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Sputtered species during ion irradiation of adenine: Implications for Titan's atmospheric chemistry

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1 Highlights

2 **Sputtered species during ion irradiation of adenine: Implications for Titan's atmospheric** 3 **chemistry**

4 Filip Matuszewski, Véronique Vuitton, Richárd Rácz, Thomas Gautier, Zoltán Juhász, Béla Sulik, Duncan V. Mifsud,
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- 6 • We analyzed the chemical composition of species sputtered into the gas-phase during keV ion irradiation on
7 adenine.
- 8 • Irradiation induces the sputtering of HCN, N₂, C₂H₂, C₂N₂, CH₄, CH₂N₂, C₃HN and C₂H₃N.
- 9 • The sputtered species are key intermediates in Titan's atmospheric chemistry, supporting a ion-induced feedback
10 mechanism.

Sputtered species during ion irradiation of adenine: Implications for Titan's atmospheric chemistry

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ABSTRACT

Cassini-Huygens detected complex molecules exceeding several thousand atomic mass units in Titan's atmosphere as well as energetic O^+ , OH^+ and H_2O^+ ions in Saturn's magnetosphere. The heavy molecules are suggested to be nitrogenous polycyclic aromatic hydrocarbons (PAHs). The energetic ions are thought to penetrate into Titan's atmosphere, potentially modifying the structure and chemistry of these macromolecules. This study investigates the composition of chemical species sputtered into the gas-phase once energetic ions impact said macromolecules. We have irradiated thin film samples of adenine ($C_5H_5N_5$), a heterocyclic aromatic, at the HUN-REN Institute for Nuclear Research (ATOMKI) in Debrecen, Hungary. The experiments varied key parameters such as ion type (Ne^{q+} , O^{q+} , OH^{q+} and H_2O^{q+}), energies (10 and 20 keV), temperatures (150 and 300 K) and fluences (up to 2×10^{15} ions $\cdot cm^{-2}$). In-situ quadrupole mass spectrometry measured the residual gas of the experimental chamber, analysing the material that was sputtered into the gas phase during irradiation. The deconvolution of these mass spectra was done using a Monte-Carlo approach, revealing a plethora of compounds including HCN, N_2 , C_2N_2 , C_2H_3N , C_3HN , CH_2N_2 , NH_3 , C_2H_2 and CH_4 . Larger species like $C_5H_5N_5$, $C_4H_4N_4$ and $C_3H_3N_3$ were only detected at the on-set of the irradiation. The sputtering of hydrocarbons and nitriles highlights a potential feedback mechanism in Titan's atmosphere. The direct formation of CO and CO_2 from PAH irradiation appears unlikely.

1. Introduction

Over the past decades, data from various space missions and ground-based observations have revealed a complex and diverse chemical composition in the atmosphere of Saturn's moon, Titan. Besides its main constituents, molecular nitrogen (N_2) and methane (CH_4), Titan's atmosphere is filled with a plethora of minor trace components like molecular hydrogen (H_2), hydrogen cyanide (HCN), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), propane (C_3H_8), cyanoacetylene (HC_3N), cyanogen (C_2N_2) (Hanel et al., 1981; Kunde et al., 1981; Samuelson et al., 1981), more complex organics like ethyl cyanide (C_2H_5CN) (Cordiner et al., 2015) as well as oxygen-bearing molecules like

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54 carbon dioxide (CO₂), carbon monoxide (CO) and water (H₂O) (Samuelson et al., 1983; Lutz et al., 1983; Coustenis
55 et al., 1998), just to name a few.

56 Two discoveries of the Cassini-Huygens mission are especially relevant to this study. First, in Titan's atmosphere,
57 negatively charged ions with masses up to thousands of atomic mass units were detected (Waite et al., 2007; Cray et al.,
58 2009). These large ions, considered precursors to the lower-altitude aerosols forming Titan's haze, are best interpreted
59 as polyaromatic nitrogen-bearing hydrocarbons (PANH), although their identification remains tentative (Lavvas et al.,
60 2013; López-Puertas et al., 2013; Haythornthwaite et al., 2021). The origin of these large ions can be traced back to
61 the dissociation and ionization of Titan's primary atmospheric compounds, N₂ and CH₄, which consequently form
62 species like C₂H₂, C₂H₄, C₂H₆ and HCN. Most of these reactions are the result of neutral reactions, although, ion
63 chemistry plays a major role in the formation of larger species (<350 Da) like benzene (C₆H₆) (Vuitton et al., 2008)
64 which has been identified through modelling efforts (Lebonnois et al., 2002; Wilson and Atreya, 2003; Lavvas et al.,
65 2008; Delitsky and McKay, 2010) and laboratory analog experiments (Trainer et al., 2013; Sciamma-O'Brien et al.,
66 2014; Sebree et al., 2014; Yoon et al., 2014) as a major precursor to polycyclic aromatic hydrocarbons (PAH).

67 The second key finding involves positively charged oxygen ions in Saturn's outer magnetosphere, which likely
68 originate from cryo-volcanic activity on Enceladus (Johnson et al., 2005; Sittler Jr et al., 2006). While O⁺ are
69 considered the abundant ions in Titan's orbit, other ions like OH⁺ and H₂O⁺ are found as well. These ions, with energies
70 between 1 and 100 keV, can deliver up to ~10⁶ ions . cm⁻² s⁻¹ into Titan's atmosphere (Hartle et al., 2006a,b) with
71 lower estimates of 0.9-4.7 × 10⁵ ions . cm⁻² s⁻¹ (Snowden et al., 2018; Snowden and Higgins, 2021). Ions of higher
72 energies are also present but at lower fluxes. As they enter Titan's atmosphere, they lose energy through electronic
73 excitation and momentum transfer to surrounding molecules, primarily N₂ (Cravens et al., 2008), with deposition
74 occurring between 1200 and 800 km in altitude. Hörst et al. (2008) demonstrated that the observed densities of CO,
75 CO₂, and H₂O in Titan's atmosphere can be explained by the influx of O⁺ and OH⁺ or H₂O⁺ ions into Titan's upper
76 atmosphere. Additionally, Sittler Jr et al. (2009) proposed that magnetospheric keV O-ions may either become trapped
77 in fullerenes or contribute to the formation of CO and CO₂ upon thermalization. Furthermore, the ions may either
78 implant or destroy the aforementioned larger and more complex organic molecules forming new potentially lighter
79 species.

80 Numerous irradiation experiments to simulate space environments have been conducted on ices (Brown et al., 1984;
81 Famá et al., 2008; Dartois et al., 2015; De Barros et al., 2022; Ivlev et al., 2023), organics (Faure et al., 2021; Quirico
82 et al., 2023), and meteorites (Brunetto et al., 2014), reporting the sputtering of small volatiles. These sputtered species
83 mostly consist of fragments of the irradiated material. For instance Quirico et al. (2023) found that the irradiation of
84 methanol ice leads to the sputtering of CO, CO₂, CH₄, H₂CO, H₂ and H₂O but not of CH₃OH itself.

85 In the ice irradiation experiments, mixtures typically composed of H₂O with organic compounds like CH₄ (Moore
86 and Hudson, 1998; Wada et al., 2006), C₂H₆ (Khare et al., 1993; De Barros et al., 2016), C₃H₈ and C₄H₁₀ (Hand and
87 Carlson, 2012), as well as, CH₃OH and CH₂O₂ (Allamandola et al., 1988; Baratta et al., 1994; Gerakines et al.,
88 1996; Hudson and Moore, 2000; Palumbo et al., 1999) were used to study the effects of irradiation on compounds
89 resembling the surfaces of icy bodies. These studies have demonstrated the formation of various organic compounds,
90 including alcohols, aldehydes and carboxylic acids. Furthermore, the irradiation of hydrogenated carbon grains,
91 benzene (C₆H₆) and more complex aromatics like indene (C₉H₈) capped with a water ice layer produces CO₂ and
92 CO as demonstrated by Mennella et al. (2004), Gomis and Strazzulla (2005) and Maté et al. (2024), respectively. In
93 these particular experiments carbonaceous material was irradiated with either He^{q+} and Ar^{q+} ions or VUV photons
94 and electrons, proving the direct irradiation-induced chemical interaction between the carbonaceous material and the
95 water recorded via FTIR.

96 Apart from the FTIR, Maté et al. (2024) as well as other studies (Brown et al., 1984; Dartois et al., 2017, 2019;
97 Faure et al., 2025) detected the decomposition products using a Quadrupole Mass Spectrometry (QMS), which has
98 proven to be a reliable tool for the analysis of volatile species released during irradiation. The use of a QMS has
99 been instrumental in providing sensitive, real-time detection of sputtered molecules, along with valuable information
100 about their composition and abundance. These studies are crucial for understanding how energetic processing in space
101 environments drives the chemical evolution of planetary surfaces, atmospheres, and interstellar materials. For instance,
102 Faure et al. (2025) analyzed the residual gas while irradiating H₂CO ice with 74 MeV ⁸⁶Kr¹⁸⁺ ions reporting the
103 sputtering of H₂CO as well as fragments of it like H₂, CO, C and O. While these studies provided valuable insights
104 into the physical and chemical effects of radiation on the ice, the use of krypton ions or electrons limits the scope of
105 the experiment to purely radiative effects without exploring potential chemical reactions with ions themselves. Using
106 ion beams with reactive species, such as oxygen, could reveal whether sputtered fragments react with oxygen ions to
107 form oxygenated species.

108 To study the effect of ion irradiation on complex organic molecules in Titan's upper atmosphere, in this work we
109 used adenine (C₅H₅N₅) as a simulant for the organic material that is present in Titan's atmosphere. Indeed, even if
110 adenine has not been detected yet on Titan, it has been detected in Titan aerosol analogs, so called tholins (Pilling et al.,
111 2009; Poch et al., 2012; Hörst et al., 2012; He and Smith, 2014; Kawai et al., 2019). It is the only nucleic base that lacks
112 oxygen and as a purine, it is a heterobicyclic aromatic compound with nitrogen. Although adenine contains a higher
113 nitrogen content (C/N = 1) than the PANHs detected in Titan's atmosphere (C/N ≥ 3, Haythornthwaite et al. (2021)),
114 its extensive experimental characterization in previous irradiation studies makes it an ideal simulant. This amount of
115 prior data allows us to build upon existing results rather than starting from first principles, for instance when estimating
116 parameters such as the thin-film sample thickness. These previous studies have examined the effect of irradiating

adenine with radiation sources like ions (Vignoli Muniz et al., 2017; Ada Bibang et al., 2019), UV-light (Peeters et al., 2003; Guan et al., 2010; Poch et al., 2014), X-rays (Pilling et al., 2011) and electrons (Evans et al., 2011) concentrating on the survivability of this nucleic base in space conditions. They determine the photodecomposition of their target samples by measuring the decrease in absorbance over irradiation time. Studies utilizing low-energy UV radiation consistently show that adenine exhibits greater **radiation**-stability than other organic compounds such as uracil and glycine, consequently not being fully destroyed as result of the irradiation. Poch et al. (2014) were the first hinting on the formation of macromolecules increasing adenine's **radiation**-stability which were later characterized using very high resolution mass spectrometry (Matuszewski et al., 2025). Studies that used higher energy sources (>150 eV) reported the destruction of adenine and fragmentation into smaller molecules (HCN, N_2 , $C_2H_4N_4$) or radicals ($\cdot CN$), in solid-phase, indicated by new appearing absorption bands (Pilling et al., 2011; Vignoli Muniz et al., 2017). Vignoli Muniz et al. (2017) pointed out that the formation of N_2 is likely but difficult to confirm as such symmetric molecules are challenging to detect through FTIR. Therefore the question remains open as to what the relative abundance of each species sputtered into the gas phase is.

