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Gabriel Vignoli Muniz, Aditya Agnihotri, Basile Augé, Rafael Martinez, Christian Mejía, et al.. Radiolysis of cytosine at cryogenic temperatures by swift heavy ion bombardments. *ACS Earth and Space Chemistry*, 2022, 6 (9), pp.2149-2157. 10.1021/acsearthspacechem.2c00036 . hal-03824306

**HAL Id: hal-03824306**

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Submitted on 21 Oct 2022

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# Radiolysis of Cytosine at Cryogenic Temperatures by Swift Heavy Ion Bombardments

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**ABSTRACT:** We investigated the radiolysis effects on the cytosine in the solid phase irradiated by swift heavy ions as galactic cosmic ray analogues (GCRs). Infrared (IR) absorption spectroscopy was employed to monitor the physical and chemical radiolytic modifications. The targets were prepared on ZnSe in two different ways: (1) by dropping a nucleobase–water–ethanol solution on the substrate and evaporating the solvent and (2) by sublimation of nucleobase powders in an oven and condensation on the windows. Both types of samples present similar IR absorption spectra. From the exponential decrease of the areas of IR absorption bands as a function of projectile fluence, apparent destruction cross sections ( $\sigma_a$ ) were determined and were found to be very similar for samples prepared using both techniques. The destruction cross section of solid cytosine at cryogenic temperatures follows an electronic stopping ( $S_e$ ) power law:  $\sigma_d = C S_e^n$ , where  $C$  is a constant and the exponential  $n$  is a dimensionless quantity. We determined  $\sigma_d = (3 \pm 1) \times 10^{-17} S_e^{(1.25 \pm 0.06)}$ . New absorption features emerge from cytosine degradation, which can be attributed to OCN<sup>-</sup>, H<sub>2</sub>CO, and HNCO. By using the observed power law, the half-life of cytosine exposed to galactic cosmic rays was estimated in the order of Mega years. The findings reported here may help a better understanding of complex organic molecule radiostability.

## 1. INTRODUCTION

Nucleobases are aromatic heterocyclic compounds that contain nitrogen. Nucleobases are divided into two groups: purines, which include two heterocyclic fused rings, and pyrimidines, which contain a single heterocyclic ring such as cytosine (Figure 1). Nucleobases are crucial to the biosphere since they are building blocks of biomolecules such as deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). These nucleic acids are responsible for the storage and transmission of genetic and hereditary information and responsible for the control of enzymatic cellular machinery. Nucleobases also play an

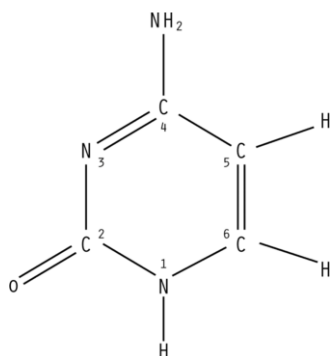


Figure 1. Schematic structure of cytosine molecules.

important role in cell energy processing and cell signalization.<sup>1</sup> Moreover, they are components of daily human nutrition, for example, caffeine and vitamins B3 and B4; additionally, they are part of important medications.<sup>2,3</sup> Thus, a better understanding of nucleobase radiolysis can have relevance in medicine<sup>4,5</sup> and the areas of radiation processing of food and drugs.<sup>6,7</sup>

The presence of nucleobases in the meteorites found on Earth strongly indicates that this class of molecules can exist in outer space.<sup>8–11</sup> Albeit attempts to detect nucleobases in outer space by radio spectroscopy were fruitless.<sup>12–14</sup> Several chemical routes were proposed to form nucleobases from simple species present in outer space under astronomical conditions of cryogenic temperature and ionizing radiation.<sup>15–19</sup> Furthermore, experimental works mimicking astronomical environments revealed the formation of complex organic molecules including nucleobases.<sup>16,20–25</sup>

The omnipresent ionizing radiation field in space raises an important question if nucleobases are formed in astronomical

Table 1. Summary of Targets and Projectile Characteristics

sample	ion	energy (MeV)	electronic stopping power (MeV $\mu\text{m}^{-1}$ )	nuclear stopping power ( $10^{-3}$ MeV $\mu\text{m}^{-1}$ )	penetration depth ( $\mu\text{m}$ )	temperature (K)	thickness ( $\mu\text{m}$ )	column density ( $10^{17}$ $\text{cm}^{-2}$ )
cytosine grainy	Xe <sup>23+</sup>	92	11.3	73	15.5	12	0.8	6.5
cytosine film	U <sup>32+</sup>	116	13.4	250	16.7	12	0.34	2.8
cytosine film	Ni <sup>8+</sup>	17	4.8	44	9.2	12	0.28	2.3
cytosine grainy	Ni <sup>8+</sup>	17	4.8	44	9.2	12	0.20	1.6
cytosine grainy	Ca <sup>10+</sup>	230	2.9	1.9	63	20	1.1	9.1

