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Ion radiation in icy space environments: Synthesis and radioresistance of complex organic molecules

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ABSTRACT

Ices are omnipresent in cold regions in space on, e.g., comets, dust grains, transneptunian objects, surfaces of planets and their satellites. The dominant molecule in such ices is water, but also other small molecules or even complex organic molecules (COMs) may be present. Ionizing radiation (UV photons, electrons, ions from cosmic rays or solar wind) induces several physico-chemical processes such as radiolysis. The fragmentation of initial molecules followed by chemical reactions between radicals may lead to formation of new molecules. Furthermore, also implanted projectiles can contribute to chemistry by forming new molecular species. Other observed effects include structural changes (compaction, amorphization) and desorption (sputtering) of particles from the surface. At CIMAP (Caen, France), using the different beam lines of the GANIL facility, and at GSI (Darmstadt, Germany), the interaction of swift highly charged heavy ions with astrophysical ices has been studied in a wide projectile energy range from keV to GeV. Here, two examples of our studies on astrophysical and astrochemical applications will be discussed in detail: 1) the synthesis of COMs under irradiation of ices made of small molecules, and 2) radiosensitivity of COMs such as pyridine, glycine and adenine, both for isolated molecules in the gas phase and in condensed phase. Special emphasis is given on pyridine and pyridine in water matrix.

1. INTRODUCTION

Complex organic molecules (COMs), including amino acids and nucleobases, can be formed under space conditions (low temperatures, typically 10–150 K) following radiolysis of mixtures of condensed small molecules (H_2O, CO, CO_2, CH_3OH, NH_3, HCOOH and others) by vacuum UV irradiation and by ion bombardment in laboratory simulations,[1–3] and references therein). Such environments exist in the interstellar medium (ISM), in particular in dense molecular clouds, and in the outer solar system, where molecules will freeze out, e.g., on dust grains or surfaces of Transneptunian objects. Similar conditions are also found at frozen surfaces in the solar system such as comets, asteroids and on several satellites of the giant planets. Indeed, glycine (NH_2CH_2COOH), the simplest amino acid,

has recently been observed among the compounds collected by the space probe STARDUST around comet Wild 2.[4] Furthermore, amino acids and nucleobases were found in the Murchison meteorite.[5] A plethora of COMs have been detected by ESA's ROSETTA mission on comet 67P/Churyumov–Gerasimenko,[6] among them several aromatic molecules and glycine.[7]

Organic matter has been and is constantly being delivered from space to Earth by, e.g., micrometeorites[1,3,8] and thus may have contributed to the emergence of life. Once COMs have been synthesized in outer space following radiolysis, they are also exposed to ionizing radiation fields. The question arises thus how long they can survive in space. It is therefore necessary to study their radiation resistance in order to determine the survival times

of complex molecules. In the following, we present laboratory studies performed at different beamlines of GANIL (Caen/France) and GSI (Darmstadt/Germany). The effects of heavy ion irradiation on ices of astrophysical interest have been studied within our collaborations since about ten years. Radiolysis of numerous simple ices and mixtures of up to four simple molecules were studied. Irradiation not only leads to fragmentation of initial molecules, but also to synthesis of COMs such as glycine. We also studied to what extend implanted projectiles contribute to the synthesis of molecules. A recent review of those results can be found in Ref. 2, the results presented below are a follow-up of sections 5.5 and 5.6 of Ref. 2.

In Sec. 2, briefly, the experimental procedures are presented. In Sec. 3, the synthesis of COMs by UV and (heavy) ion irradiation is discussed. The stability and radiation resistance of COMs both as isolated molecules (gas phase fragmentation) and in condensed phase are subject of Secs. 4 and 5, respectively. Finally, recent results obtained with pyridine and pyridine-water mixtures at low temperature are shown in Sec. 6. Such experiments address the (still open) question if the presence of water, which is omnipresent in space environments, has a protective effect or enhances radiosensitivity.

