. This characteristic can be understood by assuming that the electrons of the projectile having velocity (with respect to the atomic nucleus) lower than the projectile velocity (with respect to the target) are stripped off in the collisions (Brandt & Kitagawa 1982). Within the model, the mean charge state of the charge distribution in equilibrium depends on velocity as $Z_p [1 - \exp(-v_p/(Z_p^{2/3}v_o))]$, where v_o is the Bohr velocity (2200 km s^{-1}). For a 40 MeV Ni beam, $\langle q \rangle = 12.6^+$ is the mean charge state. More accurate calculations, using the Schiwietz and Grande equations (Schiwietz & Grande 2001), yield $\langle q \rangle = 10.7$. The charge state of the employed ion beam was $q = 11^+$, and the SRIM prediction is realistic. Therefore, the chosen nitrogen charge for the ion beam is very close to the predicted equilibrium charge.

The inspection of Figure 3 points out important confirmations:

(i) The mixture of ethane and water ices presents, at the beginning of irradiation, compaction effects for both molecular species (Figure 4(a)). The compaction process was finished at $F \sim 1 \times 10^{12}$ ions cm^{-2} ; since the ion beam flux is 1×10^9 ions $\text{cm}^{-2} \text{ s}^{-1}$, this process lasted $\sim 10^3 \text{ s} \sim 20$ minutes.

(ii) During and after the compaction, both precursor species are destroyed exponentially as a function of the beam fluence (Figure 4(b)). The compact ice track radius is about $r_c = \sqrt{\sigma_c/\pi} = 5.6 \text{ nm}$.