environments, can they survive the harsh conditions of outer space? Studying the radioresistance of nucleobases can give clues about their existence in outer space and even the possibility of their detection. Therefore, information about the radioresistance of nucleobases has pivotal importance in astrochemistry and astrobiology. Particularly, this could be relevant for the hypothesis of the RNA world; see more in.<sup>26</sup> In astrophysical environments, nucleobases are expected to exist in a low-temperature solid molecular matrix of water, CO<sub>2</sub>, and NH<sub>3</sub>.<sup>27</sup> As far as we know, a few experiments were performed under astrophysical conditions, *i.e.*, low temperature and solid phase. Adenine in a noble gas matrix was irradiated by 5 keV electrons.<sup>28</sup> Thymine with and without different water-ice contents was exposed to swift protons (0.8–1.0 MeV).<sup>29</sup> Uracil with different contents of water or CO<sub>2</sub> was irradiated by 0.9 MeV protons.<sup>30</sup> Nucleobases in a matrix of noble gas<sup>31,32</sup> and the pure solid phase (thin-film or solid samples)<sup>33–38</sup> were exposed to electromagnetic radiation.

In previous work, we investigated the radioresistance of solid adenine, a purine nucleobase, at low temperature exposed to swift heavy ions mimicking galactic cosmic rays (GCRs).<sup>39</sup>

In the present work, we investigated the radiolysis of solid cytosine at low temperatures ( $\sim 12$  K) exposed to swift heavy ions. Cytosine was prepared in two different ways for which induced effects are found to differ at low doses, mostly correlated with structural rearrangement. From experiments using several heavy ion beams provided by Grand Accelérateur National d'Ions Lourds (GANIL) in Caen, France, and by Helmholtzzentrum für Schwerionenforschung (FAIR-GSI) in Darmstadt, Germany, we studied radiolysis as a function of the electronic stopping power of the ionic projectiles.

## 2. EXPERIMENTAL METHODOLOGY

**2.1. Sample Preparation.** Cytosine ( $\geq 98\%$  pure) was purchased from Sigma-Aldrich. Cytosine powder was dissolved in a solution of ethanol and water (60.8% ethanol in water v/v) at a concentration of 1.5 mg mL<sup>-1</sup>. The solution was exposed to ultrasound until all solid particles had visibly been dissolved. Then, drops of these solutions were applied directly onto windows of ZnSe (13 mm diameter, thickness 2 mm). The windows were heated up to 100 °C until the entire evaporation of the solvent, thus obtaining a solid sample. Hereafter, samples prepared in this manner will be referred to as “grainy” because of their grainy aspect under optical microscopy (see Figure S1 in the Supporting Information).

The second method was the preparation of uniform films from the sublimation of cytosine powder at low pressure ( $10^{-5}$  mbar) using an oven at 150 °C. A similar methodology was adopted by.<sup>35–37</sup> Optical microscopy and profilometry confirm that these samples are uniform thin films, henceforth for the

sake of simplicity, we will refer to these samples as “films”. The spectra of the nucleobase films are in good agreement with those reported in the literature, see Section 3.1, demonstrating that the process of heating does not destroy these molecules.

The preparation of nucleobase films from sublimation typically takes 3 or 4 h to produce a nucleobase film of a few hundred nanometers, whereas the production of grainy nucleobase samples is much faster, not taking longer than 20 min.

**2.2. Sample Irradiation.** Solid cytosine samples were irradiated at the beamline IRRSUD (17 MeV Ni<sup>8+</sup>, 92 MeV Xe<sup>23+</sup>, and 116 MeV U<sup>32+</sup>) at GANIL (Caen, France) and the M-Branch of UNILAC (230 MeV Ca<sup>10+</sup>) at FAIR-GSI (Darmstadt, Germany) in high vacuum chambers ( $10^{-8}$  mbar). The experiments at GANIL were performed in the CASIMIR setup described in detail elsewhere.<sup>40</sup> Each target was mounted on a cold finger connected to a closed cycle helium cold head equipped with a target heater, and the samples were irradiated at 12 K. The setup used in GSI is very similar, but it allows to mount of three samples inside the vacuum chamber; the irradiation temperature was slightly higher ( $\approx 20$  K). For more details, see.<sup>40,41</sup> The average flux was about  $10^9$  ions cm<sup>-2</sup> s<sup>-1</sup> at IRRSUD and SME and  $2 \times 10^8$  ions cm<sup>-2</sup> s<sup>-1</sup> at UNILAC.

The infrared (IR) absorption spectra were obtained *in situ* before and after irradiation with a Fourier transform infrared (FTIR) spectrometer (Nicolet Magna 550, Mercury Cadmium Telluride (MCT) detector cooled with liquid nitrogen), operating in transmission mode. The spectra were acquired as an average of 128 scans with wavenumbers ranging from 4000 to 700 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>. The background of the bare window was taken at 12 K (20 K for GSI) and 300 K and used according to the temperature of the samples, thus avoiding thermal optics effects.

The projectile and target properties are summarized in Table 1. The electronic ( $S_e$ ) and nuclear stopping ( $S_n$ ) powers of the ionic projectiles in the solid nucleobase samples were calculated with the “Stopping and Ranges of Ions in Matter” (SRIM) software.<sup>42</sup> Note that for the swift projectiles used in this work, we are in the electronic regime of deposition of energy,  $S_e \gg S_n$ . Furthermore, the ion penetration depth is much larger than the sample thickness; therefore, there is no ion implantation in the solid nucleobase samples.