2. EXPERIMENTAL: LABORATORY SIMULATION OF RADIATION EFFECTS IN OUTER SPACE

To simulate cosmic radiation effects (by UV photons, electrons or ions) on condensed matter (like ice-covered dust grains or icy surfaces on larger objects) in space, one needs a suitable radiation source (UV lamp or synchrotron, ion accelerator). At GANIL, we used four different ion beam lines: ARIBE (e.g., O at 90 keV), IRRSUD (e.g., C 12 MeV and Xe 92 MeV), SME (heavy ions of about 10 MeV/u), HE (e.g., Fe 70 MeV/u). At GSI, ion irradiation experiments were performed at the M-Branch of UNILAC (see Sec. 5). It is important to perform experiments with similar samples at different accelerator facilities with different experimental set-ups in view of assuring the reproducibility of the results. A high vacuum chamber connected to those lamps or accelerator beamlines is necessary so that the radiation can reach the target without being stopped, and to limit deposition of contamination by absorption of residual gas molecules (e.g., water).

The base pressure at room temperature of such equipment is of the order of $2 \cdot 10^{-7}$ to $2 \cdot 10^{-9}$ mbar, dropping to $5 \cdot 10^{-8}$ to less than $5 \cdot 10^{-10}$ mbar with the target cooling system working. To obtain ultrahigh vacuum pressures of the order of 10^{-9} mbar or below in the irradiation chamber, it is necessary to bake out the vacuum system. Furthermore, it may be necessary to separate it from the accelerator beam lines by differential pumping stages, if the vacuum in the beam lines, which is often the cases, is in the high vacuum range of about 10^{-7} mbar.

A cryostat (e.g., liquid nitrogen or helium, or closed-cycle helium with a compressor) connected to cold head target holder is needed to provide low temperatures (typically 10–15 K). Icy layers are prepared by deposition of gases or mixtures of such on a cold substrate. A heating and temperature regulation system allows to keep the samples also at other fixed temperatures up to 300 K, and to perform a controlled slow annealing procedure.

Infrared spectroscopy is a widely used technique both for space and laboratory observations.[9] In most of our experiments, Fourier-transform infrared absorption spectroscopy (FTIR) was used. In this case, IR transparent windows serve as substrate for the deposition of small molecules or mixtures of such *in situ*. COMs may be prepared *ex situ* from powders dissolved, e.g., in methanol, dropping them on the substrate, and then evaporating the solvent by heating. Also, vapor deposition using an effusive oven was used for COMs like nucleobases. The experimental procedures of sample preparation, FTIR spectroscopy and irradiation procedures with special emphasis on precise dosimetry have been described in numerous papers (see Refs. 2 and 10–12 and references therein). We note that also UV-visible spectroscopy is a widely used technique and available at CIMAP-GANIL.[12,13]

Experiments with gas phase target molecules rely on gas targets such as effusive needles, (cold) supersonic jets and electrospray sources. In gas phase, the structure of biomolecules can be investigated by means of IR laser spectroscopy. Coupling mass spectrometry to infrared spectroscopy appears to be very promising in order to identify some intrinsic properties of small ionic model systems that could be relevant for understanding more complex mechanisms in molecular biology. To give an example, specific interactions and structures of gas-phase vancomycin antibiotics with cell-wall precursor can be investigated through InfraRed MultiPhoton Dissociation (IRMPD) spectroscopy using a free electron laser.[14]

Other techniques (available at CIMAP-GANIL) allow the identification of particles sputtered from the surface emitted by mass spectrometry. Most set-ups can be equipped with a QMS (quadrupole mass spectrometer, for a recent example see Ref. 15). Furthermore, imaging XY-TOF-SIMS (time of flight secondary ion mass spectrometry) is available; among other techniques, this set-up is described in Ref. 16. This set-up, now equipped with a cold head and sample heater (10 to 300 K), and a quartz microbalance allowing to measure the thickness of deposited layers and also mass loss (sputtering yields), was also used to study astrophysical silicates.[17]

3. RADIOLYSIS OF ICES: SYNTHESIS OF COMPLEX ORGANIC MOLECULES

Irradiation by energetic photons or ions results in excitation and ionization of target molecules. The fragmentation of the latter, often characterized by a "destruction cross section",[10] results in the appearance of new ("daughter") molecules. On the one hand, fragments of the initial molecules are observed, or newly formed species from reacting radicals formed by radiolysis. Many laboratory experiments have been performed with ices containing small molecules (e.g., H_2O, NH_3, CH_4, CO, CO_2, CH_3OH, $HCOOH$, etc.). After irradiation, in such mixtures containing the basic ingredients for synthesis of organic molecules (H, C, N, O), indeed, organic and pre-biotic molecules have been observed. Under interstellar or circumstellar conditions, COMs such as urea, nucleobases, amino acids, and ribose (a sugar) can be formed under vacuum UV, electron and ion irradiation (see, for example, Refs. 18–24, and references therein).

