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High Abundance of Ions in Cosmic Ices

Murthy S. Gudipati[*,†] and Louis J. Allamandola[†]

NASA Ames Research Center, MS 245-6, Moffett Field, CA 94035-1000 and Institute of Physical Sciences and Technology, University of Maryland, College Park, MD 20742

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Correspondence and requests for materials should be addressed to Murthy Gudipati, Email: mgudipati@mail.arc.nasa.gov; Phone: 650-604-1735.

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[*] Institute of Physical Sciences and Technology, University of Maryland, College Park, MD 20742 (also associated with Institut für Physikalische Chemie, Universität zu Köln, Köln, Germany; Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025)

[†] NASA Ames Research Center, Moffett Field, CA

Water-rich, mixed molecular ices and polycyclic aromatic hydrocarbons (PAHs) are common throughout interstellar molecular clouds and the Solar System[1-3]. Vacuum ultraviolet (VUV) irradiation and particle bombardment of these abiotic ices produces complex organic species [4-6], including important biogenic molecules such as amino acids[7,8] and functionalized PAHs[5] which may have played a role in the origin of life. This ability of such water-rich, oxygen dominated ices to promote production of complex organic species is surprising and points to an important, unusual, but previously overlooked mechanism at play within the ice. Here we report the nature of this mechanism using electronic spectroscopy. VUV-irradiation of PAH/H_2O ices leads to an unprecedented and efficient (>70%) conversion of the neutral PAHs to their cation form (PAH^+). Further, these H_2O/PAH^+ ices are stabile at temperatures below 50 K, a temperature domain common throughout interstellar clouds and the Solar System. Between 50 and 125 K they react to form the complex organics. In view of this, we conclude that charged PAHs and other molecular ions should be common and abundant in many cosmic ices. The chemical, spectroscopic and physical properties of these ion-rich ices can be of fundamental importance for objects as diverse as comets, planets, and molecular clouds and may account for several poorly understood phenomena associated with each of these object classes.

Water-rich ices, which harbor a wide variety of organic and inorganic species, are common throughout the Solar System and interstellar molecular clouds[1]. Chemical reactions induced within these cosmic ices by high-energy photons and cosmic rays, as well as thermal cycling, play a vital role in the chemical evolution of these icy objects. Indeed recent laboratory studies indicated the formation of amino acids[7,8], amphiphilic molecules[9], and functionalized PAHs[5] through such photon and thermal processing of simple cosmic ice analogs containing H_2O, CH_3OH, CO, NH_3, and PAHs. Though PAH^+ intermediacy was suspected to account for the reaction rates observed in the production of functionalized PAHs, the primary photochemical steps *within* cosmic ices evaded laboratory observations[5]. Further, water ices are not yet known to be hosts for the generation and stabilization of ionic species[10]. To address this issue we have

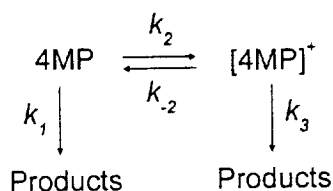studied the photo- and thermally promoted-chemistry of PAH-containing water ices with UV-visible spectroscopy.

Naphthalene ($C_{10}H_8$) and 4-methylpyrene ($C_{17}H_{12}$) containing H_2O ices were prepared in a high-vacuum, cryogenic sample chamber by co-deposition onto a LiF window at 15K. The behavior of the 4-methylpyrene (4MP)/H_2O ice is described in detail. As the experiments yielded similar results for both PAH molecules in water ice, only some of the Naphthalene (NAP)/H_2O ice results are presented.