## 3. RESULTS AND DISCUSSION

**3.1. Cytosine IR Absorption Spectra.** Grainy and film cytosine samples display similar absorption spectra, Figure 2, in terms of band position but not in absorbance values (Table S1). Moreover, the absorption bands of the cytosine film are narrower than those of grainy cytosine samples. These minor

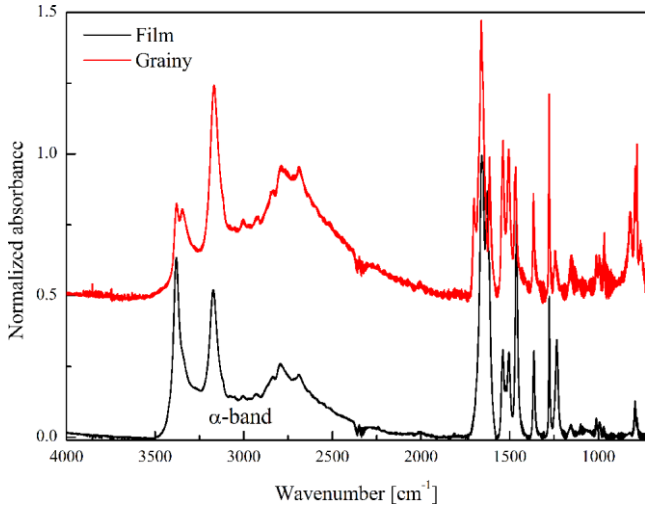


Figure 2. Normalized absorption spectra of grainy (red line) and film (black line) cytosine samples at room temperature. The grainy cytosine spectrum was shifted for clarity. The  $\alpha$ -band (3500–2000  $\text{cm}^{-1}$ ) is indicated in the figure.

variations are plausibly due to the different microenvironments of the cytosine molecules.

Table 2 summarizes the absorption bands of grainy and film cytosine spectra, including the bands reported by<sup>43</sup> for cytosine in KBr pellets.

All of the nucleobases present a large IR absorption band between 3500 and 2000  $\text{cm}^{-1}$  (the region containing characteristic vibration modes of C–H, N–H, and O–H). In the literature, this later region is called the  $\alpha$ -band or  $\beta$ -band.<sup>36,37</sup> In this work, we will refer to this cytosine absorption band (3500–2000  $\text{cm}^{-1}$ ) as the “ $\alpha$ -band”. The grainy samples do not present a smooth surface (Figure S1). We estimated their thicknesses ( $d$ ) considering the deposited mass ( $m$ ) from the previously prepared cytosine solution.  $d = m/\rho S$ , where  $\rho$  is the cytosine density (1.5  $\text{g cm}^{-3}$ ) and  $S$  is the area of the ZnSe window (see Table 1).

**3.2. Cytosine Film Thickness.** Using a “Dektak 150 surfacer” profilometer from the Veeco brand in the GREYC laboratory (ENSICAEN, Caen, France), the thickness ( $d$ ) and the roughness of cytosine film samples were measured. The samples were positioned in the center of the profilometer; using the microscope coupled to the profilometer, the profilometry tip was positioned onto a naked part of the ZnSe window. Then, the tip was moved throughout the sample, to determine the height between the ZnSe window and the edge of the film, thus giving us the thickness of the film. The thickness of each sample was determined as an average of four measurements (Table 1) corresponding to different scanned positions of the sample. A picture of a cytosine sample (film on the substrate window) and the corresponding measured profile are shown in Figure S2.

The cytosine column density ( $N$ ) was determined as follows:  $N = \frac{d \rho N_A}{MM} \times 10^{-4}$  [molecules  $\text{cm}^{-2}$ ], where  $d$  is the film thickness, in  $\mu\text{m}$ ,  $\rho$  is its density here assumed to be 1.5  $\text{g cm}^{-3}$ ,  $N_A$  is the Avogadro number, and  $MM$  is the cytosine molecular weight, 111.10  $\text{g mol}^{-1}$ . To estimate the band strength ( $A$ -value) of a given IR absorption band, we used eq 1

$$A \text{ value} = \frac{\ln 10A}{N} \quad (1)$$

Table 2. Comparison between Our Results and Those of<sup>43</sup>

assignment	vibration mode	position ( $\text{cm}^{-1}$ ) <sup>43</sup>	position ( $\text{cm}^{-1}$ ) grainy cytosine	position ( $\text{cm}^{-1}$ ) film cytosine
NH <sub>2</sub>	antisymmetric stretching	3384	3381	3381
			3351	3349
NH <sub>2</sub>	symmetric stretching	3180	3170	3173
			2840	2863
CH	stretching	2796	2793	2794
CH	stretching	2690	2686	2688
NH <sub>2</sub>	bending	1705	1703	
C <sub>2</sub> O	stretching	1667	1660	1658
				1627
C <sub>5</sub> =C <sub>6</sub>	stretching	1616	1614	1615
NH	bending in plane	1540	1539	1538
C <sub>4</sub> 5N <sub>3</sub> and C <sub>4</sub> –N <sub>4</sub>	stretching	1505	1508	1506
C <sub>4</sub> –N <sub>3</sub> and C <sub>2</sub> –N <sub>3</sub>	stretching	1469	1469	1463
C5C–H	bending	1366	1366	1365
C <sub>2</sub> –N <sub>1</sub> and C <sub>6</sub> –N <sub>1</sub>	stretching	1280	1277	1276
C <sub>4</sub> –N <sub>4</sub>	stretching	1240	1242	1235
C–O	stretching	1155	1154	1157
NH <sub>2</sub>	rocking mode	1100		1100
N <sub>1</sub> –C <sub>6</sub> –H	bending in plane	1012	1011	1010
C <sub>4</sub> –C <sub>5</sub> –H	bending in plane	995	996	993
C <sub>4</sub> –C <sub>5</sub>	stretching	966	967	961
NH	bending	822	820	825
ring	stretching breathing mode	794	793	794
			783	781
			758	762
C <sub>5</sub> –C <sub>4</sub> –N <sub>4</sub>	bending	700	700	703

Here,  $A$  is the integrated absorbance of a given IR feature and  $N$  is the column density. IR absorbance is measured on a log base-10 scale, therefore it is necessary to multiply the ratio between  $A$  and  $N$  by  $\ln 10$  to obtain the  $A$ -value. To evaluate the band strength, we used the determined thickness of three different samples. Thus, we estimate the  $A$ -value for the  $\alpha$ -band as the  $(8.8 \pm 0.7) \times 10^{-16}$   $\text{cm molecule}^{-1}$ . Additionally, we estimated the  $A$ -value for several cytosine absorption bands (Table S2). We would like to point out that the  $A$ -values estimated in this work are only valid for thin cytosine films with a thickness in the order of few hundred of nanometers.

**3.3. Film Compaction.** IR absorption spectroscopy is a suitable technique to follow the sample evolution during ion bombardment. It allows assessing the radiolytic destruction of cytosine, such as solid-phase transitions, radiolysis, sputtering, and formation of new chemical species.

Two cytosine samples were irradiated with the same projectile, 17 MeV  $\text{Ni}^{8+}$  (Table 1). Cytosine films (Figure 3a) present two different regimes with respect to target fluences. Note that the integrated absorbance at 1539  $\text{cm}^{-1}$  increases at low fluences,  $F < 6.0 \times 10^{10}$   $\text{cm}^{-2}$ ; however, at higher fluences, the integrated absorbance decreases exponentially.

The increase of integrated absorbance is correlated with the compaction process of cytosine films, *i.e.*, structural rearrangement of cytosine molecules by the irradiation, and the

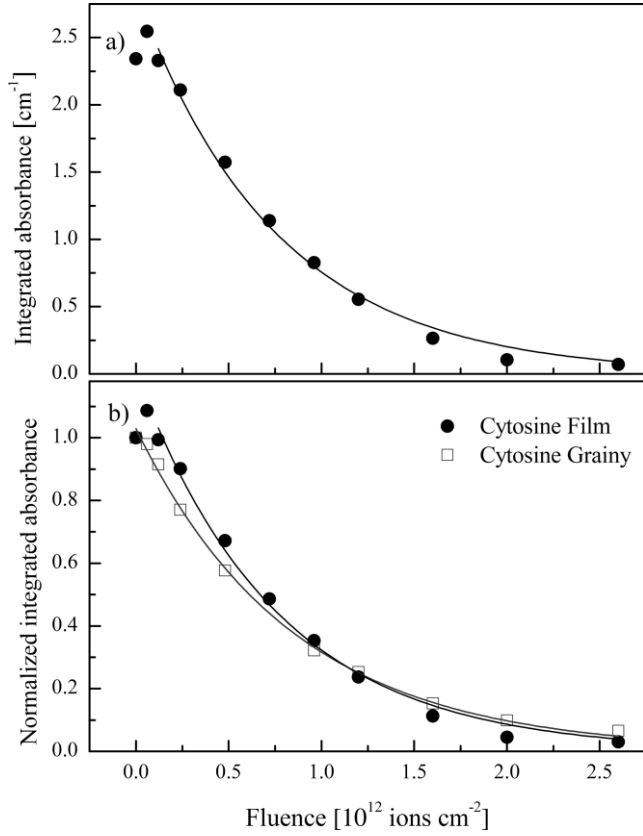


Figure 3. Integrated absorbance at  $1539\text{ cm}^{-1}$  of cytosine films as a function of the fluence of  $17\text{ MeV Ni}^{8+}$  (a). Normalized integrated absorbance at  $1539\text{ cm}^{-1}$  of the film (black circles) and grainy (open squares) cytosine samples as a function of the fluence of  $17\text{ MeV Ni}^{8+}$  (b).

subsequent changes in the band strength.<sup>40,44</sup> Assuming that the cytosine column density does not change much at low fluences, it is feasible to estimate the variation in the band strength induced by the film compaction. Under this assumption, the variation of the band strength at  $1539\text{ cm}^{-1}$  is 8%. Interestingly, the compaction effects are unobserved for grainy samples, and that cytosine decay is very similar in both film and grainy samples (Figure 3b).