Electrons also play an important role. As primary particles in the radiation field in space, they can yield a significant contribution to the deposited dose, the Galilean satellites of Jupiter being an

example.[25] As secondary particles from primary ionization induced by UV photons, primary electrons or ionic projectiles, they can lead to secondary ionization events. This is in particular true for swift ions (like occurring in cosmic rays), where the so-called δ-electrons from knock-on collisions (with energies in the keV range or more) can travel over large distances (mm or more) and lead to ionization far away from the track core (typical radius some nm). The subsequent secondary, tertiary (and so on) ionization events lead to a cascade of low-energy electrons with energies of below, say, 10 eV (see, for example, Sec. 1.4 of Ref. 2 and references therein). Low-energy electrons can contribute to bond breaking via dissociative electron attachment.[26–29] As examples of studies of keV electron beam induced effects in ices we mention the Hawaii and Karkiv groups,[30,31] see also Ref. 16 and references in Refs. 16, 30, and 31. Concerning COMs, e.g., the molecules of particular interest here, nucleobases[32] and pyridine containing icy layers[33] under electron impact have been investigated.

Several studies have compared ion irradiation and UV photolysis of ice mixtures. A major difference between UV photons and swift charged particles is the penetration depth of the ionizing radiation. If the photon energy is above the ionization threshold of the irradiated molecules, they will be rapidly absorbed in the first layer(s) of the ice (within, say, less than a nm). In contrast, swift ions penetrate deeply: depending on their energy, from some tens of nm for solar wind equivalent velocities, up to the mm range for high-energy cosmic ray equivalents (see Fig. 1 of Ref. 2). It was observed that both types of radiation generate similar changes in icy samples, although quantitative differences between the two processes have been observed. Here, we can just mention one study using GANIL-IRRSUD[22] and refer the reader to Sec. 5.5 of Ref. 2 for further discussion. Muñoz-Caro and coworkers demonstrated that radiation processing of methanol and ammonia containing ices, $CH_3OH:NH_3$, by swift heavy ions or UV photons using a similar energy dose (in eV/molecule), respectively, yield quite similar residues containing organic molecules after warm-up to room temperature. However, the applied FTIR spectroscopy does not allow to identify large COMs, this can nevertheless be achieved by ex-situ chromatographic analysis of thick residues or high resolution mass spectrometry.[23,24]

Other investigations on formation of organic matter after ion irradiation have been performed at GANIL, e.g., by Augé et al.[1] and Pilling et al.[34] Following heavy ion processing of ammonia-containing ices ($H_2O:NH_3$ and $H_2O:NH_3:CO$),[34] IR spectra exhibited lines which could be attributed to several new species including HNCO, N_2O, OCN^-, and NH_4^+. Note that OCN^- and NH_4^+ were also observed by TOF-SIMS.[35] After a slow warm-up to room temperature, the IR spectra of the residues from the irradiated $H_2O:NH_3:CO$ ice showed five bands tentatively assigned to vibration modes of the aminoacid zwitterionic glycine. Possibly, another can be attributed to hexamethylenetetramine (HMT).[34] Molecular dynamics simulations allowed to analyze the effects of MeV ion impact on an icy mixture of water, carbon dioxide, ammonia, and methanol.[36] The total number of molecules produced was found to be approximately proportional to the deposited energy density. The most complex molecules are formed at the highest energy densities, while smaller molecules (such as formaldehyde and hydrogen peroxide), are produced all along the ion track.