Analyzing the compounds that are sputtered into the gas phase during these interactions is crucial for understanding the chemical evolution of Titan's atmosphere. However, the detailed chemical interactions between these energetic ions and macromolecules remain poorly understood, highlighting the need for laboratory experiments. Such analyses can provide insight into the composition of the sputtered species, helping to bridge the gap between laboratory experiments, computational modeling and observations. In this study, we investigate the effect of irradiating adenine thin films with low energy (10 and 20 keV) Ne^{q+} , O^{q+} , OH^{q+} , H_2O^{q+} -ions with in-situ infrared (IR) spectroscopy and a strong focus on in-situ quadrupole mass spectrometry (QMS) analyzing the residual gas in the experimental chamber. A deconvolution of the mass spectra using a Monte-Carlo approach will determine the relative abundance of molecules sputtered into the gas-phase when irradiating a complex organic molecule. Here, adenine will suit us as a simulant for complex organic molecules in Titan's atmosphere, providing new insights into the effects of ion irradiation on said molecules.

2. Irradiation experiments

The irradiation experiments have been performed at HUN-REN Institute for Nuclear Research (ATOMKI) in Debrecen, Hungary. Here, the experimental astrochemistry chamber AQUILA (ATOMKI-Queen's University Ice Laboratory for Astrochemistry) (RÁCZ et al., 2024) is coupled to an electron cyclotron resonance (ECR) ion source (Biri et al., 2012, 2021). The chamber set-up permits the simultaneous production and analysis of a sample. The sample holder carried one sample window at a time with diameter of 15 mm and a thickness of 3 mm. An oven, connected to the chamber, sublimated adenine (Aldrich $\geq 99\%$) powder at a maximum temperature of 150 °C and pressure of

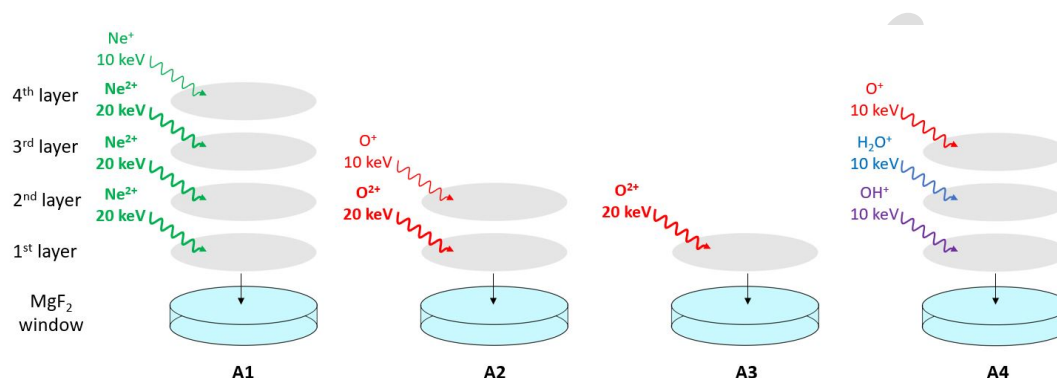


Figure 1: Schematic overview of each adenine sample, layer and ion used with the corresponding energy. Samples A1, A2 and A4 were kept at 300K, while A3 was irradiated at 150K

6×10^{-7} mbar which then condensed **uniformly** onto MgF_2 -windows that were either kept at 300 K or cooled down to 150 K. **The adenine powder was stored under ambient laboratory conditions between irradiation events and the oven was refilled with fresh adenine powder between samples. A preheating step at 80°C was performed each time the oven was refilled.** In total, four adenine thin-film samples, consisting of 1–4 layers, have been produced, as detailed further below. The ion source is able to generate a wide range of positive and negative singly or multiply charged atomic and molecular ions covering a kinetic energy range of 50 eV to 900 keV. For our experiments, single- and double-charged Ne^{q+} , O^{q+} , OH^{q+} and H_2O^{q+} ions with energies of either 10 or 20 keV were produced. From here on, we will call these ions either "ion projectiles" or simply "projectiles" to prevent confusion with ions detected with QMS. We chose these projectiles and energies to accurately mimic the conditions found in the upper atmosphere of Titan at an altitude between 800 and 900 km (Cravens et al., 2008). **The ion beam is swept across the sample area in order to get as homogeneous beam as possible with a diameter of about 10 mm.** During the irradiation, material is sputtered away, thus decreasing the thickness of the sample. In order to prevent the ions from penetrating one layer and implanting ions into either an underlying layer or the sample substrate, the maximum total fluence was chosen accordingly. Hence, the total fluence varied between 0.5×10^{15} and 20×10^{15} ions $\cdot \text{cm}^{-2}$. We note that secondary effects such as electronic cascading may still extend beyond the ion stopping range and could potentially influence deeper material. However, due to the projected range being approximately < 60 nm (calculated with SRIM (Ziegler et al., 2010) for ^{18}O ions penetrating adenine with a density of 1.5 g/cm^3) and the thickness of each layer being ≥ 300 nm, such secondary effects are negligible. Figure 1 shows a schematic overview of the samples, their layers and irradiation events. Each of these irradiation events is comprised of 4 to 9 irradiation steps. For example, the first sample A1 consists of 4 adenine layers and therefore 4 irradiation events. Each event consists of 4 irradiation steps at which the sample is irradiated with set number of ions. For irradiation event #2, e.g. 2.5×10^{14} ions $\cdot \text{cm}^{-2}$ per step which totaled in 1×10^{15} ions $\cdot \text{cm}^{-2}$ for the whole event. A detailed listing of each irradiation event and

experiment parameter can be found in Tables A.3 and A.4 in the appendix. A Fourier-transform Infrared spectrometer (FTIR, Bruker VERTEX 70v) that is installed at the chamber which allows for the acquisition of infrared (IR) spectra in between the irradiations and depositions. **The resolution of the instrument was set to 4 cm⁻¹. The IR-analyzed area equals the irradiated area.** The detector is placed at an angle of 156.5°, puts the incident angle at 23.5°. The thickness of the individual layers was monitored by IR-spectroscopy using the Beer-Lambert law:

$$z = \frac{NM}{\rho N_a} \quad (1)$$

where M is the molar mass of adenine (135.13 g/mol), ρ the density (1.47 g/cm³ ±1% Kilday (1978)), N_a the Avogadro constant, and N the column density. The column density N is calculated by:

$$N = \ln(10) \frac{S}{A} \cos(\theta) \quad (2)$$

with S being the area under the 1970-3600 cm⁻¹ of the IR-spectrum also known as the α -band and the A -value of 7.9×10^{-16} cm molecule⁻¹ ± 4 % (Saiagh et al., 2014), and θ the incident angle (23.5°). As the calculation of the area heavily depends on the baseline correction, a pessimistic error of 10 % has been chosen for the calculation of the error on the thickness.

3. QMS-data analysis

The QMS for residual gas analysis (Pfeiffer QMG 250 M3, PrismaPro Compact mass spectrometer with Vacuum RGA PrismaPro 300 sensor) is detecting the molecules that are sputtered into the gas-phase as a result of the irradiation, as well as molecules that are present at any given time. Measurements have been performed continuously throughout every deposition and irradiation. The QMS is equipped with two different detectors. In Faraday-cup (FC) mode, we are able to detect species up to a mass of 300 u. The Secondary Electron Multiplier (SEM) was set up to measure compounds up to 150 u in order to speed up the number of scans. Furthermore, the SEM possesses a higher sensitivity which is advantageous for measuring very faint signals of less abundant molecules. However, because of the heightened sensitivity, it is unsuitable for measurements during the deposition of the adenine, which were done in FC-mode.

The data present intensities for masses in the range of m/z 1-150 or m/z 1-300 over time depending on the used detector. Figure 2 shows two such plots with intensities as a function of time. On the left, the intensities of mass channels m/z 18 and m/z 135 (base peaks for water and adenine, respectively) as well as the pressure in mbar are shown before and during the deposition of adenine **in FC-mode**. In the time range of 0 to 5935 seconds, an intensity and pressure

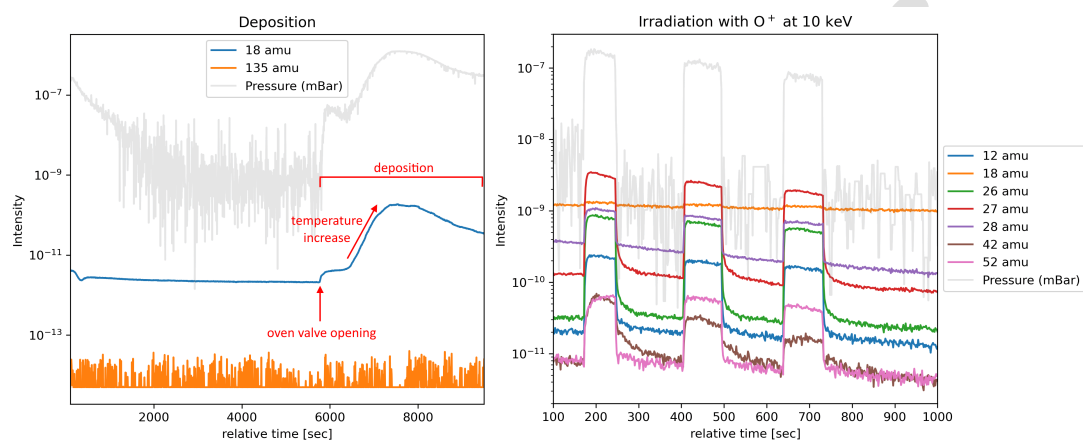


Figure 2: Intensities over relative time for the mass channels m/z 18 and 135 and the pressure in mbar for a deposition of adenine (left) and m/z 12, 18, 26, 27, 28, 42 and 52 together with the pressure in mbar for the irradiation event #6 steps 1, 2 and 3 of sample A2(right)

drop can be observed which corresponds to the initial preparation of evacuating the chamber. During that time the adenine powder is starting to heat up without being deposited yet. At 5935 s, the valve of the oven is opened. At this time, the temperature has reached 80°C, which then slowly increases to >140 °C where adenine is deposited onto the sample window. It is important to note that the signal intensity at the mass channel m/z 135 is significantly lower than that observed at m/z 18 and exhibits minimal variation over time. This is attributed to transmission efficiency of the QMS, where higher-mass species are generally less efficiently ionized and/or transmitted, resulting in substantially reduced signal intensities. The signal at m/z 135 becomes visible only after background subtraction. A more detailed discussion of this issue is provided in Section 3.1. As we suspect the adenine to be contaminated with water, the mass channel m/z 18 is a better indicator of sample sublimation and recondensation. The right plot shows the intensity of the mass channels m/z 12, 18, 26, 27, 28, 42 and 52 as well as the pressure in mbar plotted over time during an irradiation event in SEM-mode (Figure 2, right). This particular irradiation event consists of three irradiation steps during which the intensity of the mass peaks is increasing.