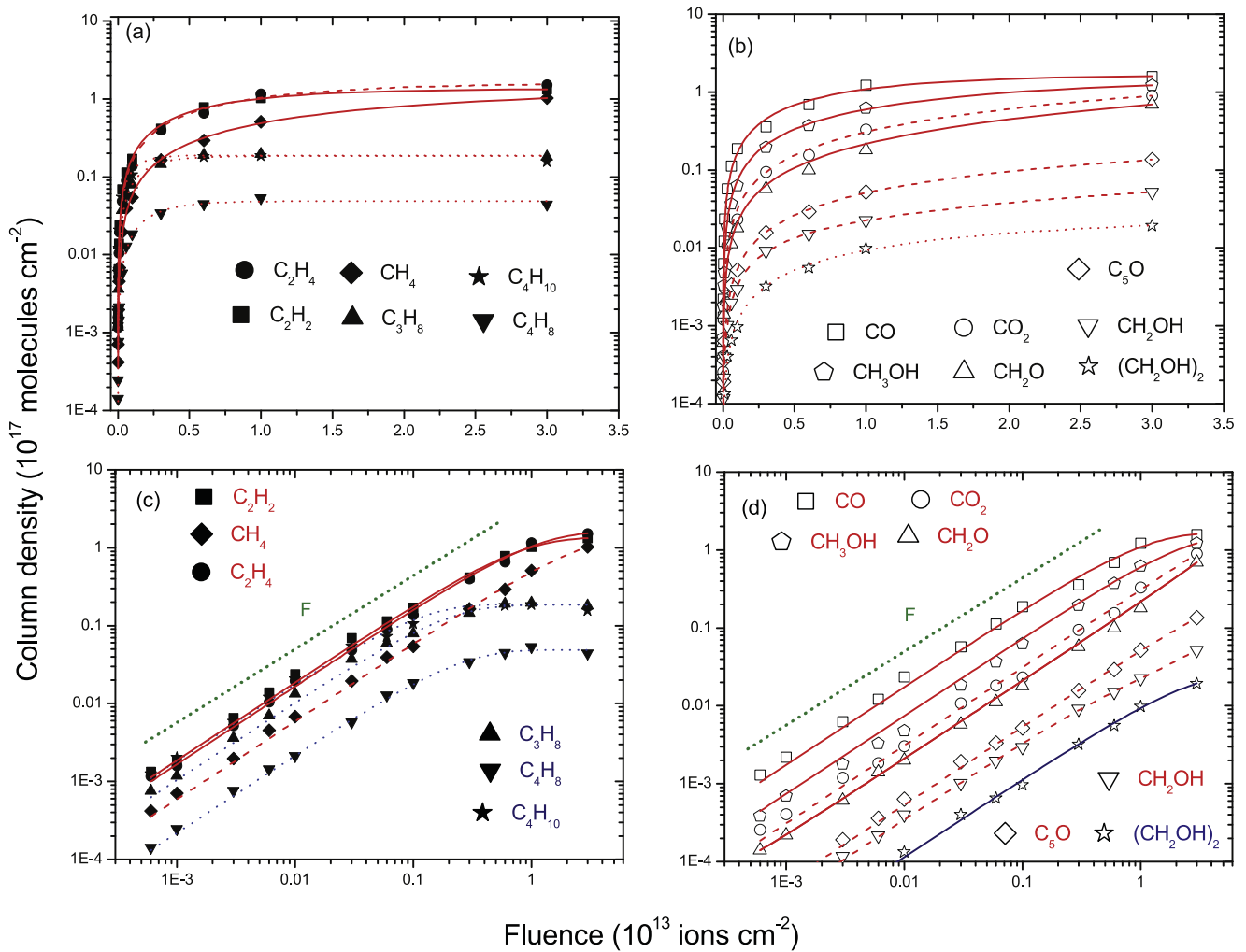


Figure 6. Evolution of the column densities of daughter species produced by the $C_2H_6:H_2O$ radiolysis. (a and c) Hydrocarbons (fragmentation of and synthesis from C_2H_6): CH_4 , C_2H_2 , C_2H_4 , C_3H_8 , C_4H_8 , and C_4H_{10} . (b and d) Hybrid molecules (products of the $C_2H_6 + H_2O$ reaction): CO , CO_2 , C_5O , CH_2O , CH_2OH , CH_3OH , and $(CH_2OH)_2$. The curves are predictions given by Equation (4); the extracted cross sections are presented in Table 4. The dotted lines in panels (c) and (d) indicate a linear dependence on F .

(iii) Eleven C_2H_6 and three H_2O IR bands show indeed the same column density evolution (Figures 3(a), (b)).

(iv) Water dangling bonds are observed in the IR spectra, confirming that the ice was initially porous (Figure 3(b), inset).

The inspection of Figures 5, 6, and 9 brings information on the daughter molecules:

(i) Thirteen species are formed by the $C_2H_6:H_2O$ ice radiolysis.

(ii) Up to $F \sim 3 \times 10^{12}$ ions cm^{-2} , their formation rates are practically constant, so that their relative abundances increase proportionally with fluence (Figure 5(a)). This means that the ion tracks in the ice have an average cross section of the order of 10^{-13} cm^2 (corresponding to $r_d = \sqrt{\sigma_d/\pi} \sim 1.7$ nm radius) and they did not overlap each other until one hour of irradiation. Note that r_c is about 3 times greater than r_d .

(iii) C_2H_2 , CH_3OH , CH_4 , and CO are the four most abundant species formed at the beginning of the irradiation (Figure 5(b)).

(iv) No H_2O_2 or O_3 IR bands were observed, indicating that the majority of oxygen atoms liberated by the water radiolysis have been directed into reactions with carbon.

(v) The hybrid products are more resistant to radiolysis than large hydrocarbons: they have a stronger structure and/or are formed closer to the track axis (Figures 6(c) and (d)). Equation (5) shows that the leveling off exhibited by C_4H_8 and C_4H_{10} is due to their high destruction cross sections.

The observation of C_3^- , C_4^- , and C_5^- products after radiolysis of small carbon-containing molecules is relevant because it provides evidence of a non-thermodynamical process for synthesizing organic molecules (see Figure 9). The formation of C_n clusters in the tracks is supported by mass spectrometry measurements, e.g., Ponciano et al. (2006) have observed the emission of C_nC^+ and C_nCO^+ (n runs from 1 to ~ 5) secondary ions when CO ice is bombarded by fast heavy projectiles.

