

## UNUSUAL STABILITY OF POLYCYCLIC AROMATIC HYDROCARBON RADICAL CATIONS IN AMORPHOUS WATER ICES UP TO 120 K: ASTRONOMICAL IMPLICATIONS

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### ABSTRACT

The PAH radical cation quaterrylene<sup>+</sup> (QTR<sup>+</sup>, C<sub>40</sub>H<sub>20</sub>) is found to be stable in amorphous water ice up to 120 K. A careful, 30 day, slow warm-up of water ice containing QTR<sup>+</sup> from 20 to 190 K revealed that QTR<sup>+</sup> does not show any sign of reactivity up to 120 K, the temperature at which the phase transition of amorphous to crystalline water ice begins. At higher temperatures the absorption due to the QTR radical cation diminishes rapidly but persists until the water ice itself sublimates around 170 K. From the absence of evidence for the recovery of neutral QTR upon warm-up or reactions with other trapped reaction intermediates in the ice, we infer that QTR<sup>+</sup> reacts with the water ice itself during warm-up above 120 K. Earlier we found that PAH ionization is quantitative in water ice and PAH ionization energy is lowered by up to 2 eV. Some implications of these unusual findings for cosmic ice chemistry and physics are briefly discussed.

*Subject headings:* ISM: clouds — methods: laboratory — molecular processes —  
radiation mechanisms: nonthermal — ultraviolet: ISM — ultraviolet: solar system

### 1. INTRODUCTION

Mixed molecular ices are a major component of the dust in dense molecular clouds (e.g., Ehrenfreund & Charnley 2000; Gibb et al. 2000; van Dishoeck 2004) and are common to planets, their satellites, and comets in the solar system and probably other planetary systems as well (e.g., Cruikshank 1997, 1999; Roush 2001; Schmitt et al. 1998 and references therein). Laboratory studies of interstellar and precometary ice analogs have shown that cosmic-ray, vacuum-ultraviolet (VUV), and thermal processing of these ices produces nonvolatile organics with a wide range of chemical complexity (e.g., Bernstein et al. 1995, 2002; Cottin et al. 2001; Dworkin et al. 2001; Gerakines et al. 2001; Greenberg et al. 2000; Hudson & Moore 2001; Kobayashi et al. 2002; Moore et al. 2001; Muñoz Caro et al. 2002; Schutte et al. 1993; Strazzulla & Palumbo 2001). The dark objects in the outer solar system and the organic crust on comets, as well as the dust in cometary comae and the interstellar medium, are likely to be rich in these materials.

Some of these complex organic species may be important for the origin of life. Since amino acids (Bernstein et al. 2002; Muñoz Caro et al. 2002), fatty-acid-like molecules that form vesicles (Dworkin et al. 2001), and functionalized biologically important polycyclic aromatic hydrocarbons (PAHs) (Bernstein et al. 1999) have all been found in these residues, the creation of complex, extraterrestrial biogenic molecules need not be confined to habitable planets and satellites but can occur in water-rich (10–150 K) ices that are common throughout interstellar molecular clouds and the solar system.

In an effort to deepen our understanding of the physics and chemistry possible in these cryogenic cosmic water-rich ice analogs beyond end-product analysis, we carried out in situ, optical (UV-vis-NIR) spectroscopic studies of PAHs in water ice. These optical studies were undertaken to overcome the limitations of severe line blending inherent with in situ infrared studies of

water-rich ices. Although infrared spectroscopy is still the method of choice for astronomical observations and studies of cosmic ices, and infrared laboratory work is essential to interpret these observations, optical spectroscopy is better suited to study in situ processes. The IR spectra of naphthalene in water ice (Sandford et al. 2004) show that the water bands dominate the PAH features, often overwhelming them at the PAH concentrations that one would expect in the ISM. Thus, using IR spectroscopy, it is extremely difficult if not impossible to follow the stepwise reaction pathways and kinetics of PAHs in water ice and to determine important properties such as the onset temperature of reaction during warm-up, the possible identities of some of the reaction intermediates, and so on.

In the course of these studies of PAH/water-ice photochemistry, we discovered the following *remarkable* phenomena: (1) PAHs are quantitatively (>70%) photoionized to their radical cations (PAH<sup>+</sup>), and (2) PAH ionization energy is lowered by at least 2 eV by the water-ice matrix (Gudipati 2004; Gudipati & Allamandola 2003, 2004). To determine the temperature range over which PAH ions might be stable in cosmic water-rich ices, we carefully monitored the QTR<sup>+</sup> absorption band in water ice during warm-up. Here we report the results of an exceptionally long experimental study that shows that ionized PAHs are very stable in water ice and that they can be stored in these ices at temperatures as high as 120 K. This remarkable stability of a large radical ion in water ice at temperatures above 100 K and the implied ion-mediated chemistry that can occur at such high temperatures will be of fundamental importance for understanding the chemistry and physics of water ice-containing objects as diverse as interstellar molecular clouds, comets, planets, and moons, and perhaps even for understanding biogenesis across the universe. Given that there is nothing special about QTR<sup>+</sup> other than size when compared with the behavior of naphthalene<sup>+</sup> and 4-methylpyrene<sup>+</sup> in water ice (Gudipati 2004; Gudipati & Allamandola 2003), similar behavior likely holds for all PAH ions of this size or larger. Such large PAHs are thought to dominate the PAH population responsible for the interstellar infrared emission features (e.g., Hudgins & Allamandola 1999 and references therein).