3.1. Raw data treatment

Despite the background pressure of $\sim 10^{-9}$ mbar, the data is underlain by signals of contaminants present in the chamber at all times (see Figure 2, signal between irradiation steps). In order to analyze and deconvolute the data, a subtraction of the background data is needed. To achieve this, the intensities of all mass channels were averaged separately over designated time ranges before and during irradiation. These time ranges were selected individually for each irradiation event to account for variations in experimental conditions. At the start and end of each irradiation event, sudden pressure changes caused by the opening and closing of the ion beam pipe valves introduced artifacts in

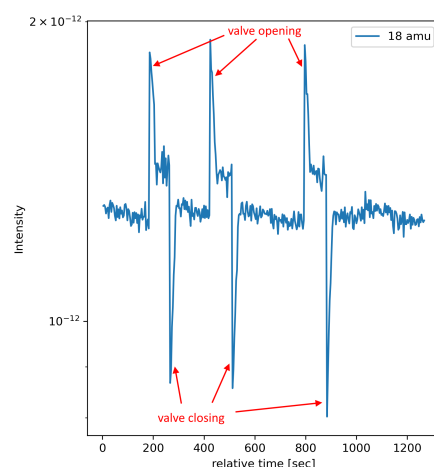


Figure 3: Intensities over relative time for the mass channels m/z 18 showing the signal artifacts before and after each irradiation stemming from opening and closing the valve of the ion beam pipe; irradiation event #9 steps 4, 5 and 6 in FC-mode

the signal, resulting in peaks and valleys. **Figure 3** shows these artifacts especially well. Here, the mass channel **18** from irradiation event #6 in FC-mode is shown as intensity over time. Especially in FC-mode, with its lower intensities, the artifact is prominent. However, the artifact does not appear in all samples or mass channels. To prevent these signal fluctuations from skewing the averaging, the initial few seconds before and after the irradiation were excluded. Afterwards, the averaged background signal is subtracted from the averaged irradiation signal (raw data).

While it might seem clear that certain mass peaks in the spectrum are associated with definite molecules (e.g. mass peak m/z 18 for H_2O), each chemical species possesses a unique mass spectrum. As molecules are ionized inside the QMS, they break apart into several fragments forming a pattern displaying multiple peaks in the mass spectrum. The more complex a molecule the more complex these fragmentation patterns become. Figure 4 shows a background subtracted mass spectrum captured during the deposition of adenine for sample A3 together with an ideal mass spectrum of adenine from the NIST database. Both of these mass spectra do not only show a peak at m/z 135 (molecular mass of adenine: 135.13 g/mol) but dozens of peaks spread across the whole mass range. Furthermore, comparing both mass spectra, **all major peaks of the fragmentation patterns coincide in position, indicating the same dominant fragments are present in both spectra.** However, the intensities of these peaks appear to be inverted, with intensities generally increasing or decreasing in opposite directions as a function of m/z . While the main peak of adenine (m/z 135) is the most intense in the NIST-mass spectrum, the same peak appears to be a minor one in the deposition mass spectrum. This is due to higher mass ions being less efficiently transmitted through the instrument. High-mass discrimination is a known phenomenon in QMS caused by fringe fields forming at the entrance of the QMS

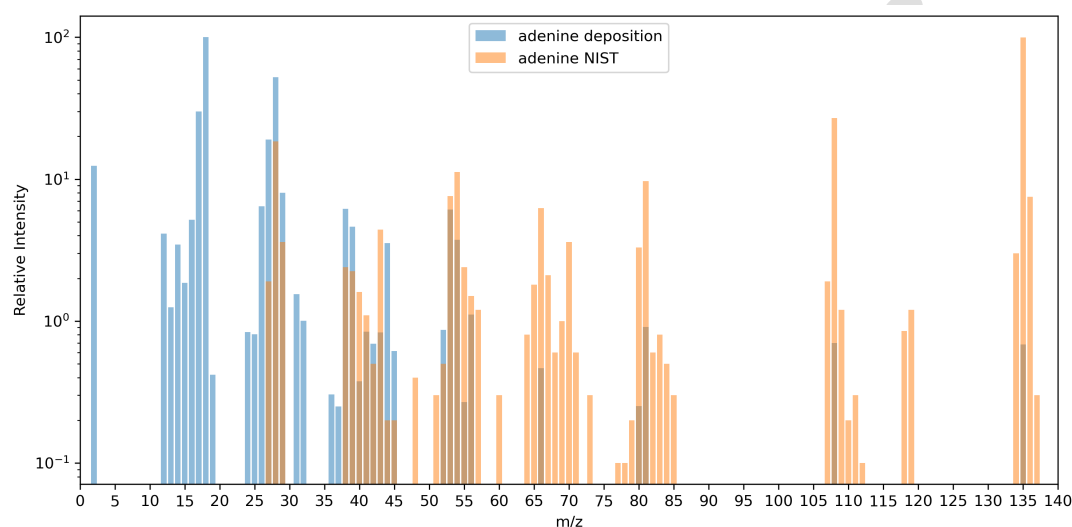


Figure 4: Mass spectrum obtained during the deposition of adenine for sample A3 (blue) and mass spectrum from the NIST database (orange). The intensities of the main peaks in each spectrum have been normalised to 100.

causing higher mass molecules to be inserted less efficiently (Brubaker, 1969). This issue in transmission has to be taken into account, requiring a correction of the mass spectra captured during irradiation. Major peaks of the adenine fragmentation pattern (m/z 28, 54, 81, 108 and 135) are used as reference points for whom factors are calculated by dividing the intensity of each major peak from the NIST-spectrum with the corresponding peak from the deposition spectrum. In order to calculate a correction factor for each mass channel, an exponential fit is generated. Figure 5 shows the calculated correction factor for each major peak together with the exponential fit. An individual calculation of correction factors was performed for each sample followed by a correction of each irradiation mass spectrum with its corresponding factors. Figure A.14 in the appendix shows the effect of the transmission correction on the deposition spectrum of adenine.

Even if two instruments have comparable sensitivities, their fragmentation patterns will likely differ in fragment intensities, because the relative abundances of fragments depend on the stability of the ionization products during dissociative ionization. This process is highly sensitive to the energy transfer between electrons and neutral molecules in the ion source, which in turn is dependent on the geometry of the ion source. Even micrometer-scale differences in said geometry can alter fragment spectra (McLafferty and Turecek, 1993).

3.2. Monte-Carlo approach

If a complex gas mixture is measured with a QMS, the fragmentation pattern of each compound are superimposed. The challenge is then to deconvolute these mass spectra of unknown chemical species mixtures. The more complex

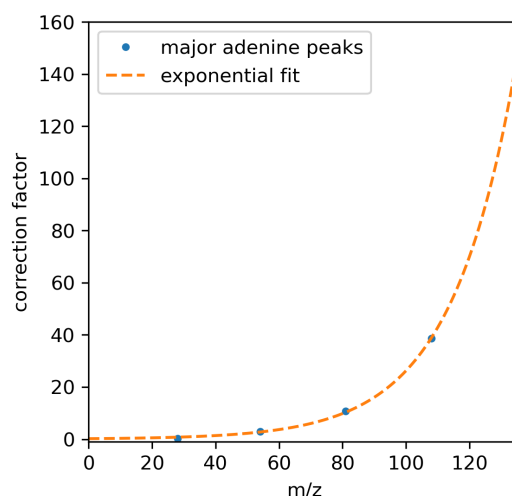


Figure 5: Correction factors for major peaks of adenine (m/z 28, 54, 81, 108 and 135) together with the exponential fit interpolating correction factors for all mass channels

the gas mixture, the more difficult this deconvolution becomes. Conventional automated deconvolutions are done under the assumption of fixed fragmentation patterns. However, individual intensities in the fragmentation patterns change depending on the instrument's geometry, which introduces a bias. Although the differences in intensities of fragmentation patterns usually are found to be in a range of 20% to 30% (Gautier et al., 2020), in extreme cases these differences can be much higher. For example, comparing the experimental fragmentation pattern from ATOMKI with the one from the NIST database, we observe differences $>100\%$ for peaks of smaller fragments (e.g. at m/z 14 for N_2 , relative intensities are at 5.1 % and 13.8 % for ATOMKI and NIST, respectively). Given these challenges, using a simple automated deconvolution process of our mass spectra would be impractical. For this reason, we have applied a Monte-Carlo approach to deconvolute these mass spectra in which the individual peaks of the fragmentation patterns are varied in each iteration. The applied software was developed with Matlab by Gautier et al. (2020) and has already been used to successfully analyze data from the Cassini's INMS (Serigano et al., 2020, 2022), Rosetta's COSAC mass spectrometer (Leseigneur et al., 2022), as well as Huygen's GCMS (Gautier et al., 2024; Das et al., 2025). Its basic function lies in solving a system of linear equations to find the best fitting chemical composition to mass spectrometry data:

$$I_i = \sum_{j=1}^n F_{i,j} N_j \quad (3)$$

Here, the measured intensity I_i for the mass channel i is calculated with the fragmentation intensity $F_{i,j}$ for species j and the species concentration N_j . This represents the conventional automated part of the process. In order to work properly, a species fragmentation pattern database is needed. The QMS used in this study ionizes molecules at 70 eV **electron impact**. It is important to choose fragmentation patterns that are in agreement with said instrument. Unfortunately, that is not always possible as we would have to obtain single measurements of each compound for our specific instrument. This is not only difficult in terms of time but also possibly dangerous when handling gases like hydrogen cyanide (HCN). For this reason, most of the fragmentation patterns of the compounds in our database originated from the NIST database. The fragmentation patterns of three of these compounds (H_2O , N_2 and CO_2) were obtained prior to the irradiation experiments by measuring pure gases with our QMS. While this dataset is considered the most reliable reference, all fragmentation patterns were treated with equal uncertainty in the Monte Carlo analysis. For the other compounds, we had to either rely on data from other studies (C_2H_2 , Plessis and Marmet (1986); NH_3 , Jiménez-Escobar et al. (2018)) or on the NIST database. The decision to select certain compounds from sources other than NIST arises from the uncertainty regarding the source of the data provided by NIST, making it difficult to assess its accuracy and reliability. Initial simulations were performed with a total of 41 different chemical compounds (Table A.5) whereby certain compounds were gradually taken out of the database if they did not contribute to the fit of the measured mass spectra. In the end, 15 compounds were left in our database for the final simulations. They are displayed in Table 1.

Apart from the fragmentation patterns, the database also includes the ionization cross sections of each compound which is important to determine the probability of a compound to ionize inside the QMS. We calculate the ionization cross section σ with an adjusted regression equation from Fitch and Sauter (1983):

$$\sigma = 0.082 + \sum_{i=1}^4 \alpha_i n_i \quad (4)$$

where α_i is the coefficient and n_i the number of each atom (H, C, N, O) in the corresponding molecule. The coefficients for H, C, N and O are 0.73, 1.43, 1.20, 1.10, respectively.