Irradiation of ($N_2–CH_4$) ices mixtures at 14 K with nitrogen content of up to 98% led to formation of HCN and CN^-, and the infrared spectra of the solid residues measured at room temperature showed similarities with that of UCAMMs (ultra-carbonaceous micrometeorites collected in Antarctica), and also with that of poly-HCN.[1] The estimated formation time scales are compatible with radiation induced processing of icy bodies orbiting in the outer Solar system, thus such a scenario of energetic radiation processing could produce precursors of organic material brought to Earth via meteorites.

4. STABILITY OF COMs IN THE GAS PHASE

Organic molecules in space exist both in gas phase as isolated molecule, and in condensed phase, in mixtures with other molecules and often in a water matrix, water being omnipresent. To understand the radiation effects on COMs, let us start with a short overview on their stability in the gas phase, mainly focusing on studies performed at GANIL, before moving on to what happens in condensed phase. It is important to note that these considerations are not only important in view of astrochemical and astro-biological considerations, but also in view of radiation biology and medicine, in particular concerning hadron-therapy for cancer treatment.

Gas phase studies of COMs have emerged in the last two decades in order to probe their intrinsic properties at the atomic and molecular level under a solvent-free or size-controlled environment. Through a *bottom-up* approach, molecules of increasing sizes are continuously investigated with the ultimate aim of describing in a comprehensive way their behaviors in the much more complex cell medium. Gas phase experiments on biological systems also inherit the powerful experimental tools developed in nuclear and atomic physics.

Processes induced by low-energy electron interaction on nucleobases and DNA strands are considered to be of relevance for radiation chemistry. The group of L. Sanche has pioneered the study of dissociative electron attachment (DEA) reaction with single and double DNA strands.[26,27] Following this seminal study, the Innsbruck team has undertaken exhaustive studies on isolated nucleobases (NB) and nucleotides through DEA by looking at the anion fragmentation yield as a function of the electron energy.[28,29] Depending on the initial energy of the electron, different fragmentation channels are observed with well-defined resonance pattern at low energy (0–20 eV). These resonances are directly related to the resonant excitation of low lying molecular orbitals on specific chemical groups of the molecule.

In the case of higher energy radiation interactions with a living cell, the identification of the physico-chemical events leading to the biological effects induced by irradiation (chromosomal aberration, mutation and/or cellular death) is more complex. The works have mainly been performed at the mesoscopic level,[37,38] by irradiating for instance cells or DNA fragments in solution and by analyzing the results with biochemical or biological methods. They have cleared up the fact that the most severe consequences of irradiation result from the damage of genetic material. Nevertheless, the physico-chemical origins of DNA damage are not yet clearly established. It is commonly accepted that radiation damage results either from direct ionizations due to the interactions with the

primary beam particles (direct effect), electrons or slow and simply charged ions, or from radical species (indirect effects) created by the primary beam interacting with the surrounding biological medium (mainly water). These *in vivo* experimental results reflect then a combination of these effects, and only give insight in the biological consequences of radiation damage. They do not allow to establish a hierarchy in the irradiation events, neither to provide a real interpretation, at the molecular level, of the origin of damages.[39]

The *bottom-up* alternative, based on low-energy ion collisions on isolated biomolecules in the gas phase, without any surrounding medium can take in account the only effects linked with the secondary particles. Physico-chemical analysis techniques (e.g., mass spectrometry) can be used to get insight into the physical processes of radiation damage. Nevertheless, this approach was strongly restrained by the difficulty to put complex molecules in the gas phase, and most of the studied systems were small molecules (amino acids, nucleobases, …) representing only elementary building blocks of the biomolecules being in the cellular medium, see, for example, Refs. [40] and [41].

Moreover, the lack of real aqueous environment is a very strong simplification and numerous important effects are clearly missing. As a consequence, a series of experiments with hydrated nucleobase mixed clusters were performed.[42,43] Like in the case of pure clusters, it has been found that the environment (surrounding molecules) has a significant influence on the fragmentation dynamics, providing an overall "protective effect": molecular fragmentation is strongly reduced. On the other hand, the environment can also favor the opening of specific fragmentation channels which have not been observed in the case of isolated molecules. Note that for hydrated clusters a series of hydrated fragments have been observed, indicating a strong interaction between biomolecule and water molecules, holding the water clusters bound to the observed molecular fragments.