Table 3 shows that relative porosity and the compaction cross section of the $C_2H_6:H_2O$ ice are roughly determined by either water or ethane data. Indeed, there is fair agreement between the values of -0.76 and -0.57 for ζ (defined in Section 3.2.1), as well as between the values 2.6×10^{-12} and 3.3×10^{-12} cm^2 for σ_c , measured from the water and ethane $S(F)$ evolution, respectively. In contrast to findings reported by Bordalo et al. (2013), besides the fast exponential decrease of OH-db absorbance, a low and long tail is also observed at

Table 5

Summary of Column Density Variation (in $\times 10^{17}$) of the Observed Species: Destruction and Formation Yields (Number of Molecules Destroyed + Sputtered or Produced per Projectile in $\times 10^4$) at the End of the Irradiation and Relative to a Fluence of 3×10^{13} ions cm^{-2}

Species	Column Density Variation	Molecular Yield	Hydrogen Yield	Carbon Yield	Oxygen Yield
	(molecules cm^{-2})	(molecules/ion)	(atoms/ion)	(atoms/ion)	(atoms/ion)
C_2H_6	-6.8 ± 0.5	2.3	13.8	4.6	...
H_2O	-11.0 ± 0.8	3.7	7.4	...	3.7
Σ		6.0	21.2	4.6	3.7
CH_4	1.0 ± 0.5	0.3	1.2	0.3	...
C_2H_2	1.3 ± 0.8	0.4	0.8	0.8	...
C_2H_4	1.5 ± 0.7	0.5	2.0	1.0	...
C_3H_8	0.18 ± 0.05	0.06	0.48	0.18	...
C_4H_8	0.04 ± 0.01	0.01	0.08	0.04	...
C_4H_{10}	0.17 ± 0.01	0.06	0.6	0.24	...
CO	1.4 ± 0.8	0.5	...	0.5	0.5
CO_2	0.9 ± 0.3	0.3	...	0.3	0.6
CH_2O	0.7 ± 0.5	0.2	0.4	0.2	0.2
CH_2OH	0.05 ± 0.1	0.02	0.06	0.02	0.02
CH_3OH	1.2 ± 0.5	0.4	1.6	0.4	0.4
$(\text{CH}_2\text{OH})_2$	0.02 ± 0.02	0.006	0.036	0.012	0.012
(C_5O)	0.13 ± 0.01	0.04	...	0.2	0.04
Σ		2.8	7.3 (34%)	4.2 (90%)	1.8 (48%)

Note. The three columns at right compare, for each atomic constituent of the molecules in the target, the atomic disappearance and appearance yields, corresponding to the missing and formed molecules, respectively.

For molecular species with more than one hydrogen, carbon, and oxygen atom, the corresponding atomic column density is obtained by multiplying the molecular column density by the number of the respective atoms in the molecule.

higher fluences and may be attributed to peak overlapping with the huge 3250 cm^{-1} water IR band.

Dartois et al. (2013) and Mejía et al. (2015) reviewed the evolution of the compaction cross section (i.e., the destruction cross section of pores, or porosity loss) for pure water ice and for water ice mixtures, respectively. They have both found that σ_c is directly proportional to the electronic stopping power in the sample and predict for $S_e = 1.41 \times 10^{-12} \text{ eV}/(\text{molecule cm}^{-2}) = 500 \text{ eV } \text{\AA}^{-1}$ a compaction cross section of $\sim 1 \times 10^{-11} \text{ cm}^2$, about the same value measured in the current work (Table 3).

Figure 5(a) shows that abundances of precursors decrease exponentially and are always higher than those of products up to $\sim 10^{14}$ ions cm^{-2} . For higher fluences, recombination of precursors probably balances their chemical destruction, and column densities tend to stay constant; nevertheless, the exponential decrease of these species indicates that so far no recombination had occurred. It is clear that the free oxygen atoms in the projectile track play a major role in the chemical reactions along the track: they eventually react with organic molecules or with their radicals. Indeed, a very different behavior was observed for pure CH_4 radiolysis: not only a much lower destruction cross section ($\sigma_d = 3.8 \times 10^{-15} \text{ cm}^2$) was measured, but the relative abundances of daughter hydrocarbons were completely different (de Barros et al. 2011a).

The well-established ion track model for MeV projectiles is invoked to justify the observed relative abundances of the most abundant daughter molecules (see, e.g., Fleischer et al. 1975; Toulemonde et al. 2000; Mejía et al. 2013). According to the model, the main phenomena that follow the projectile impact may be classified into three regimens: (I) fast (fs-ps) electronic interactions, including projectile-electron collisions, electronic molecular excitations, ionizations, and electron capture; (II)

molecular fragmentation and sputtering (ps); and (III) chemical reactions and target relaxation (ps-ns).

For the current ice mixture, the sequence of formation of molecular species is as follows:

(I) *Electronic interactions*

Formation of H_2O^+ , H_2O^{n+} , H_2O^- , C_2H_6^+ , $\text{C}_2\text{H}_6^{n+}$, and C_2H_6^- .

(II) *Molecular fragmentation and sputtering*

Production of the ionic and neutral fragments: H, OH, O, C_2H_5 , C_2H_4 , C_2H_2 , and CH_3 . Sputtering of $(\text{H}_2\text{O})_n$ and $(\text{C}_2\text{H}_6)_n$ molecular clusters and ion clusters as $(\text{H}_2\text{O})_n\text{H}^+$ + $(\text{H}_2\text{O})_n\text{O}^-$ and $(\text{H}_2\text{O})_n\text{OH}^-$ (Collado et al. 2004).

(III) *Chemical reactions*

The seven most abundant species produced in the C_2H_6 + H_2O radiolysis are C_2H_4 , C_2H_2 , CO, CH_3OH , CH_4 , CH_2O , and CO_2 .

The hydrocarbons C_2H_4 and C_2H_2 are expected to be formed directly from excited C_2H_6 molecules by multiple hydrogen losses. CH_4 may be a fragment of C_2H_6 or a result of CH_3 + H. According to Figure 6(c) data, the production rate of CH_4 remains constant all over the irradiation, that is, even after the C_2H_4 concentration leveling off at $F \sim 1 \times 10^{13}$ ions cm^{-2} ; therefore, the decay of C_2H_4^* into CH_4 is not the main mechanism. The occurrence of CH_2O and absence of CH_3 are justified by the abundant presence of free oxygen in the track: the process CH_3 + O $\rightarrow$ CH_2O + H is a very good reaction in combustion. Once formed, CH_2O may decay catalytically into CO + H_2 (Wang et al. 2014). CO_2 may be formed from free carbon and oxygen atoms, but its production from CO molecules is probably higher (Maranzana et al. 2008). OH, another abundant radical in the track, should exhaust other neighbor radicals, for instance, OH + $\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4$ + H_2O .

Figure 8 summarizes the atomic budget. The major discrepancy is found for hydrogen: only 50% of the number of atoms delivered in the ice is observed in the products (Figure 8(a)). Most probably, the missing H atoms have