The Monte-Carlo approach of the deconvolution software starts by creating a set number n of different randomized fragmentation databases based on our initial database, where $n = 500\,000$. Here, a change is only applied to the intensities of a peak and not on the position of said peaks. Due to the above mentioned discrepancy between NIST and measured fragmentation patterns, we have set the variation d in our calculations to 50 %. In the next step, each database is used to decompose the measured mass spectrum individually creating a n number of deconvoluted mass spectra. From these 500 000 iterations, the 10% with the lowest residual values are chosen to obtain a statistical result.

Table 1
Database of compounds used in the final deconvolutions

Compound name	Compound formula	Base peak [amu]	Ionization cross section [$\text{\AA}^2$]	Reference
Diazomethane	CH_2N_2	14	5.372	NIST
Methane	CH_4	16	4.432	NIST
Ammonia	NH_3	17	3.472	Jiménez-Escobar et al. (2018)
Water	H_2O	18	2.642	ATOMKI
Neon	Ne	20	0.584	NIST
Acetylene	C_2H_2	26	4.402	Plessis and Marmet (1986)
Hydrogen cyanide	HCN	27	3.442	NIST
Molecular nitrogen	N_2	28	2.482	ATOMKI
Acetonitrile	$\text{C}_2\text{H}_3\text{N}$	41	6.332	NIST
Carbon dioxide	CO_2	44	3.712	ATOMKI
Cyanoacetylene	C_3HN	51	6.302	NIST
Cyanogen	C_2N_2	52	5.342	NIST
1,3,5-Triazine	$\text{C}_3\text{H}_3\text{N}_3$	81	10.162	NIST
3-Amino-4-pyrazolecarbonitrile	$\text{C}_4\text{H}_4\text{N}_4$	108	13.522	NIST
Adenine	$\text{C}_5\text{H}_5\text{N}_5$	135	16.882	NIST

Mass channels, where $m/z < 12$, show relatively high intensities which could be explained by i) the occurrence of a double charged ions (e.g. C^{2+} and N^{2+}), ii) high-mass discrimination, where the signal produced by a lighter ion is higher than that of a heavier ion of similar abundance or iii) an unknown source of instrumental error. Furthermore, H_2 could be present in the gas-phase and would present its most intense peak at m/z 2 with possible fragmentation signals at m/z 1 for H^+ and m/z 3 and 4 for the deuterium containing isotopologs of the hydrogen molecule.

The majority of the recorded mass spectra do not exhibit peaks above m/z 57. However, in spectra where such peaks are present, typically observed during the initial stages of irradiation, distinct peaks at m/z 135, 108, and 81 can be identified. These are attributed to $\text{C}_5\text{H}_5\text{N}_5$, $\text{C}_4\text{H}_4\text{N}_4$, and $\text{C}_3\text{H}_3\text{N}_3$, respectively. Incorporating these high-mass compounds into the deconvolution process presents challenges, as the software attempts to fit their low-intensity, low-mass peaks to the dominant peaks in the measured mass spectra, leading to significant overfitting. For instance, adenine ($\text{C}_5\text{H}_5\text{N}_5$) exhibits a minor peak at m/z 28, which corresponds to a major peak in the measured QMS spectra. When the software attempts to fit this minor peak to the QMS spectrum, it results in excessive overfitting of mass channels above m/z 57. In order to mitigate this issue, we divided the QMS spectra into two mass ranges: m/z 12–57 and $m/z > 57$. The spectra exhibiting peaks above m/z 57 were fitted separately using the corresponding high-mass compounds. The contributions of these high-mass species to the intensities in the m/z 12–57 range were then subtracted from the QMS

Table 2MS-fraction of larger species for the mass range m/z 12-135

Sample	Ion	Energy [keV]	Fluence [$\times 10^{15}$ ions . cm ⁻²]	Main peak [m/z]	Compound	MS-fraction [%]
A1	Ne ²⁺	20	0.25	135	C ₅ H ₅ N ₅	2.24
	Ne ²⁺	20	0.5	81	C ₃ H ₃ N ₃	0.20
	Ne ⁺	10	0.25	135	C ₅ H ₅ N ₅	5.26
A2	O ⁺	10	0.5	108	C ₄ H ₄ N ₄	3.71
	OH ⁺	10	0.5	135	C ₅ H ₅ N ₅	2.45
A4	H ₂ O ⁺	10	0.5	81	C ₃ H ₃ N ₃	2.24
	O ⁺	10	0.5	81	C ₃ H ₃ N ₃	0.98
	O ⁺	10	1.0	108	C ₄ H ₄ N ₄	0.26

spectra. Once this correction was applied, the deconvolution analysis was performed using the remaining compounds listed in Table 1. A similar approach was employed by Serigano et al. (2022) in the analysis of Cassini data. However, in our case, the high-mass region is significantly less complex and is predominantly influenced by a single compound.

4. Deconvolution results

In total, 38 QMS spectra were deconvoluted and the MS-fractions were determined for 12+3 different compounds (12 for m/z 12-57 + 3 for $m/z > 57$). Of these spectra, 8 showed mass peaks in the high mass range. Table 2 shows the fraction of the mass spectrum and the compounds attributed to these peaks. The MS-fraction for high-mass molecules is 0.20 - 5.26 %. No discernible pattern has been identified that explains the sputtering of specific high-mass molecules as a function of ion energy or projectile type. Furthermore, the observed inconsistencies in the MS-fractions remain unexplained. These variations may be attributed to limitations in the detection sensitivity, particularly in the high-mass range, which may persist despite transmission correction. The fluence at which these spectra were taken shows that the high mass peaks are only visible in the early stages of the experiment when the deposited adenine layer is still fresh. This is why, from here on, we will concentrate our deconvolution efforts on the mass range m/z 12-57.

Our simulated mass spectra for the mass range m/z 12-57 fit on average within 3.4 ± 2.1 % for the 300 K experiments and 7.4 ± 1.8 % for the 150 K experiments. A positive value indicates that the best-fit simulations slightly underestimate the intensities of the mass spectra. For example, in the 300 K experiments, 3.4 ± 2.1 % of the mass spectrum's combined intensities are not attributed to any compound or its fragments. Further explanation as to why the cold temperature experiments are more under-fitted compared to the room temperature ones will be discussed in section 4.3. Figure 6 shows an example of a deconvoluted mass spectrum of the compounds found in the gas-phase when irradiating adenine with 10 keV O⁺ ions (bottom) and the residuals expressed as Δ normalized intensity (top). The black outline bars show

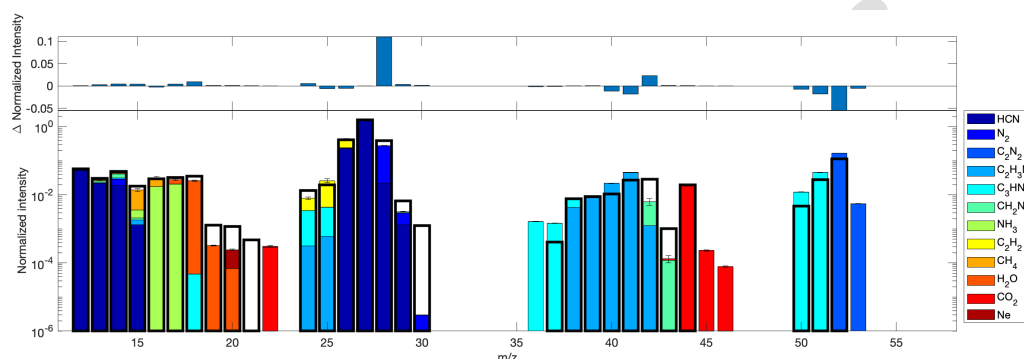


Figure 6: Mass spectrum in the range m/z 12-57 for the material sputtered into the gas-phase when irradiating an adenine thin-film with 10 keV O^+ -ions (bottom, black outline) with the median top 10 % of our best-fitting simulation (bottom, colored stacked bars) with 12 compounds. Residuals to each mass channel are shown in the top panel.

the measured mass spectrum while the stacked colored bars represent the median of the top 10 % of the best-fitting simulation which is normalized to the measured mass peak m/z 27. Each color represents one of the 12 compounds used in this simulation. In this example, the peak at m/z 28 shows highest Δ normalized intensity, making it the main contributor to the mass spectrum being slightly unter-fit. However, due to the Δ normalized intensity being relatively small compared to the summed intensity of the whole mass spectrum, this deconvolution still fits within 1.3 %.

Each following subsection presents the dependence of the results on the free parameters considered in the experiment, which include the kind of ion projectile used, the fluence, the temperature of the target adenine, and the energy of the ion beam. These results represent the MS-fraction for the mass range of m/z 12-57 and not quantitative mixing ratios of all gases in the chamber. Furthermore, the error bars in the following figures represent the statistical error of the n best-fit simulations and do not take into account the error of the intensity signals of the individual mass channels.

4.1. Influence of the ion projectile

Figure 7 shows the MS-fraction, defined as the relative contribution of each compound to the total signal in the mass spectrum, for all samples as a function of the 12 compounds identified in the mass spectrum. The energy, fluence and temperature for these particular MS-fractions are 10 keV, 0.5×10^{15} ions $\cdot$ cm $^{-2}$ and 300K, respectively.

HCN is by far the most abundant component found in the gas-phase with a MS-fraction range between 64.6 ± 5.2 % for Ne^+ and 74.6 ± 5.6 % for O^+ . HCN is followed by N_2 with a range of 18.4 ± 0.8 % and 13.8 ± 0.8 % for the same projectiles. Compounds like C_2H_2 , C_2N_2 , NH_3 , and H_2O can be found in the area of a single-digit in terms of percentage. The rest of the compounds are at a MS-fraction of <1 %. The results for neon in the gas-phase can be

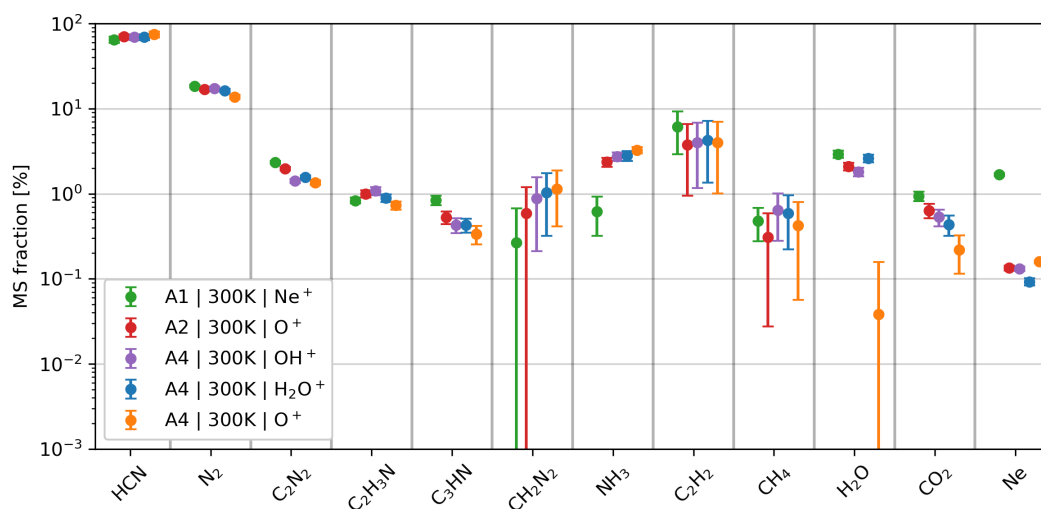


Figure 7: MS-fraction for the 12 compounds in the database for irradiations with different ions (Ne^+ , O^+ , OH^+ and H_2O^+) at an energy of 10 keV, temperature of 300 K and fluence of $0.5 \times 10^{15} \text{ ions} \cdot \text{cm}^{-2}$

viewed as the lowest threshold for detection, where samples irradiated with O-bearing projectiles yield MS-fractions of $\sim 0.1 \%$ which can not be correct as there should be no neon present in the gas-phase during these specific experiments.