Although neither cryogenic water ices nor open-shell radical ions are new to astronomers, chemists, or physicists, their

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combination has not been considered by the scientific community until recently (Bernstein et al. 1999; Gudipati 2004; Gudipati & Allamandola 2003, 2004). As early as the mid-sixties, Porter and coworkers showed that aromatic radical cations generated through photoionization can be stabilized in organic glasses at 77 K (Gibbons et al. 1965). Bennema et al. (1959) showed that PAH radical cations ( $\text{PAH}^+$ ) are stable even at room temperature in boric acid glasses. More recently, whereas  $\text{PAH}^+$  has been shown to be highly reactive in liquid water around 300 K as well as in water clusters in supersonic jets (Courty et al. 1997), there seems to be no reactivity between individual  $\text{PAH}^+$  and  $\text{H}_2\text{O}$  molecules in the gas phase (Le Page et al. 1999). On the other hand, photodissociation processes in *pure water ice* have been studied (Baragiola 2003; Johnson & Quickenden 1997), and the production and stabilization of OH radicals up to 125 K is known (Matich et al. 1993).

The work described here has been carried out to better understand the effect of temperature on the physics and chemistry of interstellar and solar system water-rich ices by in situ monitoring of the chemistry of these otherwise highly reactive open-shell radical cations trapped in water ice and the reactions between these species and with the water ice itself.

## 2. EXPERIMENTAL

The experimental setup, consisting of a cryogenic sample-holder, a spectrograph, and a detector to record absorption and emission spectra has been described in detail elsewhere (Gudipati & Allamandola 2004). For the present studies, the quaterylene (QTR,  $\text{C}_{40}\text{H}_{20}$ , molecular structure shown in Fig. 1) containing water ice was formed on a LiF window, and a 100 W quartz-tungsten halogen lamp was used to record single-beam transmission spectra.

Single-beam transmission spectra were recorded and stored in a computer after each deposition or photolysis period. These transmission spectra were then converted to absorption spectra by using the previous transmission spectrum as the reference for each step, the same procedure detailed in our earlier publication (Gudipati & Allamandola 2003). This procedure ensures removal of spectral artifacts that can slowly build up due to long-term instrumental drift and instabilities or gradual changes in the optical properties of the ices due to photolysis and, in particular, highlights any subtle changes that occur between two successive measurements. Mathematically, this procedure is identical to subtracting absorption spectra of two successive measurements that were made using an arbitrary earlier single-beam spectrum as the common reference. Using this procedure, negative absorbances indicate depletion of the molecular species, whereas positive absorbance results from creation of new molecular species. For such long experiments, in order to generate trustworthy and reliable spectra, it is absolutely critical that the optical path is not disturbed in any way for the duration of the experiment. In order to accomplish this requires simultaneous monitoring of the absorption bands of both the neutral and radical cation forms in one spectrometer setting. It is for this reason that QTR was chosen. The limits of the spectrometer were set at 510 and 950 nm. All spectra were baseline-corrected with broad smooth continua.

The ice samples were formed as follows. Water vapor was deposited at an approximate rate of  $0.02 \text{ mmol hr}^{-1}$  onto a LiF optical window kept at 30 K. QTR vapor was simultaneously condensed with the water vapor onto the LiF window. QTR vapor was generated in a glass tube containing solid QTR by heating the tube to  $300^\circ\text{C}$ . The QTR and water vapor streams were codeposited for about 4 hours, during which time transmission spectra were measured to monitor the optical depth of the ab-

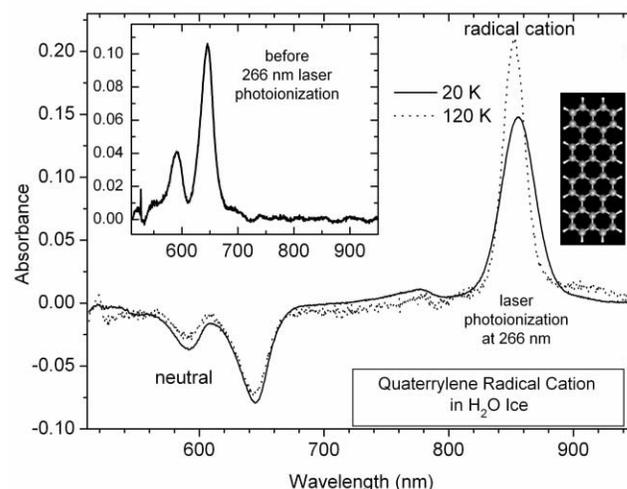


Fig. 1.—Low-energy photoionization of quaterylene in  $\text{H}_2\text{O}$  ice at 20 K. The absorption spectrum of a freshly deposited neutral quaterylene (QTR)/ $\text{H}_2\text{O}$  ice is shown in the inset. The spectrum of the same 20 K ice after photolysis with 266 nm laser light for 45 minutes is shown as the solid-line curve in the full figure. Negative bands represent depletion of the parent neutral QTR and positive bands represent generation of  $\text{QTR}^+$ , the trapped radical cation. The solid-line spectrum is the spectrum at 20 K and the dotted-line spectrum was recorded at 120 K, during the stepwise warm-up procedure over 30 days, showing  $\text{QTR}^+$  is stable in water ice at this temperature. Spectroscopic details of the selected warm-up data are shown in Fig. 2.

sorption by QTR as well as the optical quality of the ice. Once an ice of sufficient thickness and QTR optical depth was formed, it was subsequently cooled to 20 K at a rate of  $1 \text{ K minute}^{-1}$ . We have found that the cryogenic water ices prepared in this way have very good optical properties, showing no haze or cracks, and possess an optical quality comparable to rare-gas matrices. See Gudipati (2004) for details. Under these experimental conditions ices directly deposited on substrates held at lower temperatures (20 K) were optically hazy, whereas the optical quality improved when the ices are formed on a window at higher temperature. In order to keep the deposition substrate temperature as low as possible, a compromise was made to maintain the window at 30 K during deposition.