5. RADIORESISTANCE OF COMs IN CONDENSED PHASE

The life span of COMs in outer space depends on their radioresistance, i.e., their capacity to survive the impact of energetic particles to which they are continuously exposed. Measurements of destruction (or "disappearance") cross sections allow to estimate the half-life of molecules in space.[2,11,44] The goal of experiments with high energy projectiles is to simulate in laboratory the effect of cosmic rays on COMs embedded in icy mantles on dusty grains in Inter Stellar Media (ISM) or at the surface of comets. The radioresistance of molecules mixed with water or embedded in a water matrix is of great significance due to the abundance of water ices in outer space.

Among COMs, nucleobases are particularly important, since they are part of DNA. Even if nucleobases have not yet been observed directly in space, their presence on meteorites on Earth is an indication of their existence in space environments. We distinguish two kinds of nucleobases: i) purine nucleobases (guanine and adenine) formed of two heterocyclic rings, and ii) pyrimidine nucleobases (cytosine, uracil and thymine) which are formed by just one heterocyclic ring, all of which have been irradiated with swift heavy ions at GANIL (Caen, France) and GSI (Darmstadt, Germany).

As an example for such a type of experiment, we show in Fig. 1 the FTIR spectra obtained by irradiation of pyridine (Py) and of a Py–H$_2$O mixture before and after irradiation with O^{6+} (90 keV) at 15 K. Py (C$_5$H$_5$N) closely resembles the aromatic benzene ring, one of the CH groups having been replaced by a nitrogen atom. The IR spectra of pyridine ices contain several peaks and bands corresponding to different excited modes of vibrations. It is observed that the area of the peaks present in the spectra of as-deposited ice layers decrease after irradiation due to the projectile ion induced fragmentation of the initial molecules. The IR absorption lines of water and pyridine were used to determine the compositions of ices before irradiation and to monitor the evolution as a function of projectile fluence F. The quantity F is defined as the number of projectiles accumulated per surface area, i.e., the product of irradiation time and projectile flux.

Apparent destruction (disappearance) cross sections σ_d can be determined from the fluence (F) dependence of the area of selected absorption peaks, which is proportional to the column density, that is, the number of molecules per surface area. An example of the evolution of the peak area is shown in Fig. 2 for adenine. The evolution of the column density, traced as a function of the projectile fluence, can be well described (at first order) by a best fit of a simple function, $N(F) = N_0 \exp(-\sigma_d F)$ where N_0 is the initial column density of the irradiated COM layer. An important information, needed, e.g., for estimating life times of molecules exposed to cosmic rays in space, shown in Fig. 3 for adenine, is the dependence of the cross sections on the amount of deposited energy per
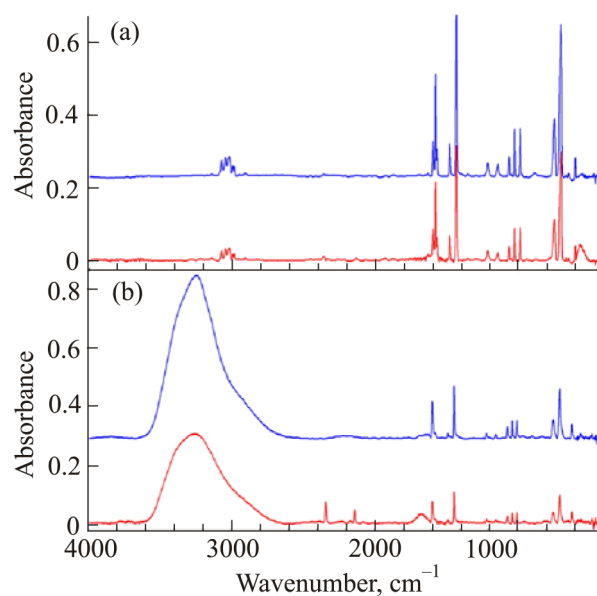