Samples A2 and A4 were both irradiated with O^+ , however for some compounds, MS-fractions differ significantly (e.g. N_2). Here, MS-fractions differ by $\sim 5 \%$ for HCN and similar behavior can be seen for for nearly all compounds. The difference between both samples is the relative time of irradiation and therefore the difference in flux of the ion beam. Even though the first irradiation step of both samples reached a fluence of $0.5 \times 10^{15} \text{ ions} \cdot \text{cm}^{-2}$, the time of the irradiation steps was ~ 71 and ~ 236 seconds for A2 and A4, respectively. This corresponds to an ion flux more than three times lower for A4 than A2 resulting in a more unstable gas density in the chamber and weaker QMS signal. Fluxes can be viewed in Tables A.3 and A.4 in the appendix. Because of that, A4 irradiated with O^+ should not be taken into account when looking at the differences in MS-fraction between different projectiles.

Significant differences in MS-fractions between samples irradiated with Ne^+ or O-bearing projectiles can be observed for the compounds C_3HN , NH_3 and CO_2 . By far the largest difference between Ne^+ and the other projectiles can be seen in the amount of NH_3 sputtered into the gas-phase. Here, MS-fractions are more than three times larger when irradiating with O-bearing projectiles. When irradiating the sample with Ne^+ , the relatively strong H_2O signal likely stems from water contamination of the adenine powder, as water could not have been produced through irradiation. **This is especially visible in figure 8, where the MS fractions of water are shown for sample A1's 1st, 2nd and 3rd adenine layer. Here, the water content drops from the 1st to the 3rd layer, indicating that each successive reheating of the adenine powder progressively removes residual water from the sample.**

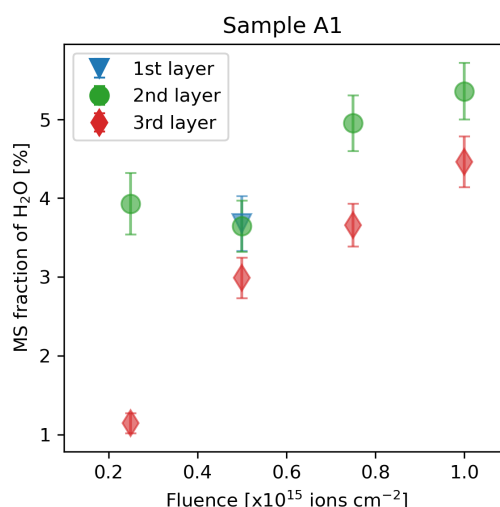


Figure 8: MS fractions of water as a function of fluence for sample A1's 1st, 2nd and 3rd adenine layer

The H₂O MS-fraction drops for sample A2 and A4, **compared to A1**, with the exception of A4 irradiated with H₂O⁺ where we see a relative increase compared to O⁺ (A2) and OH⁺ (A4). For other compounds detected in the gas phase, variations in MS-fractions fall within the bounds of mutual error margins, indicating no significant differences among them.

4.2. Effect of fluence

At varying fluence levels, we observe pronounced shifts in the relative contributions of different compounds to the mass spectral intensities, indicating substantial fluence-dependent compositional changes. Due to the averaging of intensities over the relative measurement time, the fluence represents a range for the specific irradiation step (e.g., 0–0.5 × 10¹⁵ ions . cm⁻²) rather than a fixed point value. However, for simplicity, we refer to them as discrete values (e.g., 0.5 × 10¹⁵ ions . cm⁻²) from here on. Figure 9 shows these changes for eight compounds for all mass spectra of sample A2 captured at 300 K. **Here, the results of two irradiation events (#5 & 6) with O⁺ and O²⁺ ions were combined, as certain fluence ranges were only observed either in one or the other irradiation event. Overall, the differences in MS fractions between the two events are mostly within their respective error margins. Only for smaller MS fractions, as seen for C₂N₂, do the differences between the two events show a broader spread, which nonetheless provides a general indication of the overall trend.** The compounds not shown are either not present in the gas-phase or show a high variability making it challenging to derive clear conclusions. HCN exhibits the most dramatic decrease falling from 71.3 ± 7.6% at the start of the irradiation to 39.9 ± 3.3 % at 10 × 10¹⁵ ions . cm⁻². As mentioned above, 39.9 ± 3.3 % is the average of the data acquired while irradiating from 5 × 10¹⁵ ions . cm⁻² to 10 ×

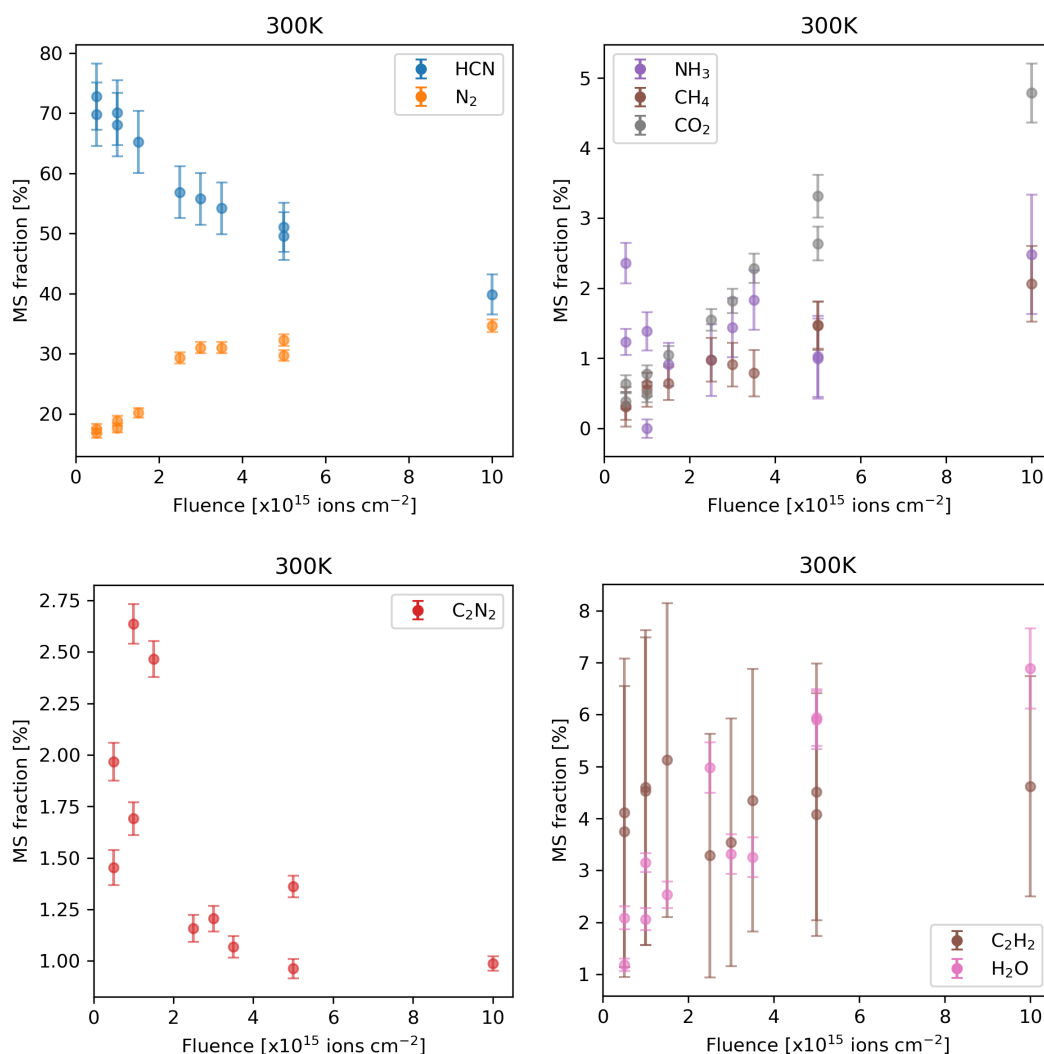


Figure 9: MS fractions as a function of fluence for sample A2 at 300K for the compounds HCN, N_2 (top left), NH_3 , CH_4 , CO_2 (top right), C_2N_2 (bottom left), and C_2H_2 with H_2O (bottom right)

10¹⁵ ions . cm⁻² (see Table A.3 irradiation event #6 step 6-7). Other compounds, such as C_2N_2 , also show a decrease, albeit to a lesser extent **while C_2H_2 show neither decrease nor increase**. N_2 , NH_3 , CH_4 and CO_2 show an increase with rising fluence. **These decreases and increases reflect changes in the relative contribution of each compound to the overall mass spectrum**. Hence, the decrease of e.g. HCN could be explained by: 1) The HCN abundance in the gas decreases, while abundances of other species increase. 2) The abundance of HCN increases but less than other species that also increase (e.g. N_2). 3) HCN decreases stronger than other species that decrease as well.

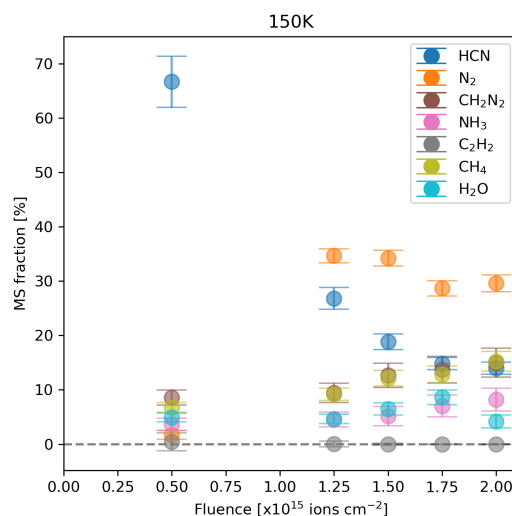


Figure 10: MS fractions as a function of fluence for the experiment **A3** at 150 K for the compounds HCN, N_2 , CH_2N_2 , NH_3 , C_2H_2 , CH_4 , H_2O

Figure 10 illustrates the results for the low-temperature sample, showing MS-fractions as a function of fluence for all gas-phase compounds detected during irradiation with O^{2+} ions at 20 keV. A similar trend to that observed at 300 K is evident: the MS-fractions for most species exhibit fluence-dependent changes. Initially, HCN dominates the mass spectrum, with $66.7 \pm 4.7\%$ at 0.5×10^{15} ions $\cdot \text{cm}^{-2}$, but it subsequently declines sharply to $14.0 \pm 1.1\%$ at 2×10^{15} ions $\cdot \text{cm}^{-2}$. N_2 , with $1.7 \pm 0.8\%$ at the start of irradiation, increases to $34.7 \pm 1.3\%$ at a fluence of 1.25×10^{15} ions $\cdot \text{cm}^{-2}$, followed by a decrease to $29.6 \pm 1.5\%$ at 2×10^{15} ions $\cdot \text{cm}^{-2}$. CH_4 , NH_3 , and H_2O present an increase over time as well. The compound C_2H_2 has the lowest abundance with $0.5 \pm 1.7\%$ at the start with none being detected by the end of the experiment. All the remaining compounds from the database could not be detected.