Figure 1 shows the UV-Vis absorption spectrum of 4MP-water ice (15 K, H_2O:4MP > 500:1) as a function of VUV *in situ* photolysis. The vibronic structure at ~340 nm corresponds to the $^1B_{3u}\leftarrow\,^1A_{1g}$ ($S_1\leftarrow S_0$) transition of neutral 4-MP[11]. Figure 1 shows the steady and nearly complete loss of neutral 4MP with VUV photolysis and the simultaneous growth of the 4MP radical-cation (4MP$^+$) that is responsible for the band centered around 450 nm. This absorption corresponds to the $^2A_u\leftarrow\,^2B_{3g}$ ($D_5\leftarrow D_0$) transition of the 4-MP$^+$[12]. In sharp contrast to the photolysis behavior customarily found in rare gas matrices (Ar, and Ne), where <15% of the neutral PAH is lost upon VUV irradiation (e.g. – Ref.[13] and references therein), as shown in the top frame of Figure 2, over 70% of the neutral 4MP is lost when it is photolyzed in water ice.

Remarkably, this loss corresponds to a nearly complete conversion to, and stabilization in, the PAH cation form. *The UV-Vis data in Figure 1 shows that PAH ionization and storage as PAH$^+$ are far and away the dominant, primary processes in VUV-photolyzed water ices at 15 K.* The integrated absorbances of 4MP and 4MP$^+$ computed as a function of photolysis time are plotted against each other in the lower frame of Figure 2. The first 2000 s of photolysis follows a linear fit with close to zero intercept and a slope of 0.72. The oscillator strengths of the electronic transitions in pyrene, the chromophore of 4MP responsible for the band at ~340 nm (f ~ 0.33)[11,14], and 4MP$^+$ at ~450 nm are thus related by $x\,f_{450nm} = 0.72\,f_{340nm}$, where x is the fraction of 4MP$^+$ generated from neutral 4MP. Assuming $x = 1$ (the case of complete neutral to cation

conversion) we get $f = 0.24$ for this transition of $4MP^+$, in reasonable agreement with the most recent theoretical estimate (0.29)[12].

The data shown in Figure 2 has also been used to derive information on the reaction kinetics during the VUV-photolysis of 4MP in water ice. Only under the assumption that x is very close to 1, and using the following kinetic scheme, can a good fit between all the experimental data and the corresponding simulations be achieved. These fits are shown as solid and dashed lines in Figure 2.

$$4MP \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [4MP]^+$$

$$k_1 \downarrow \qquad\qquad \downarrow k_3$$

$$\text{Products} \qquad \text{Products}$$

The corresponding values are: $k_2 = 1.3 \times 10^{-3}$ s^{-1}, $k_{-2}/k_2 = 0.6$, $k_1/k_2 = 0.03$ and $k_3/k_2 = 0.04$. Clearly, the dominant process corresponds to k_2, the 4MP to $4MP^+$ photoionization rate. The backward ion-electron recombination reaction is the next most significant, but accounts for only 60% of the forward reaction. Photochemical formation of other products, either directly from the 4MP or via $4MP^+$ proceeds approximately one order of magnitude slower.

Similarly, over 85 % of naphthalene (NAP) is converted to NAP^+ after 9,000 s of VUV, *in situ* photolysis of H_2O:NAP (> 200:1) ices. We attribute the facile and efficient conversion of 4MP and NAP to their cations in water ices, compared to their far less efficient production in rare-gas matrices, to the exceptional ability of H_2O ices to solvate "excess electrons"[10], in a manner similar to storing "hydrated" electrons in liquid water[15]. Thus, though electron-ion recombination is a significant competing process to ionization, electron escape from the parent ice-cage and trapping at another site is by far the dominant process in water ices upon VUV-irradiation.

Equally important is the remarkable thermal stability of PAH^+/H_2O ices at 15 K. Essentially water ices are new, low-temperature matrices for the generation, and stabilization of molecular

ions, far more efficient than the rare-gas matrices. Figure 3 presents the warm-up results obtained from $4MP^+/H_2O$ and NAP^+/H_2O ices. As revealed by these experiments, the thermal behavior of PAH^+ in water ices is marked by three distinct regions: below 50 K, between 50 and 125 K and above 125 K. Below 50 K the PAH^+ molecules are indefinitely stable in water ices. Between 50 and 125 K the ions seem to form reactive intermediates as indicated by the slow disappearance of the PAH^+ signals. Most of the PAH^+ disappears between 100 and 125 K, the temperature regime in which water ice undergoes a phase transition involving crystallization and phase separation[16,17]. Above 125 K, the neutral products start emerging and the ions disappear rapidly. The ions are completely depleted by 150 K, the temperature at which water ices undergo the crystalline to hexagonal phase transition and sublime[16].

These experiments demonstrate that, upon energetic processing, water-rich cosmic ices promote and readily store highly reactive species such as ions and electrons at concentrations significantly higher than previously thought possible. In principle, this facile ionization of neutral molecules can occur up to the point where the ionization potential of the 'guest' molecule exceeds that of H_2O-ice (~11 eV)[18]. During warm-up from 15 to 150 K, electron-cation recombination to regenerate the neutral PAH is only a minor channel compared to the formation of intermediates of hydroxylation reactions resulting in aromatic alcohols and other species, confirming the initial formation and stabilization of cations only when the permanent cage-exit of electrons occur. The final photoproducts may be due to multi-step reactions involving the trapped PAH radical cation and other species present, including those formed by photolysis such as OH, OH⁻, and perhaps O atoms.

These results have significant impact on our understanding of ices in many different astronomical environments ranging from within the Solar System to the interstellar media of the Milky Way and other galaxies. Foremost among these is that water-rich ices at temperatures below 50 K can be reservoirs of ionized PAHs and, by implication, other ionized species. Since interstellar/precometary ices in dense molecular clouds are at temperatures between 10 and 20 K, it is highly likely that they contain ionized PAHs and other molecular ions in significant

concentrations. The immediate implication is that ion-mediated reactions should be considered when modeling interstellar processes. Support for the potential importance of ions in ices is provided by the 2165 cm^{-1} interstellar ice absorption band associated with high mass protostellar regions. Reported in 1984[19] its assignment has been the subject of much debate. Laboratory experiments[20,21] over the past few years have made a compelling case that it is due to the ion (OCN)[-]. However, an outstanding issue associated with this assignment is the identity of the phantom counter ion or ions. While there is a reasonably good case for NH_4^+ in some cases[22], there are difficulties as well[23]. The presence of charged PAHs in these ices may provide part of the solution to this problem while simultaneously addressing another outstanding issue. The IR absorption spectra of these same dense molecular clouds also have unexplained band structure in the 6 to 9 μm region[23], precisely where ionized PAHs have their strongest features[13].

Closer to home, comets bridge the gap between the interstellar medium and the Solar System with a chemical history that reflects both regimes. In addition to an interstellar heritage, the outer few meters of these water-rich icy bodies will be subject to bombardment by high energy particles from the stellar wind. In the energy domain relevant to astrophysics, particle bombardment of water ice mainly produces electronic excitation[24], the type of excitation induced by VUV photons. In recent studies on mixed molecular ices, both VUV and high energy particle bombardment formed the same chemical products[6]. Thus, the conclusions we draw above for VUV irradiated, aromatic containing H_2O-rich ices regarding ionization, stabilization and reactions upon warm-up should apply to cometary ices as well.

Similarly, many other objects in the outer Solar System contain water-rich ices and beyond the orbit of Jupiter these are colder than 90 K. In addition, aromatics are also likely to be delivered to the surfaces of most Solar System objects in significant quantities by meteorites and interplanetary dust particles (IDPs)[25,26]. Since these surfaces are also exposed to ionizing radiation, they may also be prone to richer, ion-mediated organic chemistry, which can give rise to a suite of complex organics. Furthermore, since ionized PAHs are strongly colored (e.g.

Figure 1), entrapped ions, particularly aromatic ions, could contribute to the rich coloration of some water rich icy bodies such as Europa.

Lastly, low-temperature interstellar and Solar System PAH-containing ices processed by VUV or particle radiation are likely to be energetically rich reservoirs of excess electrons, positively and negatively charged ionic species, and neutral radicals. Upon warm-up, either due to external temperature gradients or internal processes such as accumulation of excessive charge resulting in electric discharge or electron-ion or ion-ion recombination, oxygen and nitrogen containing organic molecules such as alcohols, ketones[5], amines, and amino acids[1] may be expelled from the subliming ices. These ion-assisted ejection processes may play some role in two other poorly understood phenomena, the outgassing of comets at large heliocentric distances and the long-standing puzzle that some portion of interstellar molecules are in the gas phase and not all frozen out onto the grains[27].

Summarizing, the facile but unanticipated, *in situ* generation and stabilization of PAH cations in water ices will have significant impact in our understanding of the physics and chemistry of cosmic ices and the evolution of prebiotic material.

Methods

Materials:
The water was purified by three freeze-pump-thaw cycles under vacuum before vacuum transfer into a glass bulb prior to deposition. Naphthalene and 4-methylpyrene (Aldrich, 99.99% purity) were used without further purification.

Sample Preparation:
The cryogenic sample chamber and UV-Vis spectroscopy system is described in detail elsewhere[17]. For the H_2O:NAP (>200:1) studies, the premixed gas sample was deposited under vacuum directly onto the onto the 15 K MgF_2 substrate. For the H_2O:4MP studies, water vapor

was passed over 4MP at room temperature resulting in H_2O:4MP (~500:1)[28]. Samples were typically deposited at a flow rate of 0.02 mmole/hour for 2 to 4 hours. After deposition, absorption and emission spectra of the ice were measured. The sample was then VUV-irradiated using a microwave-powered, flowing hydrogen-discharge lamp which produces radiation at Lyman α (121.6 nm) and a roughly 20 nm wide molecular transition centered at 160 nm.

Analysis:

Single-beam transmission spectra were measured by passing the light from a Xe arc-lamp attenuated with a 3.0 O.D. (optical density) neutral density filter through the ice sample, dispersing it with a 0.25 m spectrograph, and recording the spectrum on a CCD camera. For luminescence measurements, the excitation source was the same Xe arc-lamp, now prefiltered through a 0.2 m monochromator. The band pass in this configuration was 10 nm. Initial experimental trials showed that the optical quality of the ices was very sensitive to the VUV irradiation and thermal history. To standardize the data, absorption spectra were computed from the single-beam transmission spectra by referencing to the previous single-beam spectrum at any given time. These spectra were baseline-corrected and co-added to generate the absorption spectra presented here. This technique permitted the straightforward detection of absorbances on the order of 10^{-3}. A detailed description of this optics is provided elsewhere[17].
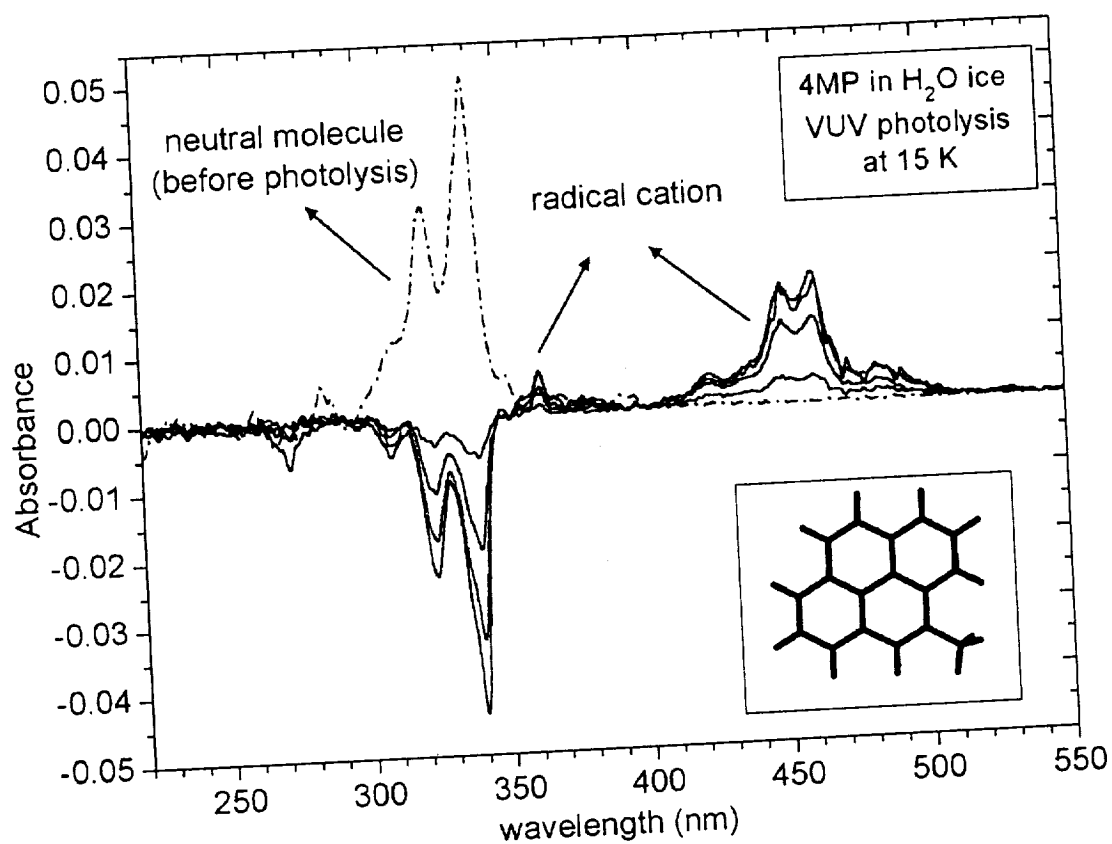
Figure 1: Spectral evolution of the H_2O:4MP (>500:1) ice at 15 K as a function of VUV irradiation time. Spectra are shown before (dot-dash line) and after 30, 300, 1200, and 4800 seconds (black, red, green, and blue, solid lines respectively) of *in situ* VUV irradiation. The vibronic bands peaking near 340 nm correspond to 4MP, those near 450 nm to $4MP^+$.
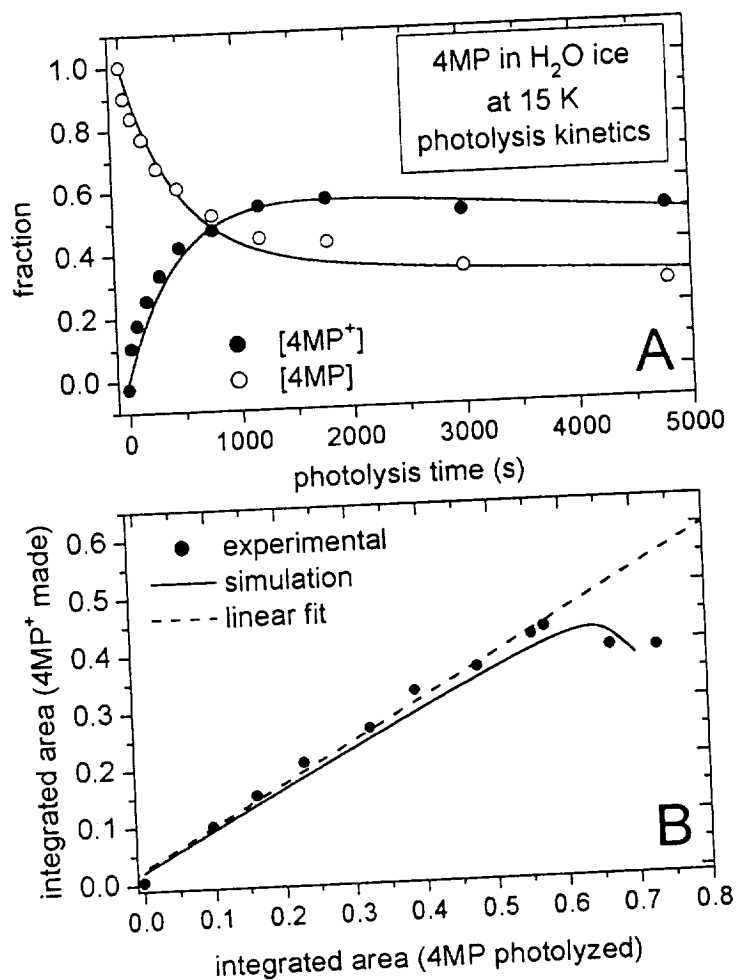
Figure 2: Kinetics of VUV irradiation of the H_2O:4MP (>500:1) ice at 15 K. Solid and open circles are experimental data, whereas the solid and dashed lines are from numerical fits (see text). Absorption bands were integrated and normalized to the integrated absorbance of 4MP before photolysis. Top: The fractions of 4MP lost and $4MP^+$ produced are plotted against photolysis time. Bottom: Normalized integrated absorbance of 4MP plotted against $4MP^+$ as a function of photolysis sequence. A linear fit from 0 to 2000 seconds (dashed line) yields the slope of 0.72, which relates the oscillator strengths of the neutral with the cation for the corresponding transitions (see text).
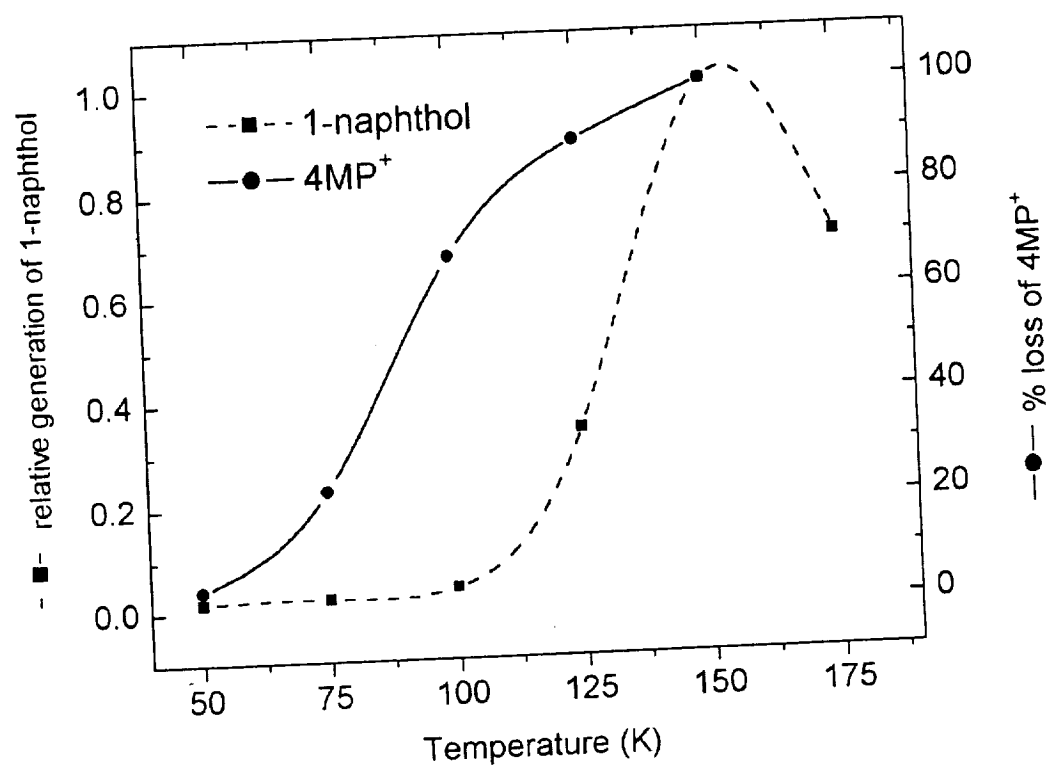
Figure 3: Thermal behavior of $4MP^+/H_2O$ and NAP^+/H_2O ices. For the $4MP^+/H_2O$ ices the percentage loss of $4MP^+$ was monitored through its absorption between 415 and 500 nm. For the NAP^+/H_2O ices the growth of the neutral product 1-naphthol was monitored through its fluorescence at 322 nm.

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