FIG. 1. FTIR spectra obtained by irradiation of (a) pyridine (Py) and of a (b) Py–H$_2$O mixture before and after irradiation with O^{6+} (90 keV) at 15 K during 50 min. The range of 90 keV oxygen projectiles is about 0.4 μm, the thickness of the deposited layers of the order of 1 μm. The final projectile fluence amounts to 10^{15} cm^{-1}. Spectra "before irradiation" were slightly shifted on the absorbance axis for better visibility.
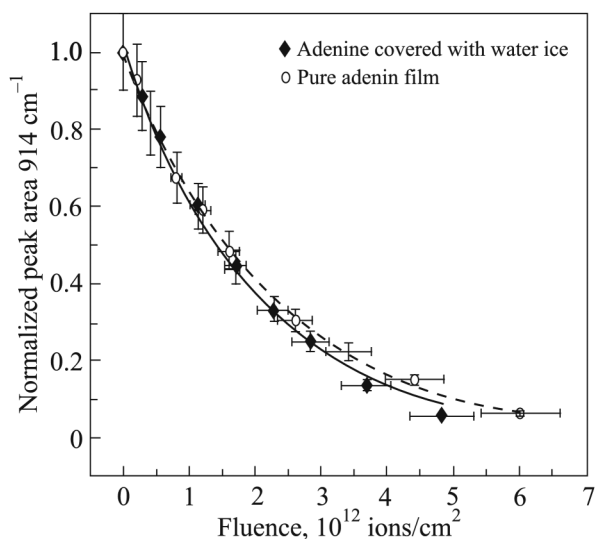
FIG. 2. Evolution of the area of one of the IR absorption peaks of adenine (914 cm^{-1}) with projectile fluence F for pure adenine, and adenine covered with a water layer (as indicated, from Ref. 44).

FIG. 3. Apparent destruction (disappearance) cross sections σ_d obtained with adenine as a function of electronic stopping power. The cross sections are found to follow a power law as a function of the electronic stopping power, $\sigma_d \sim S_e^n$ with a stronger than linear dependence, $n = 1.17$ in this case. [11,44]

molecule (dose, here expressed as the electronic stopping power, see Refs. 1, 2, 11, and 44 for a detailed discussion). The cross sections are found to follow a power law as a function of the electronic stopping power, $\sigma_d \sim S_e^n$, with a stronger than linear dependence, $n = 1.17$ in this case.[11,44] This scaling law also holds if data for electron irradiation are included.[11,32,44] The corresponding destruction cross sections for the other nucleobases are of the same order of magnitude. Nevertheless, the destruction cross sections of purine nucleobases are smaller than those of pyrimidine nucleobases.[44]

Taking into account the above scaling (power law) and the flux distribution of cosmic rays, the half lifetime of adenine can be estimated.[11,44] Deep inside a dense molecular cloud, where primary UV radiation cannot penetrate and only secondary UV photons induced by cosmic rays are present, the survival time of solid adenine exposed to cosmic rays was estimated as $(10 \pm 8) \cdot 10^6$ years, thus it would be of the order of 10 Myr. This is comparable to the lifetime of such molecular clouds. Therefore, it seems likely that adenine may survive in those "nurseries" of star formation.

A further interesting finding is that a water layer on top of the adenine sample seems to not significantly reduce or enhance the radiosensitivity, as shown in Fig. 2 (from Ref. 44). We also note that, as an example for the fragmentation of a COM, with adenine, the formation of HCN, CN^-, CH_3CN, $C_2H_4N_4$, and $(CH_3)_3CNC$ fragments has been observed by FTIR. Finally, we mention that the radiation resistance of another COM, the amino acid glycine (in its crystalline α-glycine form) has been investigated with swift heavy ion beams by Portugal et al.[45]

6. PYRIDINE–WATER

In a second type of experiments, the COM pyridine has been prepared by condensing it *in situ* at low temperature (10 K).
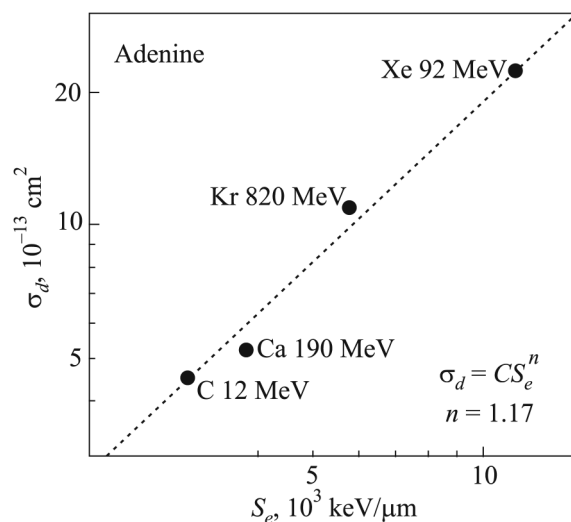
Pyridine is liquid at room temperature, as is water, and therefore, a mixture of both at defined ratio can be prepared. The vapor of pure pyridine or the water–pyridine vapor mixture can be introduced into the TOF-SIMS irradiation chamber[16,17] and condenses on the cold head (copper substrate). First, pure pyridine, and then an ice film of the organic molecules mixed with water were investigated. At low concentrations of pyridine, this would correspond to a COM embedded in a water matrix. This comes close to real conditions in space and allows us to verify if the icy environment modifies the radiation resistance of the initial molecule and/or the synthesis of daughter molecules. The layers were irradiated with O^{6+} (90 keV). The TOF-SIMS mass spectrum is displayed in Fig. 4. An example of corresponding FTIR spectra is shown in Fig. 1.

In the mass spectrum of Fig. 4, pyridine itself exhibits the most prominent peak at $m_{\text{Py}} = 79$ u. At lower masses $m < m_{\text{Py}}$, fragments due to the collisional fragmentation by the 90 keV O^{6+} projectiles are observed. At higher masses $m > m_{\text{Py}}$, clusters of pyridine $(\text{Py})_n$ with n up to 4 are visible. The relative cluster yields $Y(n)$ normalized to that of pure pyridine, $Y(1) = 1$, are plotted as a function of cluster size n in Fig. 5. The emission of sputtered particles (which are mostly emitted as neutrals, not as charged secondary ions) in the form of molecules and clusters is common. In some cases, the cluster yields $Y(n)$ follow a power law $Y(n) \sim n^\delta$ in other cases, an exponential law $Y(n) \sim \exp(n)$ is observed. Possible mechanisms for cluster emission include the emission of preformed species as single entities after impact following a collective phenomenon such as a shock wave. An observed power law dependence is a hint for such a collective mechanism. Exponential laws in contrast reflect "statistical processes" like (in-flight) fragmentation or agglomeration after strong electronic excitation leading to the formation of a local plasma (see Ref. 46 for a more thorough discussion).
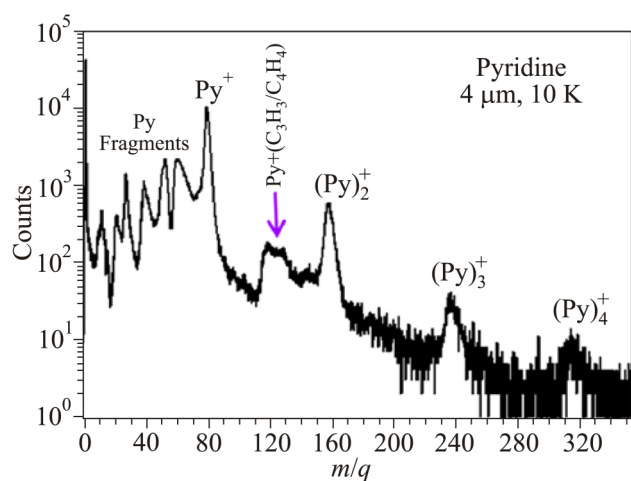
FIG. 4. TOF-SIMS mass spectrum of pyridine condensed at 10 K under impact of the 90 keV O^{6+} projectiles. Py is observed at $m_{Py} = 79$ u. At masses $m < m_{Py}$, Py fragments, and at masses $m > m_{Py}$, clusters of pyridine $(Py)_n$ with n up to 4 are visible.

The cluster size dependence of the yields of sputtered secondary ions could in many examples, and in particular with condensed molecules (ices)[2,47] but also with LiF,[46] be described by the sum of two exponential functions. The number of data points here is, however, too small to allow to distinguish between those possibilities. Nevertheless, an interesting result is observed with the Py–H_2O mixture: although the smallest cluster $(Py)_2$ is still observed, this is not the case for the larger cluster $n > 2$. This finding, in view of the
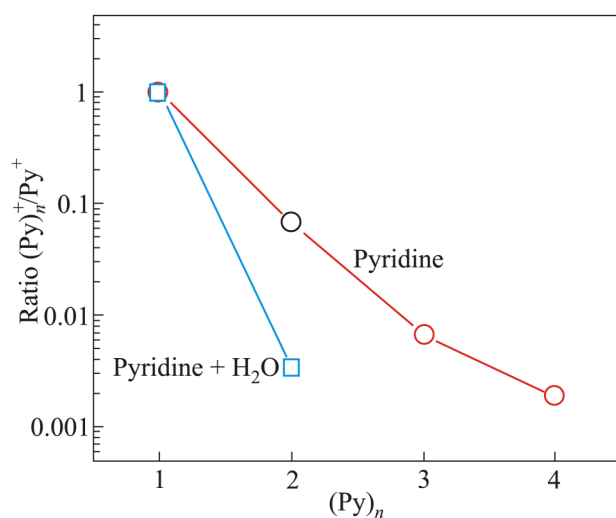

FIG. 5. Relative cluster yields $Y(n)$ of pure Py and a Py–H_2O mixture (as indicated), normalized to that of pure pyridine, $Y(1) = 1$, as a function of cluster size n.

question if the presence of water has a protective effect or enhances radiosensitivity, is still under investigation.

7. OUTLOOK

In order to perform laboratory simulations of ion irradiation effects (in space due to cosmic rays, solar wind and flares, ions trapped in giant planet's magnetospheres) on COMs, it is mandatory to work in ultrahigh vacuum conditions to ensure a controlled preparation of the targets. This also ensures a clean monitoring of the chemical and physical evolution under irradiation in such "online" experiments with *in situ* analysis. This is particularly true for mass spectrometry, a technique relying on sputtering, a surface related process (in contrast to FTIR which probes the bulk of the samples), because contamination by water may influence cross section and sputter yield measurements. Recently, a new ultrahigh vacuum device has been built at CIMAP-GANIL. The performances of this new device are described in Ref. 12. It is equipped with 3 spectrometers (FTIR, UV and quadrupole mass spectrometer) and can be installed on several GANIL beam lines (and those of other radiation facilities). This setup is now open to the scientific community[48,49] and will help to address new challenges about irradiation effects in ices, COMs, and other materials.

These challenges are quite numerous: as an example, we need to study the radiation processing of COMs in more realistic situations. In ISM, grains are covered with a thin icy mantle mainly composed of H_2O molecules. To reproduce such conditions, it is important to study irradiation effects on COMs trapped in a water matrix at low temperature in order to characterize the effect of the matrix. First experiments in this direction were started at CIMAP (Sec. 6). A second challenge consists in increasing the size and the complexity of the COMs. New experiments concern nucleotides (nucleobase + sugar). This kind of studies should be extended to more complex molecules (e.g., peptides). Polycyclic aromatic hydrocarbons (PAH) are really important complex molecules in view of astro-physical and astrochemical applications (Sec. 4). They have been detected in space and represent an important source of carbon in space (up to 30%). Since carbon is the key element in evolution of prebiotic materials,[50] it would be most interesting to study the PAH radio-resistance and the associated radiolysis products in water matrix with different percentages.

The temperatures of objects on which COMs occur cover a wide range, from 10 K in dense molecular clouds, from 25 to 150 K in the outer Solar system, up to 300 K (or higher) in the inner Solar system. First experiments with the amino acid glycine at temperatures of 14 and 300 K bombarded with swift heavy ions[45] indicate that the stability of glycine in solid phase (crystalline α-glycine form) to ion irradiation depends on the temperature. Puzzling results have been reported concerning nucleobases as discussed in Ref. 44. This subject needs more, thorough investigation. Note that experiments at higher temperature are not only relevant for astrochemistry and biology, but also for radiation biology and in particular, the application of ion beams for cancer treatment (hadrontherapy).

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