**3.4. Cytosine Radiolysis.** Henceforth, we studied cytosine radiolysis at cryogenic temperatures with the electronic energy loss ranging from  $2.9$  to  $13.4\text{ MeV }\mu\text{m}^{-1}$ . For this task, we used two facilities with two similar setups and three different ion beamlines (GANIL and GSI).

We observe that for doses higher than  $0.35\text{ eV}$  per molecule, the overall IR absorption intensity decreases exponentially with the accumulated number of projectiles (fluence). For example, Figure 4 displays the evolution of grainy and film cytosine samples bombarded by  $17\text{ MeV Ni}^{8+}$  at  $12\text{ K}$ .

The decrease of the IR absorbance values is due to the disappearance of the initial molecule caused by either destruction or sputtering. Both effects, destruction and sputtering, can be quantified by introducing the apparent destruction cross section ( $\sigma_a$ );  $\sigma_a$  is defined as a sum between the molecule destruction cross section and the sputtering per incoming ion. For more details, see.<sup>39,45,46</sup>

The integrated absorbance ( $A$ ) evolution as an ion fluence function can be written according to eq 2

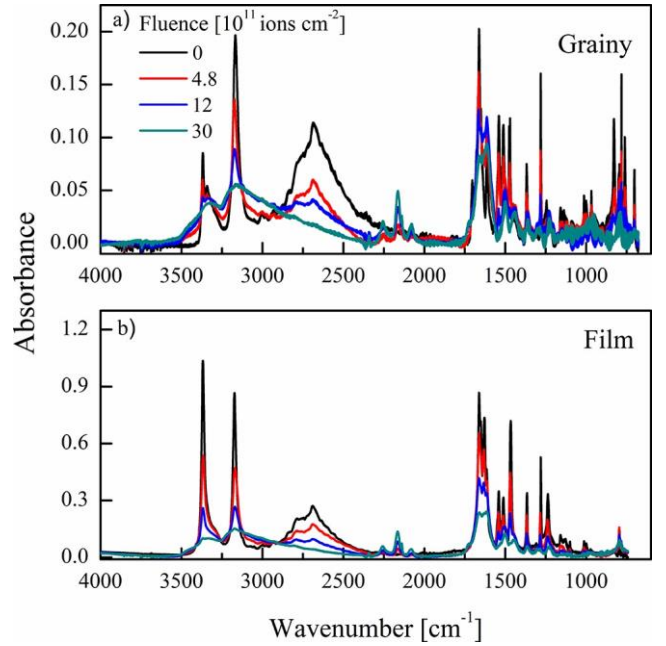


Figure 4. Spectra of grainy (a) and film (b) cytosine samples at  $12\text{ K}$ . The samples were irradiated by  $17\text{ MeV Ni}^{8+}$  at different fluences.

$$A = A_0 e^{-\sigma_a F} \quad (2)$$

where  $F$  is the fluence and  $A_0$  is the initial integrated absorbance of a given IR band.

Figure 5 displays the evolution of the normalized integrated absorbance at  $1539\text{ cm}^{-1}$  as a function of the accumulated ions

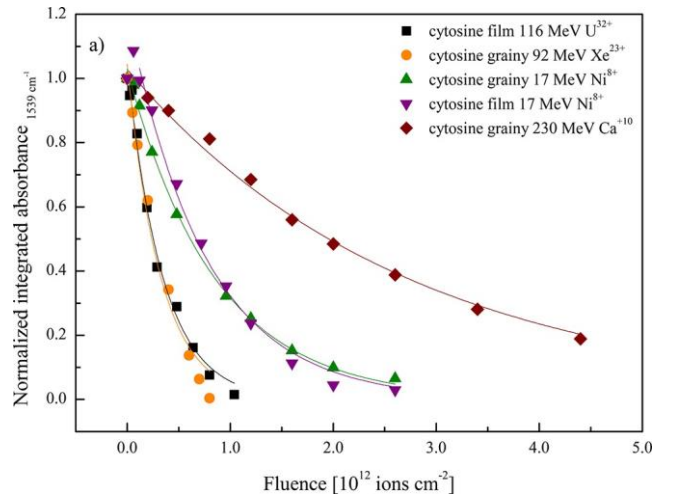


Figure 5. Normalized integrated absorbance at  $1539\text{ cm}^{-1}$  as a function of the projectile fluence. The full lines correspond to the fitting of the data with eq 2.

per square centimeter. This figure shows that the projectiles with higher electronic energy loss (Table 1) cause a faster and stronger decay of the IR integrated absorbance.

The evolution of several absorption bands was monitored during the heavy ion bombardment, and the respective destruction cross sections were determined by fitting eq 2 (see Table 3). The IR feature at  $1539\text{ cm}^{-1}$  yielded the highest cross section values (Table S3). It is important to mention that, in principle, all of the bands should yield the

Table 3. Destruction Cross Sections of Cytosine for Different Projectiles

projectile	$\sigma_d$ [ $10^{-12}$ cm $^2$ ]	sample
116 MeV U $^{32+}$	(3.50 $\pm$ 0.09)	film
92 MeV Xe $^{23+}$	(3.0 $\pm$ 0.3)	grainy
17 MeV Ni $^{8+}$	(1.17 $\pm$ 0.03)	grainy
17 MeV Ni $^{8+}$	(1.31 $\pm$ 0.06)	film
230 MeV Ca $^{10+}$	(0.51 $\pm$ 0.01)	grainy

same cross section values. We speculate that the different cross section values are due to the presence of IR absorption features from the radioproducts and/or the changes in the band strength induced by the irradiation and the subsequent changes in cytosine's local chemical environment. Therefore, for our calculations, we will use the highest cross section values, that is, the cross sections determined from the decay of the IR absorption band at 1539 cm $^{-1}$  (Table 3).

Note that grainy and film cytosine samples were irradiated by the same projectiles (17 MeV Ni $^{8+}$ ) leading to very similar cross sections (Tables 3 and S3).

As pointed out by,<sup>47</sup> it has been reported, for more than four decades, that the destruction cross sections for swift ions follow a power law on the electronic stopping power under the form  $\sigma_d = C S_e^n$ , where  $C$  is a constant and  $n$  is a dimensionless quantity. Additionally, it has been observed that the parameter  $n$  ranges from 1.0 to 1.5 for different molecules; for more details, see<sup>47,48</sup> and the references therein.

Figure 6 shows the destruction cross section of cytosine as a function of the electronic stopping power by using the following power law:  $\sigma_d = C S_e^n$ .

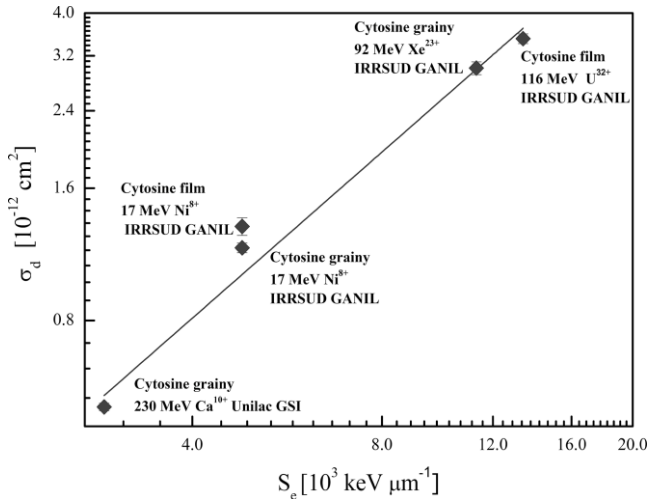


Figure 6. Apparent destruction cross section of cytosine as a function of the electronic stopping power.

The best fitting processes yielded  $\sigma_d = (3 \pm 1) \times 10^{-17} S_e^{(1.25 \pm 0.06)}$  with  $S_e$  in keV  $\mu\text{m}^{-1}$  for  $\sigma_d$  in cm $^2$ . The fitting yielded a  $\chi^2 = 0.97$ .

**3.5. Radioproducts: New Molecules from Cytosine Radiolysis.** Although the goal of this paper is not to investigate the radioproducts from cytosine degradation, we observed that swift ion irradiation not only leads to the decrease in nucleobase IR absorption lines, but new absorption bands arise in the IR spectra. We will highlight the new absorption bands and possible candidates for these IR bands.

Cytosine displays a very complex vibrational spectrum, making it hard to identify the molecules responsible for the new absorption features unequivocally. It is nevertheless possible to propose that some candidates of new molecular species are responsible for the observed absorption. We observe that new absorption features emerge from all nucleobase spectra due to sample radio degradation.

Grainy and film samples exhibit the same new absorption features for the same deposited local dose. Figure 7 displays the evolution of the IR absorption spectra of cytosine before and during the bombardment by 116 MeV U $^{32+}$  at different fluences. The IR spectra were shifted for better visualization.

The energetic processing of cytosine samples produced new absorption bands in the region of 2300–2000 cm $^{-1}$  (Figure 7a). Note that cytosine does not display absorption peaks in that region; this region is characteristic of nitrile and isonitrile vibrations.<sup>49</sup>

At lower wavenumbers (Figure 7b), small peaks emerge between 1720 and 1500 cm $^{-1}$ , which can be attributed to H $_2$ CO,<sup>45,50</sup> as indicated in Figure 7b.

To identify the radioproducts, the absorption band between 2300 and 2000 cm $^{-1}$  was deconvoluted (Figure 8c). The following absorption peaks are observed: 2077, 2138, 2164, 2227, and 2256 cm $^{-1}$ . The FWHH of the absorption peak at 2139 cm $^{-1}$  is 4.4 cm $^{-1}$ ; accordingly, this seems to be the IR absorption peak of CO.<sup>51</sup> The absorption band at 2165 cm $^{-1}$  may be assigned to OCN $^-$ .<sup>52</sup> Indeed, the formation of OCN $^-$  from the destruction of the cytosine ring is plausible (see Figure 1). The absorption band at 2258 cm $^{-1}$  is attributed to HNCO.<sup>52,53</sup>

#### 4. ASTROPHYSICAL IMPLICATIONS

From the astrophysical point of view, it is important to estimate the half-life ( $\tau_{1/2}$ ) of molecules exposed to ionizing radiation fields. This can indicate the probability of detecting a given molecule in an astronomical environment and the possibility of a molecule composing the inventory of molecules in a planetary disk.

To estimate the half-life of solid cytosine exposed to galactic cosmic rays (GCRs), we calculate the cytosine destruction rate, *i.e.*, the product of the destruction cross section, and the flux of cosmic rays. We selected the 10 most-abundant ions that compose the GCRs and determined the destruction cross section as a function of the energy per nucleon ( $E$ ) using the code SRIM<sup>55</sup> and the observed power law (see Section 3.4 (Figure S3)). As expected, heavier elements display higher destruction cross sections since, for swift ions, the stopping power is proportional to the square of the projectile atomic number and approximately inversely proportional to the square of the projectile velocity.<sup>54,55</sup>

The distribution of cosmic rays ( $\Phi(Z, E)$ ) is well-determined at energies above 1 GeV per nucleon (GeV/ $n$ ). Though, the differential flux at low energies is less accurate, due to the interaction between the charged particles, the heliosphere, and the planetary magnetic fields.<sup>56</sup> In this work, the GCR differential flux was calculated using the model proposed by<sup>56,57</sup> according to eq 3.

$$\Phi(Z, E) = C(Z)E^{0.3}/(E_0 + E)^3 \quad (3)$$

$C(Z)$  is a normalization constant. The numerical values of  $C(Z)$  were adapted from<sup>58</sup> (see Table S4). In this model,  $E_0$  is a parameter that modulates the differential fluxes only at low

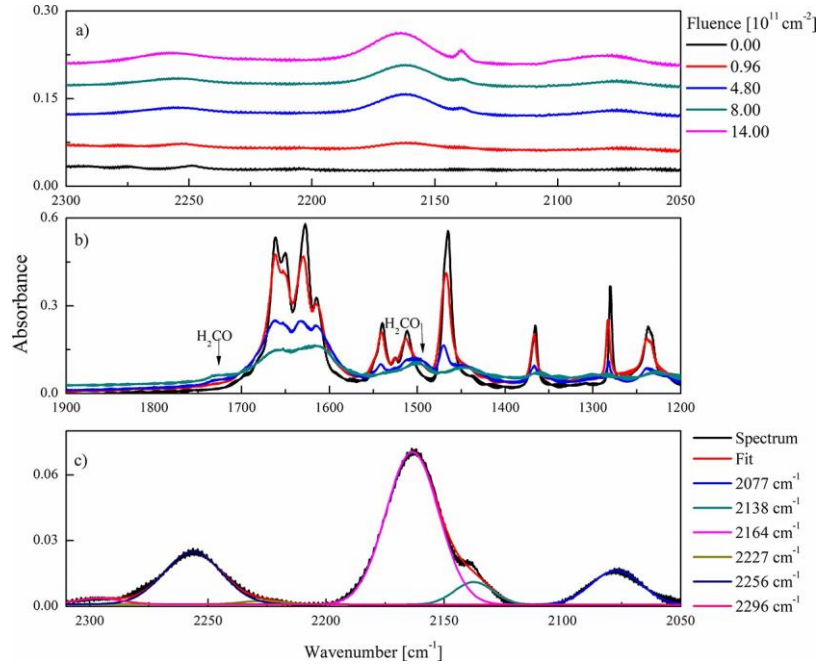


Figure 7. IR spectra of the cytosine film irradiated by 116 MeV  $U^{32+}$  at different fluences. The sample was irradiated by 116 MeV  $U^{32+}$  at different fluences, within wavenumbers ranging from 2300 to 2050  $cm^{-1}$  (a) and from 1900 to 1200  $cm^{-1}$  (b). Deconvolution of the band between 2300–2050  $cm^{-1}$  of the cytosine film irradiated by 116 MeV  $U^{32+}$  at the fluence of  $1.44 \times 10^{12}$  ions  $cm^{-2}$  (19.6 eV per molecule) at 12 K (c).

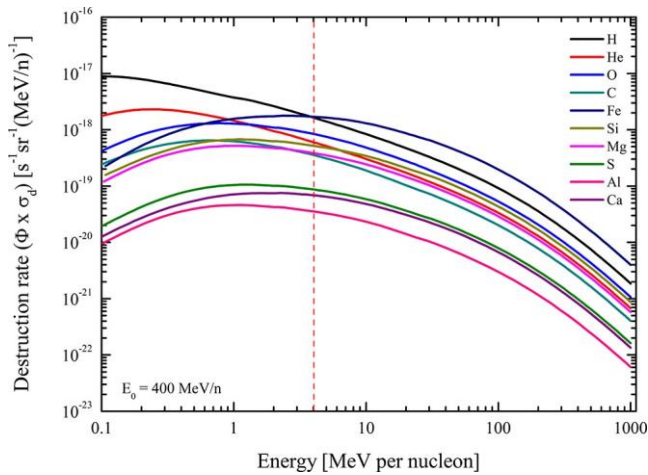


Figure 8. Cytosine destruction rate for the 10 most-abundant elements of the galactic cosmic rays as an energy function. The dashed red line is only a guide for the eyes.  $E_0 = 400$  MeV/n.