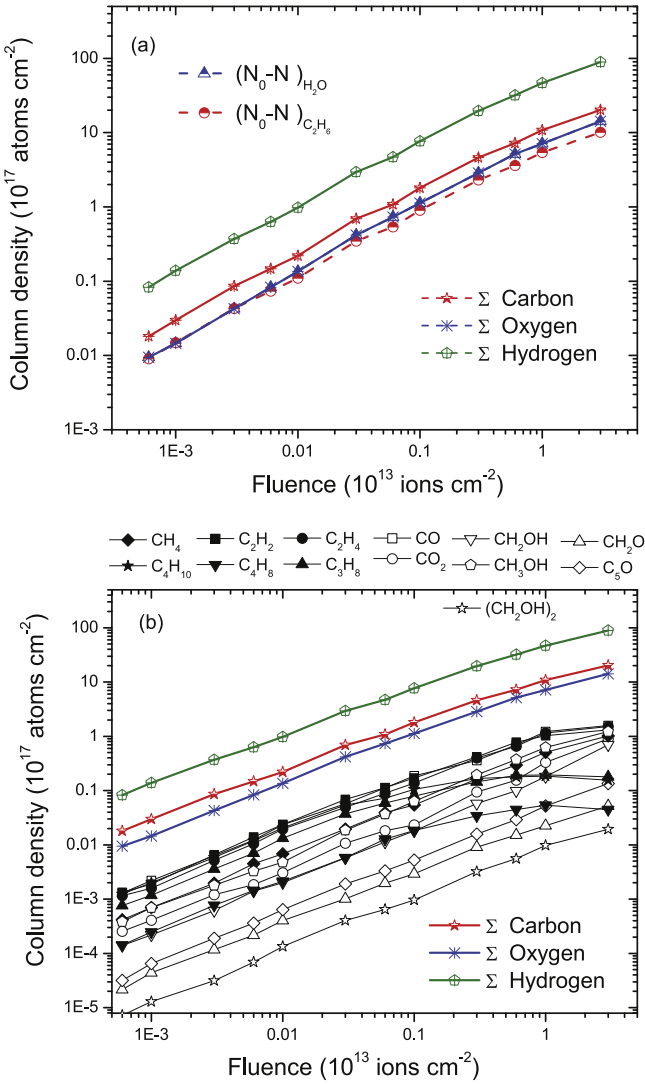


Figure 7. Total and partial hydrogen, carbon, and oxygen column density as a function of beam fluence. The partial values are determined according to their stoichiometry at the most abundant species. Each total atom column density is the sum of elemental column densities over all the species and is labeled Σ element. (a) Decrease of column densities of the precursor species, that is, $N_0 - N(F)$; (b) column densities of the daughter species, $N(F)$.

diffused through the ice, producing H_2 inside or outside. For carbon atoms (Figure 8(b)), almost all the produced atoms could be followed ($\sim 97\%$). Figure 8(c) shows the comparison precursor-daughter molecules for oxygen atoms: $\sim 74\%$ of these are located in the formed species. Contrary to hydrogen, which cannot condense, O_2 may be trapped in grains during diffusion; naturally, O_2 molecules are expected to be produced, but they are hardly observed directly by IR spectroscopy.

4. ASTROPHYSICAL IMPLICATIONS AND CONCLUSIONS

Solid water ice has been observed on the surface of many different astronomical objects and is the dominant ice present in the universe. In the solar system water ice has been detected on the surface of some asteroids, planets and their satellites, Centaurs, TNOs, and comets (see, e.g., Dalton 2010; Mumma & Charnley 2011; Öberg et al. 2011; Tielens 2013; Boogert et al. 2015). In dense, cold interstellar clouds, infrared

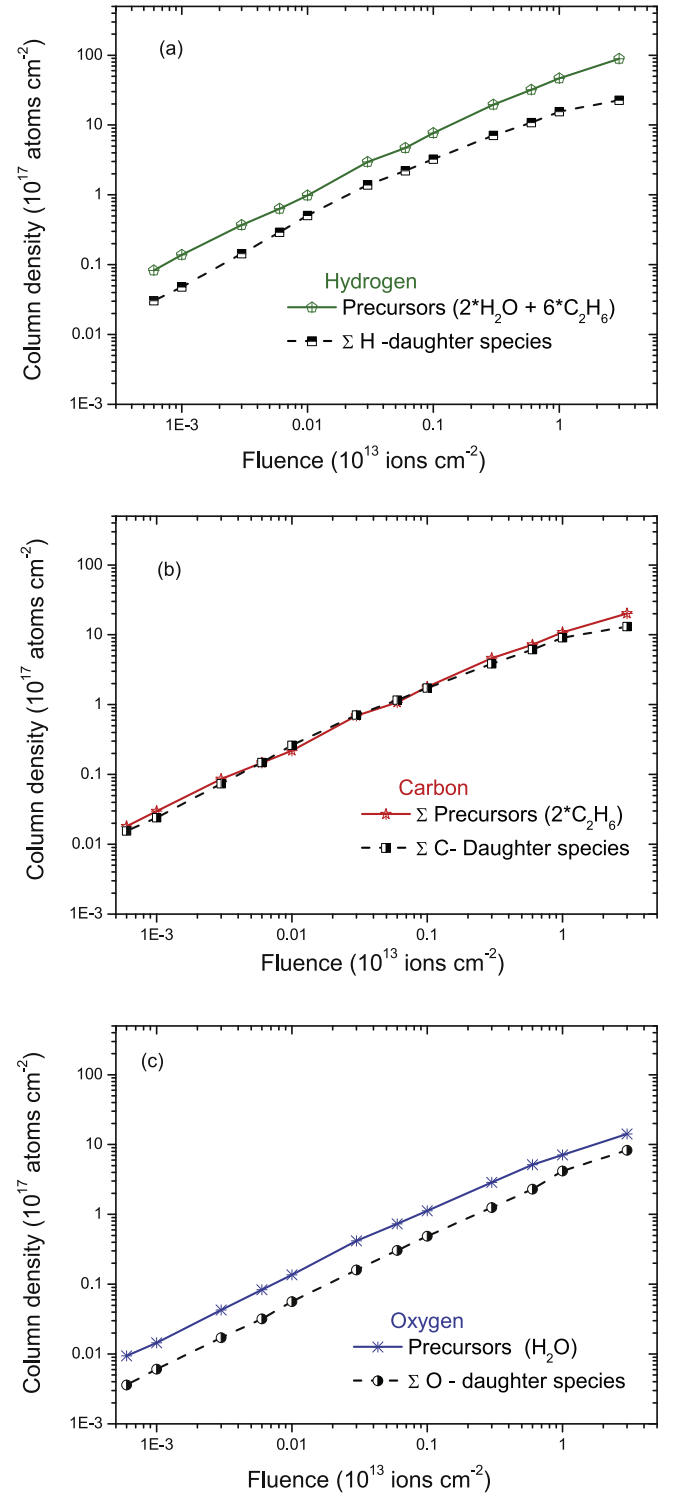


Figure 8. Total and partial hydrogen, carbon, and oxygen column densities as a function of beam fluence. The atom column density decrease for precursors is compared with the sum of atom column densities of daughter species: (a) hydrogen, (b) carbon, and (c) oxygen.

observations show that interstellar dust grains are covered with water-rich ices. Also ethane has been detected across the solar system, from the atmosphere of the giant planets and the surface of Saturn's satellite Titan to various comets (more than 10 to date) and TNOs (see, e.g., Coustenis et al. 2003; Mumma et al. 2003; Sasaki et al. 2005; Griffith et al. 2006; Schaller &

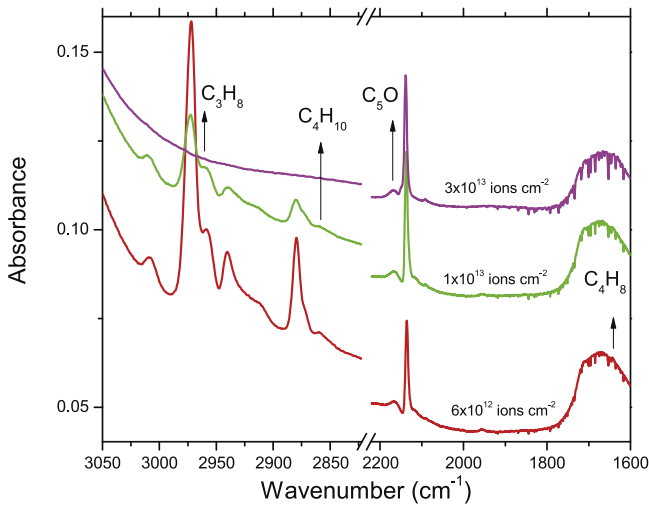


Figure 9. Two regions of the $\text{C}_2\text{H}_6:\text{H}_2\text{O}$ FTIR spectrum at 1.0×10^{12} ions cm^{-2} fluence. Bands of C_3 -, C_4 -, and C_5 -products are seen.

Brown 2007; Mumma & Charnley 2011; Cruikshank et al. 2015), and, even though it is not as abundant and spread as water, plays an important role in the chemical evolution of the solar system and the ISM.

Ices in these space environments are continually exposed to solar winds and to galactic cosmic rays. The passage of energetic ions through the ice causes ionization, which triggers chemical reactions and physical processes. These reactions can be simulated in the laboratory by bombarding ices of astrophysical interest with keV/MeV ion beams (see, e.g., Moore & Hudson 1998; Kaiser & Roessler 1998; Strazzulla et al. 2002; Palumbo et al. 2008; Hudson et al. 2009; Fulvio et al. 2010; Lv et al. 2012; Raut & Baragiola 2013). In this study, the interaction of 40 MeV nickel ions with a mixture of C_2H_6 and H_2O ice at 15 K has been analyzed. To the best of our knowledge, this is the first study focused on a C_2H_6 and H_2O icy mixture exposed to ion irradiation simulating cosmic rays.

Chemical reactions induced by ion processing in the $\text{C}_2\text{H}_6:\text{H}_2\text{O}$ icy mixture produce the daughter species CH_4 (methane), C_2H_4 (ethylene), C_2H_2 (acetylene), C_3H_8 (propane), C_4H_8 (isobutene), C_4H_{10} (butane), CO (carbon monoxide), CO_2 (carbon dioxide), C_5O (pentacarbon monoxide), CH_2O (formaldehyde), CH_2OH (hydroxymethyl radical), CH_3OH (methanol), and some more complex molecules such as $(\text{CH}_2\text{OH})_2$ (ethylene glycol). Among these newly formed species, the most abundant are CO , CH_4 , C_2H_4 , C_2H_2 , CH_3OH , and CO_2 . It should be stressed that, together with water and ethane, all these molecules have been detected after their sublimation from the interior of comets and all of them are regarded as primary cometary volatiles. Representative ranges of molecular abundances for these molecules in comets are as follows (expressed in percent relative to water): carbon monoxide (0.4%–30%), methane (0.4%–1.6%), acetylene (0.1%–0.5%), formaldehyde (0.1%–4%), and carbon dioxide (2%–30%). In the current measurements, a small production of higher molecular weight hydrocarbons (C_3H_8 , C_4H_8 , and C_2H_{10}) that are not detected in comets occurs. These hydrocarbons have the highest destruction cross sections (Table 4), i.e., they are the most fragile species. The relative ease with which they are destroyed by irradiation can explain why they have not yet been identified in comets. After irradiation, two other molecular species have been produced with intermediate abundances: CH_2OH and

C_2H_4 . Concerning CH_2OH , it is worthwhile to note that, despite the fact that it has never been detected in comets, in our experiment the $(\text{CH}_2\text{OH})_2$ is observed. The common idea is that radicals such as CH_2OH can associate in radical–radical reactions to produce more complex organics, such as $(\text{CH}_2\text{OH})_2$. Concerning C_2H_4 , it has never been detected in comets, and we suggest that this could be due to the specific composition of the starting mixture in comets, which favors some reaction pathways over others. To elucidate this point, a systematic laboratory study on the effect of radiation on (at least) binary and ternary mixtures involving C_2H_6 and H_2O should be done and detailed reaction schemes studied. We have also observed the production of small amounts of CH_3OH , a species that has been detected in many comets and is regarded as a primary cometary volatile, with a representative range of molecular abundances (relative to water) of 0.2%–7% (see Mumma & Charnley 2011 and references therein). In view of the importance of the discussed molecules on the understanding of cometary chemistry, the study presented here should be regarded as a first step into laboratory works dedicated to simulating the effect of cosmic radiation on multicomponent mixtures involving C_2H_6 and H_2O .

One should also keep in mind that constraints on the origin and evolution of cometary molecules have also strong implications for the ISM chemistry. Indeed, all cometary material was once in the ISM; understanding the similarities and differences between cometary and interstellar composition and processes would shed light on the physics and chemistry of these environments. In this view, it is interesting to note that, up to the present date, among the molecules considered in this study (including all molecules, before and after irradiation), only CO , CO_2 , CH_4 , CH_3OH , and CH_2O have been surely detected in interstellar ices, besides water ice (see, e.g., Boogert et al. 2015 and references therein). The molecules CO , CH_4 , and CH_3OH are the most abundant products of the current irradiation, and despite not being very abundant, the production of CO_2 and CH_2O is also observed. As remarked before, we have also observed the production of hydrocarbons not seen yet in the ISM: C_2H_2 , C_2H_6 , C_3H_8 , C_4H_8 , and C_4H_{10} . For the last three molecules what has already been said about their undetectability in comets applies: they have high destruction cross sections (see Table 4); therefore, being fragile molecules, they are easily destroyed by irradiation.

Special mention should be given to C_2H_2 and C_2H_6 , being molecules that have been detected in comets but not in the ISM. The current results show that when mixed with water, C_2H_6 is easily destroyed and converted in the many daughter molecules observed here. A similar result was found by Moore & Hudson (1998) when considering icy mixtures of $\text{H}_2\text{O}:\text{C}_2\text{H}_2$, $\text{H}_2\text{O}:\text{C}_2\text{H}_2:\text{CH}_4$, and $\text{H}_2\text{O}:\text{C}_2\text{H}_2:\text{CH}_4:\text{CO}$. In all of those mixtures, Moore & Hudson (1998) saw the total destruction of C_2H_2 in favor of many daughter molecules such as CH_3OH . With this in mind, we propose here that the explanation why C_2H_2 and C_2H_6 have been detected in comets but not in the ISM could be related to the fact that in the last case they have been promptly converted in other molecules by means of radiation processing, while in comets their emission originates from the internal and unprocessed pristine ices. In this picture, the present data clearly indicate that other experiments on multicomponent mixtures involving C_2H_6 and H_2O are also of great interest for the understanding of the chemistry of the ISM and its relationship to cometary chemistry.

Finally, one should consider that the current results are also of interest for the study and understanding of TNOs. Indeed, keeping in mind the small number of TNOs for which reflectance spectra are available (to date), it looks interesting that in a number of them CH_4 and C_2H_6 have already been detected. In particular, among the species discussed in this study: (i) frozen CH_4 has already been detected on the surface of Quaoar (Schaller & Brown 2007), Eris (Dumas et al. 2007), Makemake (Licandro et al. 2006; Brown et al. 2007), and (probably) 2007 OR10 (Brown et al. 2011); (ii) C_2H_6 has been observed on Quaoar (Schaller & Brown 2007), Makemake (Sasaki et al. 2005; Brown et al. 2007), and (has been suggested for) Orcus (Delsanti et al. 2010); and (iii) frozen CH_4 , CO , and C_2H_6 have been detected on the surface of Pluto (see, e.g., Cruikshank et al. 2015 and references therein). This suggests that the daughter species produced in the current irradiation could have played and may still play an important role on the surface of TNOs; therefore, experiments on mixtures involving C_2H_6 and H_2O will be of great interest for the understanding of their chemical evolution.

To date, only few laboratory experiments have been conducted to investigate the interaction of ionizing radiation with pure ethane ices (Strazzulla et al. 2002; Hudson et al. 2009; Kim et al. 2010), and, to the best of our knowledge, there have been no experiments focused on icy mixtures of ethane and water, a closer case study for many astronomical environments in which C_2H_6 has been detected. We have shown here the importance of considering experiments on icy mixtures of C_2H_6 and H_2O exposed to ion irradiation simulating cosmic rays. Similar experiments on multicomponent mixtures involving C_2H_6 and H_2O are required for a deeper understanding of the chemistry of the solar system and the ISM.

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