4.3. Temperature

The deconvolution of mass spectra acquired at 150 K proved significantly more challenging compared to those taken at 300 K, because peak intensities reduced by an order of magnitude at low temperature compared to room temperature. The reason for this is that the abundance of sputtered material is influenced by temperature, as demonstrated by Davis et al. (2021). For instance, Chandra et al. (2025) reported that the sputtering yield of CO_2 from irradiated organic–water mixtures is three times lower at 80 K compared to 100 K and 120 K. As a result, certain smaller mass peaks fell below the noise threshold, making accurate analysis more challenging and leading to larger error margins. Despite this, we observe a significant difference in the MS fractions when comparing the measurements conducted at 150 K versus 300 K.

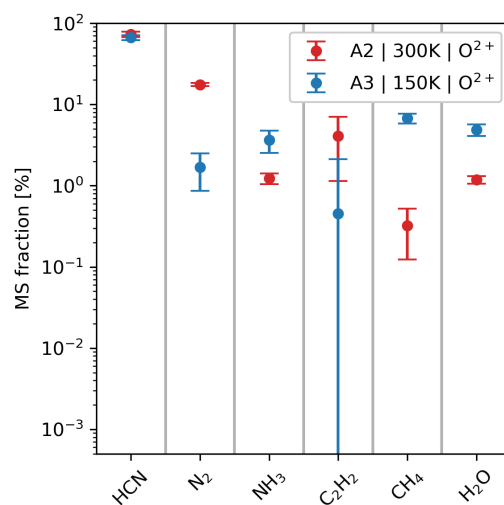


Figure 11: MS-fraction for 7 compounds for different ions at an energy of 20 keV, temperature of 150 and 300 K and fluence of 0.5×10^{15} ions $\cdot$ cm⁻²

Similarly to Figure 7, Figure 11 presents the MS fractions for all measured compounds. However, instead of comparing different ion projectiles, this figure illustrates the differences between samples A2 and A3, which were both irradiated with 20 keV O₂⁺ ions at 0.5×10^{15} ions $\cdot$ cm⁻², but at temperatures of 300 K and 150 K, respectively. Almost all compounds exhibit variations in their MS fractions when comparing the two different temperatures. The only exception is HCN, the primary component of the gas mixture, which consistently constitutes approximately 70% of the MS signal. Compounds like N₂ and C₂H₂ show higher MS fractions in the 300 K sample compared to the 150 K. The opposite is true for NH₃, H₂O and CH₄. All other compounds from Table 1, have not been found in the cold temperature experiment.

4.4. Energy

The samples A1 and A2 were irradiated with two different ion beam energies: 10 and 20 keV. Upon examining the impact of these varying energies on the MS fraction, it is challenging to draw definitive conclusions regarding their influence. The reason for this is, in part, due to an insufficient amount of data points. Based on the available data points, no significant changes in MS fractions are observed, likely due to the energy difference being too small.

5. Discussion

5.1. Ambiguities in the molecular interpretation of mass channel m/z 44

Interpreting mass spectra of complex chemical mixtures presents inherent challenges due to the overlapping fragmentation patterns of different molecular compounds. While certain mass channels may initially appear to correspond to specific molecules, fragmentation during ionization produces multiple peaks, leading to ambiguities in molecular identification. Consequently, a given mass channel may not uniquely correspond to a single molecular species. This section discusses the difficulties associated with molecular interpretation for specific mass channels.

We tested C_3H_8 , CO_2 and N_2O as potential contributors to the signal at m/z 44. Although these compounds have the same nominal mass, their fragmentation patterns differ significantly: CO_2 and N_2O exhibit their main peak at m/z 44, while C_3H_8 shows a dominant fragment at m/z 29. Best-fit simulations incorporating each compound were performed. Given the number of hydrogen atoms in adenine, the formation of a highly hydrogenated compound like C_3H_8 is chemically implausible under sputtering conditions. This reasoning also applies to other hydrogen-rich species with similar mass, such as C_2H_6N , for which no fragmentation pattern was available to include in our fits. Another candidate for the m/z 44 signal, N_2O , is chemically more consistent with nitrogen-rich fragmentation pathways. However, simulations including N_2O led to higher MS fractions in the Ne^{q+} experiments compared to those with O-bearing projectiles. Simulations including only CO_2 produced similarly unexpected high MS-fractions in the Ne^{q+} irradiation experiments, surpassing those observed in experiments using oxygen-bearing projectiles (see Figure 7). As neither the adenine sample nor the Ne^{q+} projectiles contain oxygen, the formation of CO_2 in this set-up is surprising. The relatively high MS-fractions across all projectile types together with an oxygen-free system suggest the attribution may be incorrect. Small error bars indicate statistical confidence in the measurement, but they do not necessarily rule out misassignments in the spectral deconvolution. However, as described in the introduction, many studies have shown that water ices mixed with organic (oxygen-free) compounds lead to the sputtering of CO_2 (Mennella et al., 2004; Gomis and Strazzulla, 2005; Maté et al., 2024). From the relatively strong H_2O signal in the Ne- projectile experiment, we know that the adenine is highly contaminated with water. This suggests that we could have a similar process of CO_2 formation at hand, in which the formation of CO_2 is limited to the interaction between the sample and its contamination being excited by the energy delivered via irradiation. Hence, the sputtering of CO_2 is not a direct product of the ion projectiles bonding with atoms from the adenine. Given these ambiguities, we regard the identification of CO_2 at m/z 44 as the only valid candidate, however, its origin is the result of unwanted water contamination interacting with the adenine.

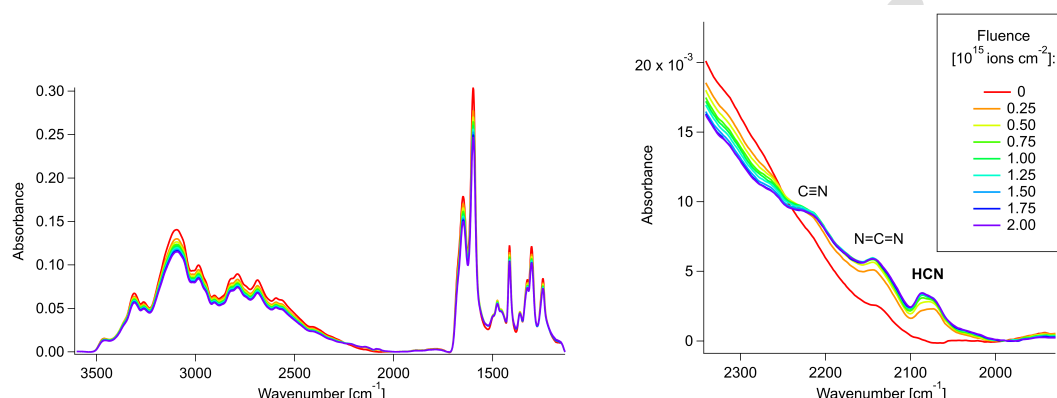


Figure 12: IR-spectra of sample A3 for the fluences from 0 to 2×10^{15} ions $\cdot$ cm $^{-2}$; full spectrum (left), zoomed-in area at 2340-1930 cm $^{-1}$, highlighting the growth of new bands with progressing irradiation.

5.2. The role of gas-phase species in the formation of complex organic matter

The most significant factor impacting changes in MS-fractions is the irradiation fluence. Nearly all presented species show either an increase or decrease in MS-fractions with rising fluence. Figure 12 shows combined IR-spectra for sample A3 at 150 K. The left, shows the full wavenumber range while the right shows the zoomed-in wavenumber range at 2340-1930 cm $^{-1}$ of the same spectra. Here, each line represents the absorbance over the chosen wavenumber range for fluences from 0 to 2×10^{15} ions $\cdot$ cm $^{-2}$. Normally, during the irradiation of adenine, we observe a gradual decrease of absorbance over the time of irradiation as the sample is being destroyed. In Figure 12, this can be observed from ~ 3500 to ~ 2300 cm $^{-1}$ and $\lesssim 1700$ cm $^{-1}$. However, at 2250-2000 cm $^{-1}$ we see an increase of absorbance over time which indicates the creation of new material. Three new peaks can be observed here at 2216, 2143 and 2088 cm $^{-1}$ which correspond to C $\equiv$ N, N=C=N and HCN, respectively. The peak at 2088 cm $^{-1}$ is only observed at 150 K and corresponds to HCN-ice forming on the surface of the sample (Moore and Hudson, 2003; Noble et al., 2013; Gerakines et al., 2022). In this IR-spectrum, we see a significant increase of absorbance between 0 and 0.25×10^{15} ions $\cdot$ cm $^{-2}$ indicating that the formation of HCN-ice is manifesting with the on-set of irradiation and slows later in the experiment.

The increase of absorbance for the nitrile band is an indicator for complex polymer-like organic molecules forming from adenine during irradiation. These novel molecules were initially proposed by Poch et al. (2014) and are likely to have two key effects on the MS fractions. Firstly, they are believed to enhance the **radiation**-stability of adenine, thereby reducing the sputtering of material into the gas phase. Secondly, as new complex secondary material forms, the sputtering rate of HCN and C $_2$ N $_2$ decreases, likely due to the increased **radiation**-stability provided by the newly formed material. This is indicated by a decrease in MS-fractions of these species with rising fluence. These species are

more readily sputtered from fresh adenine, whereas their release becomes less efficient as the irradiation progresses and the sample undergoes chemical restructuring forming complex secondary material.