## 3. RESULTS

Figure 1 shows the absorption spectrum of neutral QTR in amorphous water ice (20 K,  $\text{H}_2\text{O} : \text{QTR} > 500 : 1$ ) before (*inset*) and after (*full figure*) undergoing in situ photoionization at 20 K with defocused 266 nm laser light for 45 minutes. Figure 1 also presents the spectrum taken of this ice sample at 120 K (*dotted line, full figure*), during the stepwise warm-up to 190 K. The absorbance maxima at 645 and 595 nm (*inset*) correspond to the  ${}^1B_{3u} \leftarrow {}^1A_{1g}(S_1 \leftarrow S_0)$  transition of neutral QTR (Halasinski et al. 2003). The absorption spectrum shown as the solid line in the full figure also contains negative bands that are due to the depletion of the neutral QTR bands at 645 and 595 nm and a strong positive band at 850 nm due to the appearance of the singly ionized QTR radical cation ( $\text{QTR}^+$ , simplified here to  $\text{QTR}^+$ ) upon laser photoionization. The absorption at 850 nm (Halasinski et al. 2003) corresponds to the  ${}^2A_u \leftarrow {}^2B_{3g}(D_2 \leftarrow D_0)$  transition of  $\text{QTR}^+$ . In sharp contrast to the photolysis behavior common in rare gas matrices (Ar and Ne), where at most only  $\sim 15\%$  of the neutral PAH molecules are photoionized (Hudgins et al. 2000), over 70% of the neutral QTR molecules are ionized in water ice, similar to our earlier