energies but does not have an impact at high energies.  $E_0$  values range from 0 to 940 MeV/n. It was shown that the  $E_0 = (300 \pm 100)$  MeV/n is the best parameter to explain the  $^3He/^4He$  measured ratio.<sup>57</sup> Here, we decided to investigate how different  $E_0$  values, namely, 200, 400, and 600 MeV/n, would impact the cytosine half-life. Therefore, here we adopted these three values for the  $E_0$  parameter to simulate the GCR fluxes and estimate the half-life of cytosine exposed to GCRs. Figure S4 shows the GCRs calculated using these three values of the parameter  $E_0$ .

The cytosine destruction rate ( $\sigma_d(Z, E) \times \Phi(Z, E)$ ) is exhibited in Figure 8. Interestingly, at energies higher than 4 MeV/n, iron is the most effective element to destroy cytosine (see the red dashed line in Figure 8). Note that in the energy range of 4–1000 MeV/n, iron displays cross sections about 4

orders of magnitude higher than hydrogen (Figure S3), thus iron compensates for its low abundance and becomes the most efficient cosmic ray element to destroy cytosine.

The half-life of cytosine can be calculated by  $\tau_{1/2}(Z) = \ln 2 / (4 \pi \sum_Z \int \sigma_d(E, Z) \Phi(E, Z) dE)$ , and the integral was performed from 0.1 to 1000 MeV/n. The factor  $4\pi$  is due to the fact that the GCR flux is isotropic; however, this value is small in comparison with the uncertainties of the GCR distribution (see Figure S4). For the total half-life, it is necessary to perform a summation of each element. Table 4

Table 4. Half-life of Cytosine Exposed to Cosmic Rays for Different Values of the Parameter  $E_0$

$E_0$ (MeV/n)	$\tau_{1/2}$ (Myers)
200	1.2
400	7.3
600	20.5

displays the half-life of cytosine exposed to cosmic rays for distinct values of  $E_0$ . It is important to point out that the values here are only an estimation given the uncertainties of the GCR flux.

Taking into consideration the same GCR distributions, cytosine was found slightly more radio susceptible than adenine.<sup>39</sup> Indeed, more experimental and theoretical approaches are necessary to better understand the susceptibility of purine and pyrimidine nucleobases to ionizing radiation.

## 5. CONCLUSIONS

In this work, the processing of solid cytosine at cryogenic temperatures by swift heavy ions was investigated. Cytosine targets were produced by two different methods: (1) by dropping a water–ethanol nucleobase solution on ZnSe windows followed by heating and solvent evaporation and

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(2) by sublimation of the nucleobase and condensation on a ZnSe window. This latter method produces a thin smooth solid nucleobase film. By using profilometry and combining with IR data, band strengths for several IR absorption bands of the cytosine film were estimated at room temperature, with the  $\alpha$ -band (3500–2000  $\text{cm}^{-1}$ ) presenting an  $A$ -value that equals  $(8.8 \pm 0.7) \times 10^{-16} \text{ cm molecule}^{-1}$ .

At low fluences ( $F < 1 \times 10^{11} \text{ cm}^{-2}$ ), cytosine films present an increase in the IR absorbance; this is probably correlated with molecular rearrangement and changes in their band strength. For both types of samples, film and grainy, the evolution of the IR spectra under heavy ion bombardment is very similar, yielding destruction cross sections equal within error bars. Furthermore, as observed for many organic molecules, cytosine destruction cross section follows an electronic stopping ( $S_e$ ) power law under the form:  $(3 \pm 1) \times 10^{-17} S_e^{(1.25 \pm 0.06)}$ . The half-life of cytosine exposed to GCRs was estimated using different GCR fluxes; the values estimated here are in order of Mega years. The results here suggest that the search for nucleobases by radio spectroscopy should be performed.

## ACKNOWLEDGMENTS

This work was supported by Brazilian agencies CNPq (INEspaço and Science without Borders) and FAPERJ, as well as the CAPES-COFECUB French-Brazilian exchange program, the European Commission, FP7 for RTD Capacities Programme (Contract No. 262010, ENSAR), and the EU's Horizon 2020 Research and Innovation Programme (grant agreement no. 654002 ENSAR2). It is a pleasure to thank Thierry Been, Jean-Marc Ramillon, Toiamou Madi, and Dr. Clara Grygiel for their invaluable support. The authors wish to acknowledge the staff of GANIL and GSI for their invaluable help throughout the course of the experiments. The authors are particularly thankful to Prof. Dr. Christina Trautmann, Dr. Daniel Severin, Dr. Markus Bender, Alexander Warth, and Arne Siegmund at GSI. The experiments were performed at *Grand Accélérateur National d'Ions Lourds* (GANIL) Caen, France, and at (GSI) *Helmholtzzentrum für Schwerionenfor-*  
*schung*, Darmstadt, Germany. The authors also thank the reviewers for their constructive remarks.



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