Based on prior experiments in which adenine was irradiated with neon and oxygen ions, high resolution mass spectrometry analysis on the solid sample, as well as IR-spectroscopy, indicate the formation of new complex organic molecules (NCOM)(Matuszewski et al., 2025). These experiments show that ion irradiation induces molecular restructuring, leading to the synthesis of up to 2000 NCOM per sample. All NCOM exhibit a high degree of aromaticity with aromaticity equivalent values over 2.7, classifying them as condensed aromatic structures or PANHs (Yassine et al., 2014). Furthermore, NCOM demonstrate efficient nitrogen incorporation with the N/C ratios being close, however, still smaller compared to the starting material adenine. The mechanisms underlying the formation of these molecules remain only partially understood. The presence of all the measured compounds in the gas phase indicates that they are a direct product of adenine decomposition, where its molecular structure is broken apart and reorganized into new molecular frameworks. However, some of these compounds may also remain on the surface or subsurface and contribute to the formation of NCOMs. Additionally, the loss of N_2 and other nitrogen-rich compounds explains the slightly lower N/C ratio compared to adenine in the newly formed complex organic molecules. This suggests that the irradiation process selectively removes nitrogen-rich fragments, leading to a final product with a different elemental composition than the original adenine. **We observe that the decrease in sample thickness slows significantly with progressing irradiation (see table A.3). For instance, after the first deposition in sample A2 the thickness decreases dramatically by ~ 45 nm after the first irradiation step, while the next irradiation step only removes ~ 13 nm, decreasing further with more irradiation steps. This behavior is consistent with the formation of NCOM, which have been shown to increase the radiation-stability of adenine by protecting it from further degradation (Matuszewski et al., 2025).**

5.3. Implications for organics in Titan's atmosphere

Nearly all compounds that were sputtered into the gas-phase during our experiments can be found in Titan's atmosphere (Hörst, 2017). The exception is CH_2N_2 which has not been detected in its atmosphere. However, for CH_2N_2 , upper limits of abundance have been determined from observations (Nixon et al., 2010; Teanby et al., 2013; Khelifi et al., 1996). **The detection of CH_2N_2 in our experiments is consistent with nitrogen-rich fragmentation pathways of adenine (Shafranyosh et al., 2015), and with the presence of diazo-ion $CH_2N_2^+$ signals reported experimentally in Titan aerosol analogs through the reaction $N_2^+ + CH_3$ (Carrasco et al., 2022).** Among the trace compounds found in Titan's atmosphere, C_2H_4 and C_2H_6 are of relative high abundance, however we could not definitely attribute them to our mass spectra (see section 5.1), suggesting that they are not being produced via oxygen irradiation of PANHs.

Figure 13 shows a schematic overview of the chemical processes in Titan's atmosphere that lead to the formation of aerosols. Here, Figure 4 from Waite et al. (2007) is supplemented and modified to fit the process of sputtering from this study. Complex organics in the mass range of <300 Da (e.g. adenine) are irradiated with low energy ions triggering the sputtering of compounds that are similar to the ones resulting from the dissociation of N_2 and CH_4 . Notably, both N_2 and CH_4 are also produced through sputtering processes during the experiment. This indicates that ion irradiation contributes to a feedback mechanism, where sputtered species can further participate in the atmospheric chemistry of Titan's atmosphere. This irradiation-induced feedback process has not been investigated before and is presented here for the first time.

Recent studies suggest that there is a discrepancy between observed and modeled mixing ratios of HCN in Titan's upper atmosphere. Current model calculations estimate HCN mixing ratios at an altitude of 900 km to be in the range of around 1×10^{-4} to 6×10^{-4} (Lavvas et al., 2008; Krasnopolsky, 2009; Hébrard et al., 2012; Loison et al., 2015; Vuitton et al., 2019), whereas observations indicate significantly higher values, ranging from approximately 5×10^{-4} to 3×10^{-3} (Vervack Jr et al., 2004; Gurwell, 2004; Shemansky et al., 2005; Kim et al., 2005; Adriani et al., 2011). These models do not yet consider the sputtering of HCN from PANHs, as our irradiation experiments demonstrated. These suggest that similar sputtering processes could take place in Titan's upper atmosphere and could serve as an additional source of HCN, among other compounds. However, considering that the difference in observational and modeling mixing ratios for HCN is $\sim 1.5 \times 10^{-3}$ that would amount to a density of $\sim 7.24 \times 10^7$ molecules cm^{-3} (10^{-4} Pa pressure and 150 K temperature at ~ 900 km altitude from Hörst (2017)) that are unaccounted for. Temperature and pressure are corresponding to the condition of Titan's atmosphere at ~ 900 km altitude (Hörst, 2017). Assuming a density of $2-3 \times 10^4$ particles cm^{-3} for PANH molecules (López-Puertas et al., 2013), each individual PANH molecule would need to sputter approximately 3,000 HCN molecules in order to account for the gap between observations and modeling efforts. Given that PANH usually contain < 100 C atoms, the contribution of HCN production via ion-induced sputtering from PANHs can, at best, be considered minor. However, instead of PANH, larger and more massive negative ions may be susceptible to ion-induced sputtering and could represent another source. Coates et al. (2007) quantified the density of such negative ions with masses of $< 10,000$ amu to be ~ 200 cm^{-3} . Assuming this density, each negative ion would have to sputter 362,000 HCN molecules to account for the gap, an amount that seems highly unrealistic. **Taking a representative ion precipitation flux of 10^6 ions $cm^{-2} s^{-1}$ (Hartle et al., 2006a,b), our major results correspond to a fluence of 0.5×10^{15} ions cm^{-2} , which is equivalent to an irradiation timescale of approximately 5×10^8 s, or roughly 16 years. At most, the fluence reaches 20×10^{15} ions cm^{-2} , which corresponds to roughly 630 years. However, these timescales are not central to the conclusions of our study. Sputtering begins immediately upon the onset of irradiation, and identifying the species released into the gas phase from these earliest stages is the key result of this work. The fluence-dependent evolution we report further characterizes how this sputtered**

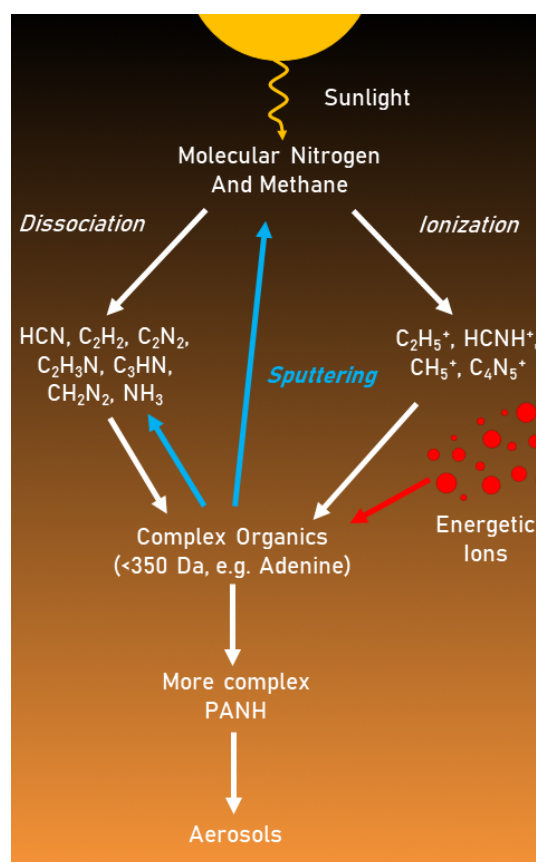


Figure 13: Schematic overview of the chemical processes leading to the formation of aerosols in Titan's atmosphere by Waite et al. (2007), modified to include the process of sputtering (blue) induced by energetic ions (red).

inventory develops with dose, but the identification itself does not depend on the total accumulated fluence or its equivalent real-time duration on Titan.

Future calculations of absolute sputtering yields, based on cross-section calculations, together with the determination of precise mixing ratios of the sputtered species will be essential for quantifying the contribution of sputtering to modelling efforts.

6. Summary and Conclusion

In this study, we have irradiated 4 multi-layered adenine thin-film samples with Ne^{q+} , O^{q+} , OH^{q+} and H_2O^{q+} -ions with energies of 10 or 20 keV at the HUN-REN ATOMKI facility in Debrecen, Hungary. Adenine was chosen as a simulant for complex organic molecules, namely PANHs, found in Titan's atmosphere. During the course of the experiment, QMS-measurements of the compounds which were sputtered into the gas phase have been performed. The

deconvolution of the mass spectra was done using a Monte-Carlo approach, resulting in MS-fractions for 12 different chemical species. The following conclusions can be made:

1. The ion irradiation of adenine leads to the sputtering of HCN, N₂, NH₃, C₂H₂, C₂N₂, CH₄, CH₂N₂, C₃HN and C₂H₃N. The sputtering of H₂O can be mostly attributed to the sputtering of water contamination of the adenine thin-film. Similarly, the origin of CO₂ in the gas-phase originates from purely irradiation-induced chemistry between adenine and water contamination.
2. The sputtered compounds like HCN, N₂, C₂H₂ and CH₄ are key intermediates in Titan's atmospheric chemistry. This suggests that sputtering not only contributes to the molecular inventory of the atmosphere but also acts as a feedback mechanism, replenishing reactive species that can further participate in the synthesis of complex organics and aerosols.
3. With increasing fluence, the abundances of HCN and C₂N₂ in the gas phase decrease, indicating that their sputtering efficiency is higher in fresh adenine but decreases as irradiation-induced chemical restructuring and the formation of secondary material progress, while simultaneously, the abundances of N₂, NH₃, and CH₄ in the gas phase increase.
4. Larger species like C₅H₅N₅, C₄H₄N₄ and C₃H₃N₃ are predominantly sputtered into the gas phase during the initial stages of irradiation, when the adenine thin films remain unaltered and secondary material formation has not yet occurred.
5. The sputtering of HCN is not included in chemical models of Titan's atmosphere, which might explain the lower estimates of HCN abundance in Titan's upper atmosphere in said models. However, the amount of PANH and high-mass ions in Titan's upper atmosphere as well as the amount of sputtered HCN is not sufficient to explain this gap between observations and models. Therefore, the effect of material sputtered of PANHs and high-mass ions can be considered minor.
6. Oxygen-bearing compounds like CO and CO₂, which play an integral part in the chemistry of Titan's atmosphere, are unlikely to be the result of oxygen ion irradiation of PANH-like molecules at 10-20 keV. However, this behavior may be different for other PANHs or energies.

The accuracy of our results could be enhanced by calculating instrument-specific ionization cross sections for several compounds that are presented in this study. For instance, temperature-programmed desorption (TPD) can be employed, wherein a solid sample is gradually heated while the desorbed species are monitored using a mass spectrometer as a function of temperature. This approach may also allow the extrapolation of ionization cross sections for hazardous compounds, such as HCN, which are otherwise challenging to handle directly (Díaz, 2024). Such calculations would allow for the determination of accurate mixing ratios which are vital for follow-up modeling efforts involving complex organic matter in Titan's atmosphere.