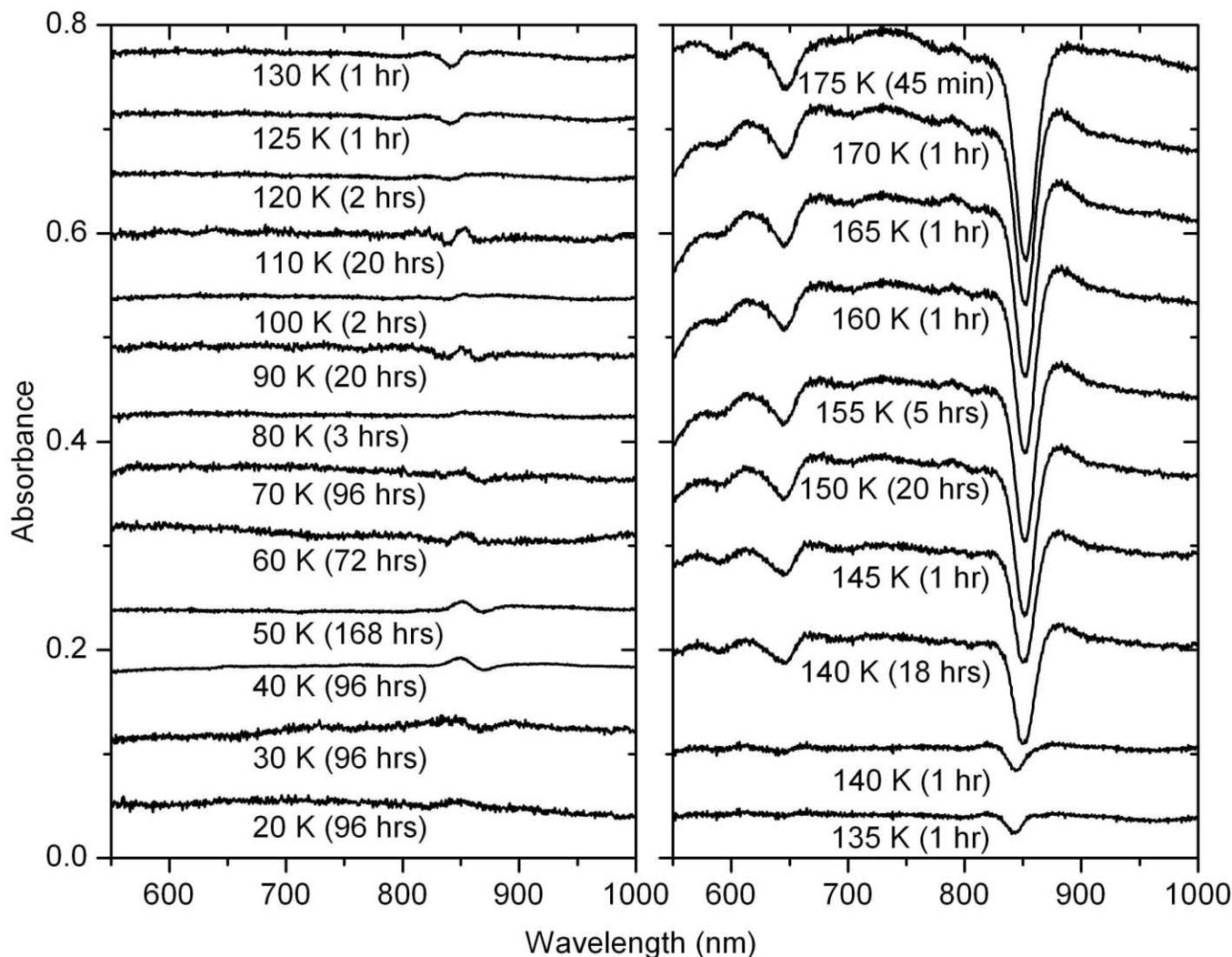


FIG. 2.—Selected absorption spectra obtained during the slow warm-up procedure after photoionization of QTR in amorphous water ice at 20 K. The labels given below the curves indicate the temperature of the ice at which the spectrum was taken and the amount of time the sample was held at that temperature. Below 120 K, the absorption spectra shown were obtained using the single-beam spectrum of the sample from the immediately preceding temperature as reference for the single-beam spectrum at the labeled temperature. This increases the sensitivity between each temperature step, and subtle changes would not go unnoticed. For all spectra measured above 120 K, the spectrum at 120 K was taken as the reference because the changes from one spectrum to the next were sufficiently large above this temperature, the  $T$  at which QTR<sup>+</sup> loss becomes first evident. Spectra are offset for clarity.

findings with the PAHs naphthalene and 4-methylpyrene (Gudipati 2004; Gudipati & Allamandola 2003). The dotted-line absorption curve shown in Figure 1 was taken at 120 K, after a nearly 1 month slow and stepwise warm-up procedure of the same ice sample. This spectrum unequivocally shows that the QTR<sup>+</sup> is indeed still very much stable in water ice up to this temperature. The narrower line widths (FWHM = 27 nm at 20 K and 18 nm at 120 K) increase in absorption maximum from an absorbance of roughly 0.15 to slightly over 0.2, and slight blue-shift (from 855.7 nm at 20 K to 852.5 nm at 120 K) between the QTR<sup>+</sup> absorption band taken at these two temperatures reflect changes in the microenvironment around the QTR<sup>+</sup> as the amorphous water ice is annealed. These changes are addressed below.

Close to 100 spectra of the sample were measured at 25 different temperatures during a deliberately slow, 30 day warm-up from 20 to 190 K. Spectra were taken at 10 K intervals between 20 and 120 K and 5 K intervals thereafter. The spectra plotted in Figure 2 were selected from these measurements and show the gradual changes that occurred upon warm-up between 20 and 175 K, the temperature at which water ice sublimates rapidly

under high vacuum. Under the experimental conditions reported here, the water ice is completely gone at 190 K.

As the ice is warmed from 20 to 120 K, the major process occurring within the ice is that of annealing. This reduces the number of different water matrix-sites, a process that is manifested by absorbance band narrowing as shown in Figure 1 and derivative-like (wave-shaped) spectral features between temperature steps as shown in Figure 2. Upon warm-up from 20 to about 120 K, reorientation of the H<sub>2</sub>O molecules that form the host cavity (site) around the guest QTR<sup>+</sup> leads to an increase in ground-state host-guest stabilization as indicated by the overall shift to the blue side of the initial QTR<sup>+</sup> absorption band shown in Figure 1. Regardless of this site structure reorientation, the integrated absorbance of the 860 nm band of QTR<sup>+</sup> shown in Figure 1 at 20 and 120 K is the same to within 5% uncertainty. Thus, remarkably, the water-ice matrix remains effectively inert towards the otherwise normally highly reactive, open-shell QTR<sup>+</sup> (radical cation) up to 120 K.

The spectra presented in Figure 2 show that the shape of the 850 nm absorption band of QTR<sup>+</sup> changes from a derivative profile to a peak profile when the sample is warmed from 110 to

120 K. This is the temperature at which amorphous water ice starts crystallizing (Jenniskens & Blake 1996), and it is only during such crystallization that large-scale mobility at the molecular level can start to occur in water ice. The drop in absorption due to the QTR radical cation ( $\text{QTR}^+$ ) is due to its loss by reactions occurring in the water ice. We consider the following three  $\text{QTR}^+$  reaction channels below: recombination with trapped electrons, reactions with other species trapped in the ice, and reactions with the water ice itself.

The lack of simultaneous growth in the 650 nm absorption band of neutral QTR as the absorption band of  $\text{QTR}^+$  drops clearly rules out the possibility of ion-electron recombination as the  $\text{QTR}^+$  loss mechanism. The electron affinity of water ice is known to be in the range of 2–3 eV (Khan 2004; Novakovskaya & Stepanov 2004), values corresponding to thermal energies of several thousand kelvin. Since the excess electrons generated through photoionization of neutral QTR are trapped in such deep energy wells of the host water-ice lattice, they are unable to recombine with and neutralize the  $\text{QTR}^+$ . *Thus, recombination with trapped electrons is not the  $\text{QTR}^+$  loss mechanism.*

To investigate whether other photoproducts might play a role,  $\text{QTR}^+$  trapped in  $\text{H}_2\text{O}$  ice was also produced by in situ photolysis with  $\text{Ly}\alpha$  photons ( $\lambda = 121.6$  nm) followed by warm-up. Reactive species such as  $\text{OH}^-$ , OH, O, and H are formed through photolysis of water with 10.2 eV  $\text{Ly}\alpha$  photons, but not with the 4.66 eV defocused laser light photons ( $\lambda = 266$  nm) used in the experiments described in detail above. Photoproducts from water cannot be produced by using defocused laser light at 266 nm because the possibility of multiple photon photolytic events is eliminated by defocusing, water does not absorb significantly at wavelengths beyond about 190 nm, nor is water photolysis energetically possible at wavelengths longer than 242 nm (5.1 eV; Calvert & Pitts 1966). Remarkably, we find no difference in the warm-up behavior of the  $\text{QTR}^+$  band produced by photolysis of QTR trapped in water ices with  $\text{Ly}\alpha$  or 266 nm radiation and conclude that reactions between  $\text{QTR}^+$  and other reactive species trapped in the ice is not the  $\text{QTR}^+$  loss mechanism. *If such highly reactive species as  $\text{OH}^-$ , OH, O, and H do not play a role in the loss of  $\text{QTR}^+$ , the possibility that the presence or absence of other radicals and ions influencing the stability of  $\text{QTR}^+$  in the ice below 120 K is essentially ruled out.*

Our earlier optical studies of the reactions of the radical cations of the PAHs naphthalene ( $\text{C}_{10}\text{H}_8$ ) and 4-methyl-pyrene ( $\text{C}_{17}\text{H}_{12}$ ) show that these smaller PAHs are also stable at unexpectedly high temperatures when trapped in water ice and are converted to stable species such as alcohols only at these higher temperatures, either by reactions with other photoproduct species in the ice or with the water molecules comprising the ice (Gudipati 2004; Gudipati & Allamandola 2003). Indeed, the optical bands due to an alcohol of naphthalene (naphthol) only appear when the irradiated water ice containing  $\text{C}_{10}\text{H}_8^+$  is warmed above 100 K (Gudipati 2004). The QTR/ $\text{QTR}^+$  warm-up spectroscopic series presented in Figure 2 shows that between 140 and 170 K, in addition to the rapid disappearance of  $\text{QTR}^+$  absorption and slow depletion of the remaining neutral QTR absorption, new broad absorptions grow in between about 650 and 800 nm and near 880 nm. These changes in absorption, both band loss and growth, should be due to reactions of neutral and ionized QTR with the host matrix. Consistent with this behavior, Bernstein et al. (1999, 2001) showed that when irradiated water ices containing naphthalene or coronene are warmed to room temperature, the residues remaining contain aromatic alcohols and ketones (quinones). *Thus, for aromatic cations trapped in water ice, all the evidence is consistent with reactions only occurring upon*

*warm-up and at temperatures above about 100 K.* Further studies are underway to gain a detailed understanding of these processes for PAHs of various sizes.

#### 4. DISCUSSION

In this section we discuss the results presented above in the broader context of the physical and chemical processes occurring in water-rich ices containing organic impurities. Four fundamental questions pertaining to cosmic ice processes arise from this work: (1) what is the fate of electrons that are released into the ices upon PAH photoionization and, by implication, any electrons in these ices? (2) What is the physics behind PAH ionization energy lowering in water ice compared to PAHs in the gas phase? (3) What is behind the high thermal stability of  $\text{PAH}^+$  ions in these ices? and (4) What reactions occur at temperatures higher than 120 K? The answers to these fundamental questions bear strongly on our understanding of cosmic ices. Here we address each of these questions but point out that to fully address these issues will require very specific and somewhat sophisticated follow-up laboratory work.

1. *Fate of electrons in water ice.*—Although the phenomenon of electrons solvated in water (also known as hydrated electrons) has been known for over several decades (Boyle et al. 1969), understanding the molecular physics of the hydrated electron remains an active area of research (Verlet et al. 2005). Pulsed radiolysis experiments of pure water ices revealed that the optical absorption due to free electrons in water ice decay on the timescale of a few nanoseconds to a few microseconds. The lower the temperature, the longer the lifetime of the free electrons in this range (Gillis & Quickenden 2001). Thus, under our experimental conditions of long-term UV photolysis followed by slow spectral scanning we would expect that there would be no free electrons present in these ices at 20 K. Electrons would have more than ample time to become attached to  $\text{H}_2\text{O}$  or OH within the ice, forming trapped  $\text{H}_2\text{O}^-$  or  $\text{OH}^-$  negative ions (anions). While the electron affinity of water ice is estimated to be around 2–3 eV (Khan 2004; Novakovskaya & Stepanov 2004), the electron affinity for OH in water ice is computed to be 5.06 eV, a value far larger than the 1.75 eV electron affinity for OH in the gas phase (Woon & Park 2004). These energies are far greater than the thermal energy available at 30 or even at 120 K. Thus, unless the  $\text{PAH}^+$  or any other ionized species possesses a larger electron affinity than that of  $\text{H}_2\text{O}$  or OH, electrons will be present in the water ice in the form of  $\text{H}_2\text{O}^-$  or  $\text{OH}^-$ . If photon energies that are below 5.1 eV ( $>242$  nm) are used to irradiate the ice, as with the 266 nm defocused laser irradiation reported here,  $\text{H}_2\text{O}$  photodissociation does not occur, leaving  $\text{H}_2\text{O}^-$  as the only negative counter ion in the water ices containing ionized PAHs. At high photon energies, where the kinetic energy of the photoelectrons generated from PAHs overcomes the electron affinity of water ice, electron ejection from the ice can occur.

2. *Ionization energy lowering in water ice.*—The 2–3 eV electron affinity of water ice seems to be the most important factor in determining the PAH/ $\text{H}_2\text{O}$  ice irradiation and warm-up behavior reported above: high PAH ionization efficiency, lowering PAH ionization energy, and high thermal stability of the ionized aromatic/ $\text{H}_2\text{O}$  ice systems. Theoretical computations carried out by Woon & Park (2004) provided insight into the molecular physics behind the ionization potential lowering we observed and predicted this is applicable to other aromatic systems as well. Interestingly, their predictions suggest that the lowering of ionization energy does not go hand in hand with PAH polarizability (which increases with increasing PAH size).

For example, benzene ( $C_6H_6$ ), the aromatic molecule with the lowest polarizability of those considered by Woon & Park (2004), has the largest ionization energy reduction ( $-2.1$  eV) of the PAHs they treated, while pyrene, a fused four-ring PAH and the largest they treated, has an ionization potential reduction of  $-1.5$  eV. Benzene has a ground state polarizability of  $11 \text{ \AA}^3$ , the two-ring aromatic molecule naphthalene has a ground state polarizability of  $20 \text{ \AA}^3$ , and the three-ring aromatic molecule anthracene has a ground state polarizability of  $35 \text{ \AA}^3$  (Cheng et al. 1972; Mathies & Albrecht 1974 and references therein). Thus, while one might intuit that PAH ionization potential lowering in water ice would correlate with PAH polarization, the trend appears to be opposite, indicating that the physics at play is more complex.

Theoretically, the ionization threshold of an impurity in a condensed medium can be treated as the difference between the ionization threshold of that impurity in the gas phase ( $IE_{GAS}$ ) and the sum of the polarization ( $P_+$ ) due to the ion in the medium and the electron affinity ( $EA_{ICE}$ ) of the medium (here, water ice):

$$IE_{PAH-ICE} = IE_{PAH-GAS} - \left(1 - \frac{1}{\epsilon_\infty}\right) \frac{e^2}{2R} - EA_{ICE}. \quad (1)$$

Here the second term is the induced polarization ( $P_+$ ), in which  $\epsilon_\infty$  is the optical dielectric constant of the medium (water ice),  $e$  the electron charge, and  $R$  the effective radius of the ion. The optical dielectric constant of water is known in the literature to be small, around 1.8 compared to the static dielectric constant ( $\epsilon$ ) of around 80 (Coe 2001; Makov & Nitzan 1994). For QTR, whose molecular volume is  $341 \text{ \AA}^3$ ,  $R$  is approximately  $4.33 \text{ \AA}$ . From the above equation we obtain the polarization due to QTR<sup>+</sup> in water ice,  $P_+$  of 0.74 eV, and the overall theoretical lowering of the ionization threshold to be around 2.74 eV. Because decreasing PAH size results in decreasing  $R$ , which in turn increases  $P_+$ , smaller PAHs are expected to have larger reduction in ionization energy, which is in agreement with the trend in the theoretical computations described above (Woon & Park 2004). Full understanding of this behavior will require further careful and systematic laboratory and theoretical work.

3. *Stability of ionized PAHs in water ice.*—The data presented in Figure 2 can provide semiquantitative information on the physics and chemistry of amorphous water ices containing ionized PAH impurities. Figure 3, which presents the integrated intensity of the QTR<sup>+</sup> ion absorption band plotted against temperature, shows that there are three distinct regimes of behavior. From 20 to 120 K there is no significant loss of the ion (see Fig. 2). Between 120 and 140 K there is a very slow disappearance of QTR<sup>+</sup> as shown by the small slope. At 140 K, where the sample was kept for over 18 hours, there is significant reduction in the QTR<sup>+</sup> absorption band. As described above, we infer that this is due to QTR<sup>+</sup> reactivity with the water matrix. Amorphous water ice starts crystallizing around 120 K (Jenniskens & Blake 1996). Apparently, this crystallization phase transition (which is associated with a large rearrangement of water molecules) makes the orientation between the incorporated QTR<sup>+</sup> and potential reaction partners ( $OH$ ,  $OH^-$ ,  $H_2O$ ,  $H_2O^-$ , etc.) favorable for reaction. Thus, it appears the rate of QTR<sup>+</sup> disappearance during the amorphous to crystalline phase transition is proportional to the rate of rearrangement of water molecules. In this regard, note the QTR<sup>+</sup> band loss behavior at 150 and 155 K. During this long warm-up experiment, once it was recognized that QTR<sup>+</sup> was diminishing slowly even at such high temperatures, the temperature was kept constant at 150 K for over 20 hours and then held at 155 K for over 5 hours. Remarkably, even at these temperatures, the QTR<sup>+</sup> concentration did not drop significantly as shown by

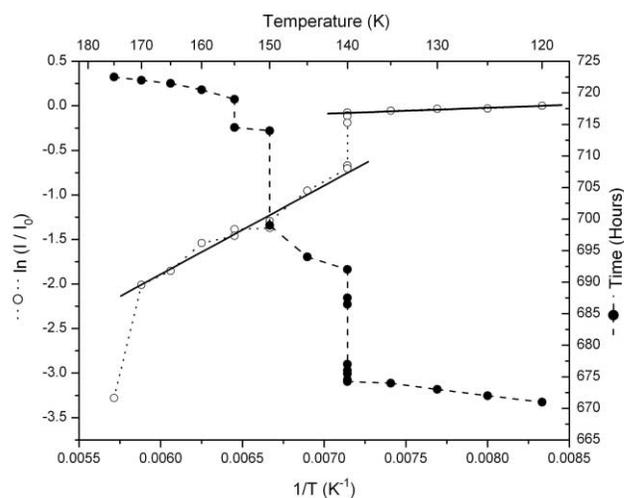


FIG. 3.—Plot of the integrated strength of the QTR<sup>+</sup> 850 nm absorption band loss (open circles) and the corresponding elapsed time since the generation of the QTR<sup>+</sup> at 20 K to the given temperature (filled circles) as a function of temperature. There is no change in band strength up to 120 K, and there is relatively small change from 120 to 140 K, the temperature range in which crystallization starts and the crystallization rate increases with temperature. At 140 K there is an initial faster rate of QTR<sup>+</sup> loss followed by a steady, but slower decline up to 175 K. Note that there is no significant drop in QTR<sup>+</sup> concentration during a 20 hour halt in warm-up at 150 K or a 5 hour halt at 155 K. We infer therefore that crystallization is completed during this slow warm-up between 140 and 150 K and further loss of QTR<sup>+</sup> upon warm-up results from partial sublimation of the ice along with the embedded impurities (QTR<sup>+</sup>/QTR).

the path followed by the open circles in Figure 3. This seems to imply that at this slow warm-up rate, crystallization is completed after reaching 150 K. Above 155 K the slow sublimation along with chemical reactions contributes to the drop in QTR<sup>+</sup> concentration. Sublimation becomes more prominent at 170 K, peaks at 180 K, and is complete at 190 K.

Since  $e^-$  recombination with QTR<sup>+</sup>, which would lead to the generation of neutral QTR (the starting material), has not been observed during the warm-up between 20 and 140 K, the fate of electrons that are generated through photoionization of QTR is not clear and needs to be further investigated with other spectroscopic methods. Similarly, the disappearance of neutral, unphotolyzed QTR evident from the 18 hour warm-up at 140 K needs further understanding. It is either due to the reaction between neutral QTR and other species in the ice, i.e., QTR<sup>+</sup>,  $H_2O^-$ , or  $OH^-$ , or physical processes such as the slow sublimation of the outer layers of the ice film.

In order to derive thermodynamic quantities such as crystallization and sublimation enthalpies and the reaction barrier between QTR<sup>+</sup> and the other reactants, it is necessary to follow PAH<sup>+</sup> loss at specific temperatures between 120 and 180 K. Such experiments demand both significant resources and time and are planned to be carried out in the future.

4. *PAH cation–water ice reactions above 120 K.*—We found no difference in the thermal stability and warm-up behavior of QTR<sup>+</sup> when QTR/ $H_2O$  ices were photolyzed with defocused laser light at 266 nm or Ly $\alpha$  radiation at 121.6 nm. As pointed out above, the 266 nm light does not photodissociate  $H_2O$  to  $H + OH$ , while Ly $\alpha$  radiation does. The observation of similar warm-up behavior in both cases shows that the reactivity of  $OH$  and  $OH^-$  with QTR<sup>+</sup> is not significant below 120 K, the temperature at which the amorphous to crystalline phase transition begins and the architecture of the entire ice starts to transform. Reaction below this temperature does not occur because there

may be a barrier (inherent activation energy) or stereochemical requirement of proximity and reorientation that need significant ice structural changes before reactions can take place. Some computations predict barrierless reactions between PAH<sup>+</sup> and OH (Ricca & Bauchlicher 2000; Woon & Park 2004), others predict a barrierless deprotonation of PAH<sup>+</sup> with H<sub>2</sub>O producing H<sub>3</sub>O<sup>+</sup> and the PAH<sub>(n-1)</sub> radical (Ibrahim et al. 2005), while others predict a 7.35 kcal mol<sup>-1</sup> barrier for the reaction of PAH neutral with OH (DeMatteo et al. 2005). More theoretical work, including studies of the reactivity of OH<sup>-</sup>, H<sub>2</sub>O<sup>-</sup> with both neutral and ionized PAHs in water ice, is clearly warranted.

Laboratory experiments on the photolysis of PAHs imbedded in water ices (Bernstein et al. 1999, 2001, 2003), show that both oxidized and reduced aromatic species are present in the residue remaining after the sample is warmed to at room temperature. This residue contains species such as aromatic alcohols, ketones, and partially aliphatic ring systems. Thus, on the basis of the results reported here, we expect the PAH<sup>+</sup> that are generated through UV processing react with H<sub>2</sub>O, H<sub>2</sub>O<sup>-</sup>, OH, or OH<sup>-</sup> at relatively higher temperatures (~120 K) than previously thought. In addition to studying the PAH loss rate at specific temperatures, a better understanding of the processes at play will require systematic studies on PAHs of various sizes and at different concentrations to determine whether PAH size and concentration have any influence on the high thermal stability of ionized PAHs in water ices. This elaborate experimental program is now underway.

## 5. ASTROPHYSICAL IMPLICATIONS

It is generally assumed that interstellar and many other extraterrestrial ices are primarily composed of *neutral* molecules and radicals. As such, the chemistry and ice physics treated in various interstellar chemistry models consider only neutral species (e.g., Charnley 2001; Charnley et al. 1992; d'Hendecourt et al. 1982; Stantcheva & Herbst 2004). The result presented here that the most common ice in the cosmos, frozen water, can contain ionized PAHs up to temperatures as high as 120 K questions that general assumption, and all the more since this ability of water ice to trap and store ions and electrons to temperatures above 100 K likely holds for other organic ions as well. Such energy-rich ices can play a role in many different radiation-rich astronomical environments ranging from the interstellar media of the Milky Way and other galaxies to the icy objects within these galaxies. Here we discuss some implications for interstellar chemistry in dense molecular clouds and briefly mention some possible solar system considerations.

There is now a wealth of information about the composition of ices in dense interstellar molecular clouds thanks to a legacy of infrared observations spanning over 20 years. It is now clear that these interstellar ices are water-rich, mixed molecular ices (Gibb et al. 2004). While some species such as CO, CO<sub>2</sub>, and CH<sub>3</sub>OH can have abundances on the order of tens of percent along various lines of sight, the majority of species produce infrared absorptions that imply concentrations of a few percent. Of course, given the difficulty of line overlap mentioned earlier, other species must be present at lower concentrations as well. It is likely that PAHs are among these species (e.g., Bernstein et al. 2001).

There is already observational evidence for the presence of ions trapped in this interstellar ice. Among the well-known ice features, the 2165 cm<sup>-1</sup> (4.62 μm) interstellar ice absorption band has been convincingly assigned to (OCN<sup>-</sup>) salts (Demyk et al. 2001; Novozamsky et al. 2001). However, identifying the counter-ion or -ions has been elusive and controversial. While there is reasonably good evidence for NH<sub>4</sub><sup>+</sup> in some cases (Novozamsky et al. 2001), there are important difficulties as well

(Keane et al. 2001). The relative ease with which PAH<sup>+</sup> can be formed and stabilized in water ice and the high temperatures at which these ions can remain trapped suggest that these, and perhaps other organic cations, may provide part of the solution to this problem. Furthermore, this work, which shows the ease of aromatic ion formation and stabilization in cryogenic water-rich ices, taken in conjunction with the evidence for OCN<sup>-</sup>, suggests that ion-mediated chemistry and physics might play a far more important role in interstellar chemistry and grain physics than normally considered.

The suggested presence of PAH ions trapped in cosmic ice may simultaneously address another issue. The IR absorption spectra of these same dense molecular clouds also show unexplained band structure in the 6–9 μm region (Keane et al. 2001). This is the region in which PAH ions have their strongest features (e.g., Hudgins et al. 2000). Unpublished results from the Ames Astrochemistry Laboratory show that PAH cation trapped in water ice also show band enhancement in this region. Thus, PAH cations could serve as the OCN<sup>-</sup> counter-ion *and* contribute to the unexplained band structure in the 6–9 μm region.

Interstellar ice features are strongest in dense clouds along sight lines to star-forming regions and are also likely important in the ice-containing planet forming disks surrounding the protostar. Recent observations (Boogert et al. 2004) with the *Spitzer Space Telescope* show the temperature of much of the ice and dust across these disks can range between 50 and 150 K, the temperature range that encompasses the range studied here. Since the regions from which the PAH mid-IR emission features originate are often closely associated with icy interstellar regions, it is reasonable to assume that PAHs are mixed in these ices as well. Consequently, the ease of formation of PAH radical ions, their stabilization in water-rich ices, and their reactions with the ice when they are warmed above about 100 K suggests that PAH<sup>+</sup> containing water ice may be common in many different cosmic environments and that ion-mediated ice chemistry could be important in water ices throughout the universe.

This work should also be relevant for solar system processes because many solar system objects contain water-rich ices, and their surface temperatures are low enough to contain trapped aromatic ions. For example, the albedo-dependent temperatures of the water-rich Galilean satellites fall roughly between 120 and 150 K, and for objects beyond the orbit of Jupiter temperatures are below 90 K (Grundy et al. 1999). Even shaded craters on the Moon are thought to be near 40 K. Since significant quantities of aromatics are also delivered to most of these objects by meteorites and interplanetary dust particles (Clemett et al. 1993), it is to be expected that their surfaces also contain trapped aromatic ions. Thus, for example, it is possible that a rich and previously unrecognized chemistry can occur on the icy Galilean satellites due to energetic and thermal processing of ionized species in water ices even at temperatures above 120 K. In contrast, storage of these strongly colored, ionized organic species is expected to dominate on Saturnian icy rings and satellites, and trans-Saturnian icy bodies. Perhaps the rich colors of some of the rings of Saturn (Estrada et al. 2003) could be due to the entrapment of colorful PAH or other organic ions.

The experimental observation that both the large PAH cation QTR<sup>+</sup> and the smallest PAH cation, naphthalene<sup>+</sup>, do not react with species such as OH, OH<sup>-</sup>, and O until the temperature at which amorphous water ice starts crystallizing (Jenniskens & Blake 1996) shows that it is the unique hydrogen bonding and complex formation capability of the water molecules in the water ice that controls the process. Nonpolar species such as CO and N<sub>2</sub> readily rearrange in, and escape through, the amorphous

ice pores at much lower temperatures as it is warmed from 10 to 20 K to the crystallization point (Bar-Nun et al. 1985, 1987; Laufer et al. 1987; Sandford & Allamandola 1988; Allamandola et al. 1988). The special interactions possible between aromatic species with water molecules and subsequent changes in chemistry and molecular physics of these species is now a topic of interest in chemical physics (e.g., DeMatteo et al. 2005; Ibrahim et al. 2005; Woon & Park 2004) and will influence our understanding of the chemistry and physics of cosmic ices.

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