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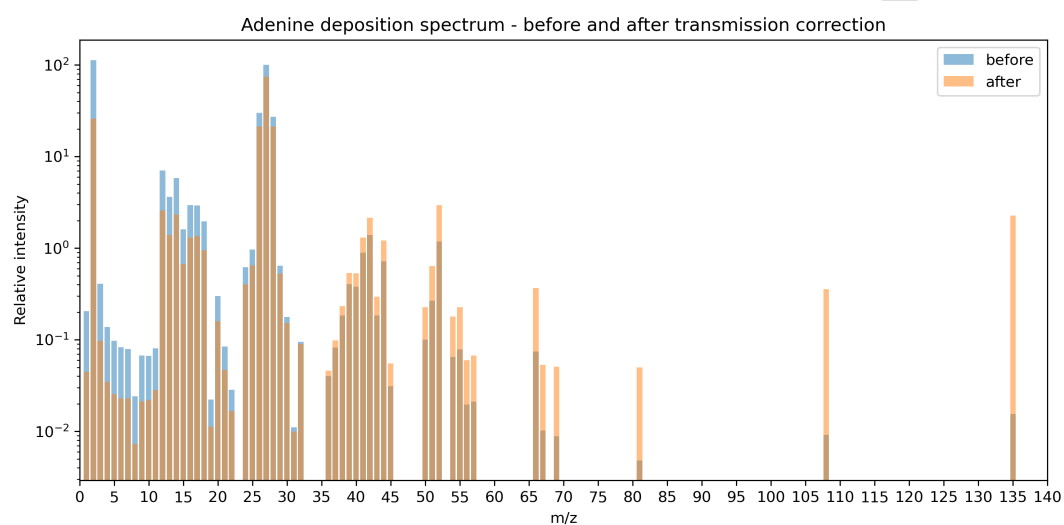


Figure A.14: Mass spectra of the adenine deposition before (blue) and after (orange) the transmission correction was applied

823 **A. Supplementary**

Table A.3

List of samples (A1 and A2) with irradiation events, steps, ions used, as well as fluences, energies, temperatures and thicknesses of the adenine thin-films; irradiation steps marked with a "*" have deconvoluted mass spectra

	Ion	irradiation event	Energy [keV]	Irradiation step	Fluence [$\times 10^{15}$ ions cm^{-2}]	Flux [10^{12} ions cm^{-2} s]	Temperature [K]	Thickness [nm]	QMS detector
A1 (18.03.2024)	deposition						300	261 $\pm$ 28	FC
								277 $\pm$ 30	
	Ne ²⁺	#1	20	1	0.005	2.03		274 $\pm$ 30	FC
				2	0.01	1.91		269 $\pm$ 29	
				3	0.02	2.06		262 $\pm$ 28	SEM
				4*	0.50	2.63		190 $\pm$ 21	
	deposition							464 $\pm$ 50	FC
								450 $\pm$ 49	
	Ne ²⁺	#2	20	1*	0.25	2.49		424 $\pm$ 46	SEM
				2*	0.50	2.39		413 $\pm$ 45	
				3*	0.75	2.35		402 $\pm$ 43	
				4*	1.00	2.33		392 $\pm$ 42	
	deposition							605 $\pm$ 65	FC
								945 $\pm$ 102	
	Ne ²⁺	#3	20	1*	0.25	2.38		889 $\pm$ 96	SEM
				2*	0.50	2.31		867 $\pm$ 94	
				3*	0.75	2.27		849 $\pm$ 92	
				4*	1.00	2.24		836 $\pm$ 90	
	deposition							1444 $\pm$ 156	FC
	Ne ⁺	#4	10	1*	0.25	2.41		1426 $\pm$ 154	SEM
				2*	0.50	2.36		1417 $\pm$ 153	
				3*	0.75	2.32		1410 $\pm$ 152	
				4*	1.00	2.28		1406 $\pm$ 152	
A2 (19.03.2024)	deposition						300	576 $\pm$ 62	FC
	O ²⁺	#5	20	1*	0.50	3.09		531 $\pm$ 57	SEM
				2*	1.00	3.02		518 $\pm$ 56	
				3	1.50	3.04		506 $\pm$ 55	
				4	2.00	3.01		498 $\pm$ 54	FC
				5*	2.50	3.05		493 $\pm$ 53	
				6*	3.00	3.04		486 $\pm$ 53	
				7*	3.50	3.04		481 $\pm$ 52	
				8*	5.00	3.00		469 $\pm$ 51	
				9	8.50	2.96		449 $\pm$ 49	FC
	deposition							493 $\pm$ 53	FC
								840 $\pm$ 91	
	O ⁺	#6	10	1*	0.50	6.82		1087 $\pm$ 118	SEM
				2*	1.00	6.18		1050 $\pm$ 114	
				3*	1.50	5.91		1036 $\pm$ 112	
				4	2.00	5.84		1026 $\pm$ 111	FC
				5	2.50	5.72		1018 $\pm$ 110	
				6*	5.00	5.71		1009 $\pm$ 109	SEM
				7*	10.00	5.28		980 $\pm$ 106	
				8	15.00	5.12		955 $\pm$ 103	FC
				9	20.00	5.02		939 $\pm$ 102	
								926 $\pm$ 100	FC

Table A.4

List of samples (A3 and A4) with irradiation events, steps, ions used, as well as fluences, energies, temperatures and thicknesses of the adenine thin-films; irradiation steps marked with a "*" have deconvoluted mass spectra

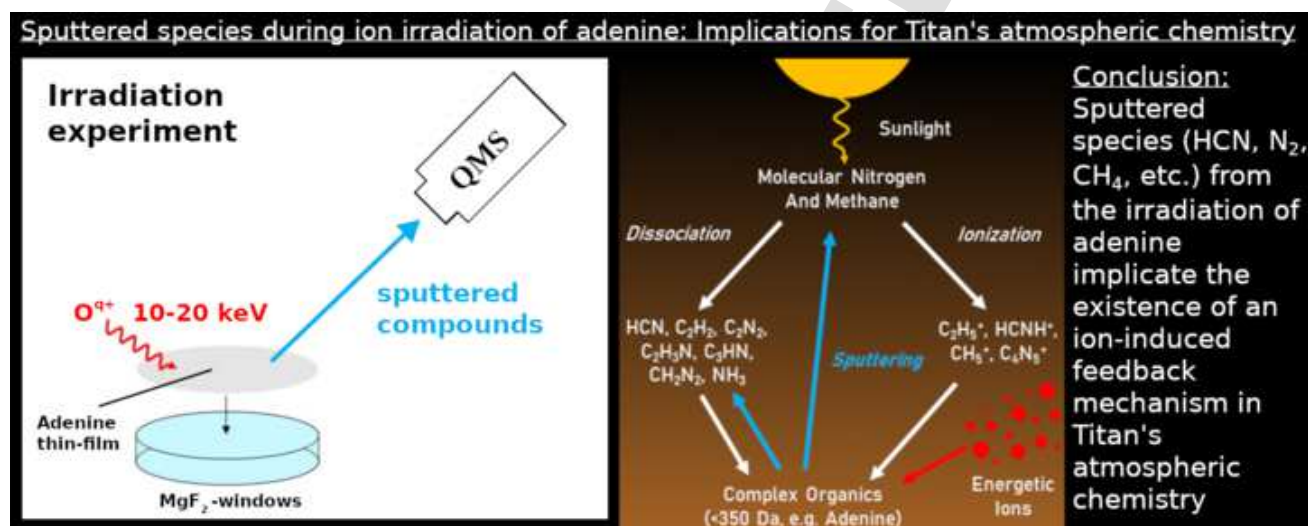
	Ion	irradiation event	Energy [keV]	Irradiation step	Fluence [× 10 ¹⁵ ions cm ⁻²]	Flux [× 10 ¹² ions cm ⁻² s]	Temperature [K]	Thickness [nm]	QMS detector	
A3 (20.03.2024)	deposition						150	170 ± 18	FC	
								312 ± 34		
	O ²⁺	#7	20	1	0.25	2.44		296 ± 32	SEM	
				2*	0.50	2.35		289 ± 31		
				3	0.75	2.28		283 ± 31	FC	
				4	1.00	2.21		279 ± 30		
				5*	1.25	2.18		274 ± 30	SEM	
				6*	1.50	2.14		270 ± 29		
				7*	1.75	2.11		266 ± 29		
				8*	2.00	2.09		264 ± 29		
	reheating 1K/min							150-300		FC
	A4 (22.03.2024)	deposition						300	424 ± 46	FC
OH ⁺		#8	10	1*	0.50	5.3	382 ± 41		SEM	
				2*	1.00	5.18	361 ± 39			
				3*	1.50	5.09	342 ± 37			
				4	2.00	5.04	328 ± 35		FC	
				5	2.50	4.94	314 ± 34			
				6	3.00	4.86	302 ± 33			
deposition						536 ± 58	FC			
						688 ± 74				
H ₂ O ⁺		#9	10	1*	0.50	6.88	669 ± 72		SEM	
				2*	1.00	6.58	661 ± 72			
				3*	1.50	6.44	655 ± 71			
				4	2.00	6.40	651 ± 70		FC	
				5	2.50	6.29	647 ± 70			
				6	3.00	6.20	644 ± 70			
deposition						832 ± 90	FC			
						1022 ± 111				
O ⁺		#10	10	1*	0.50	2.09	983 ± 106		SEM	
				2*	1.00	1.98	964 ± 104			
				3*	1.50	1.90	947 ± 102			
				4	2.00	1.85	934 ± 101		FC	
				5	2.50	1.79	925 ± 100			
	6			3.00	1.75	916 ± 99				

Table A.5

Initial database that has been reduced to 12 compounds over the course of the trial deconvolutions

Nr.	Compound name	Compound formula	Ionization cross section [$\text{\AA}^2$]
1	Hydrogen cyanide	HCN	3.442
2	Molecular nitrogen	N ₂	2.482
3	Acetylene	C ₂ H ₂	4.402
4	Hydrogen peroxide	H ₂ O ₂	3.742
5	Water	H ₂ O	2.642
6	Ammonia	NH ₃	3.472
7	Methane	CH ₄	4.432
8	Propane	C ₃ H ₈	10.212
9	Diazomethane	CH ₂ N ₂	5.372
10	Cyanogen	C ₂ N ₂	5.342
11	Acetonitrile	C ₂ H ₃ N	6.332
12	Neon	Ne	0.584
13	Cyanoacetylene	C ₃ HN	6.302
14	Molecular oxygen	O ₂	2.282
15	Carbon dioxide	CO ₂	3.712
16	Argon	Ar	2.96
18	Methylamine	CH ₃ N	6.362
19	Nitrous oxide	N ₂ O	3.582
20	Acetamide	C ₂ H ₅ NO	8.892
21	Ethylene oxide	C ₂ H ₄ O	6.962
22	Acetone	C ₃ H ₆ O	9.852
23	Formamide	CH ₃ NO	6.002
24	Formaldehyde	CH ₂ O	4.072
25	Methane isocyanato	C ₂ H ₃ NO	7.432
26	Ethylene	C ₂ H ₄	5.862
27	Carbon monoxide	CO	2.612
28	Hydrogen azide	N ₃ H	4.412
29	Popanenitrile	C ₃ H ₅ N	9.222
30	Adenine	C ₅ H ₅ N ₅	16.882
31	Diacetylene	C ₄ H ₂	7.262
32	Formic acid	CH ₂ O ₂	5.172
33	Methanimine	CH ₃ N	4.902
34	Aminoacetonitrile	C ₂ H ₄ N ₂	8.262
35	Venylacetylene	C ₄ H ₄	8.722
36	Ethane	C ₂ H ₆	7.322
37	Allene	C ₃ H ₄	7.292
38	Propyne	C ₃ H ₄	7.292
39	3-Amino-4-pyrazolecarbonitrile	C ₄ H ₄ N ₄	13.522
40	1,3,5-Triazine	C ₃ H ₃ N ₃	10.162
41	1,2,4-Triazine	C ₃ H ₃ N ₃	10.162

Graphical Abstract

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Author contributions: CRediT

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Véronique Vuitton: Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Validation, Writing - review and editing

Richárd Rácz: Methodology, Validation, Data curation, Writing - review and editing

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: