POLYCYCLIC AROMATIC HYDROCARBON IONIZATION ENERGY LOWERING IN WATER ICES

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ABSTRACT

In studying various interstellar and solar system ice analogs, we have recently found that upon vacuum ultraviolet photolysis, polycyclic aromatic hydrocarbons (PAHs) frozen in water ice at low temperatures are easily ionized and indefinitely stabilized as trapped ions (Gudipati; Gudipati & Allamandola). Here we report the first experimental study that shows that PAH ionization energy is significantly lowered in PAH/H$_2$O ices, in agreement with recent theoretical work (Woon & Park). The ionization energy (IE) of the PAH studied here, quaterrylene (C$_{40}$H$_{20}$, IE = 6.11 eV), is lowered by up to 2.11 eV in water ice. PAH ionization energy reduction in low-temperature water ice substantially expands the astronomical regions in which trapped ions and electrons may be important. This reduction in ionization energy should also hold for other types of trapped species in water-rich interstellar, circumstellar, and solar system ices.

Subject headings: ISM: clouds — methods: laboratory — molecular processes —
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1. INTRODUCTION

Water-rich mixed molecular ices and polycyclic aromatic hydrocarbons (PAHs) are common throughout interstellar molecular clouds and the solar system (Cruikshank et al. 1998; Roush 2001; van Dishoeck 2004). Laboratory analog experiments have shown that vacuum ultraviolet (VUV) irradiation and particle bombardment of these ices produces complex organic species, including important biogenic molecules such as amino acids and functionalized PAHs that may have played a role in the origin of life (Bernstein et al. 1995, 1999, 2002; Gerakines et al. 1996, 2001; Muñoz Caro et al. 2002). In view of the ubiquity of these cosmic ices and their important role in astrochemistry (Charnley 2004; Charnley et al. 1992, 2001; Ruffle & Herbst 2000; Stantcheva & Herbst 2004), the processes through which these water-rich, oxygen-dominated ices promote the production of complex organic species from simple molecules calls for deeper understanding.

In exploring these processes, we recently discovered that PAHs embedded in water-rich cryogenic ices are easily and efficiently ionized (>80%, i.e., near-quantitative ion yields) by VUV photons (Gudipati 2004; Gudipati & Allamandola 2003, hereafter GA03). These experiments showed that when a PAH is frozen in water ice at low temperature, ionization leads to the quantitative conversion of the neutral PAH species to the positively charged radical cation. These PAH radical cations (PAH$^+$) are indefinitely stabilized in the cryogenic ice. As previously pointed out, this result provides important new insight into the chemistry and physics of water ices, especially in radiation-rich environments. The unexpected presence of organic ions and electrons trapped in cosmic ices will significantly alter our understanding of chemistry, physics, and spectroscopy of these cosmic ices (GA03).

In response to these experimental results, Woon & Park (2004) carried out time-dependent density functional theory calculations to model the PAH/water ice system. In addition to confirming our experimental findings, this theoretical study

found that the PAH ions in H$_2$O ices can be stabilized by as much as 2 eV compared to the respective gas-phase ion energies. Consequently, PAHs, which typically have gas-phase ionization energies falling in the 6–10 eV range (corresponding to VUV photons), may have ionization energies lowered to 4–8 eV (corresponding to near-UV photons) when frozen in water ice, which is transparent at these wavelengths. Thus, while VUV radiation ($\lambda < 200$ nm) would be required to ionize PAHs in the gas, when PAHs are frozen in water ice, near-UV radiation ($\lambda < 300$ nm) is all that would be necessary. In such a scenario, the ionization of a variety of impurities in water-rich cosmic ices becomes an important process even in regions of lower energy photons typically classified as nonionizing in the astronomical literature. Such a lowering of the ionization energies has important ramifications in our understanding of physical and chemical processes that occur in water-rich cryogenic ices both in the interstellar medium and in the outer solar system.

We have studied the PAH quaterrylene (QTR; C$_{40}$H$_{20}$) frozen in water ice to experimentally determine how far the ionization energy would be lowered when these molecules are imbedded in cryogenic water ices. We carefully selected QTR (C$_{40}$H$_{20}$) as the test system because of the combination of its ionization energy of 6.11 eV (Carl & Schmidt 1978) and strong absorption in the visible near-infrared by both the neutral molecule (around 640 nm) and the radical cation (around 850 nm; Halasinski et al. 2003). As described below, we indeed found that QTR is ionized very efficiently at 266 nm (4.66 eV) and to a small degree even at wavelengths greater than 310 nm (4 eV), confirming that the ionization energy of QTR is lowered by up to 2.11 eV when it is frozen in water.

2. EXPERIMENTAL

The experimental setup, consisting of a cryogenic sample-holder and a spectrograph and detector to record absorption and emission spectra, has been described in detail in an earlier publication (Gudipati et al. 2003). For the present studies, the QTR containing water ice was deposited onto a LiF window, and a 100 W quartz-tungsten halogen lamp was used to record single-beam transmission spectra.

Photoionization of the selected PAH, QTR, has been carried out at wavelengths longer than 310 nm (<4 eV) using a deuterium lamp equipped with a crown-glass filter and at $\lambda = 266$ nm

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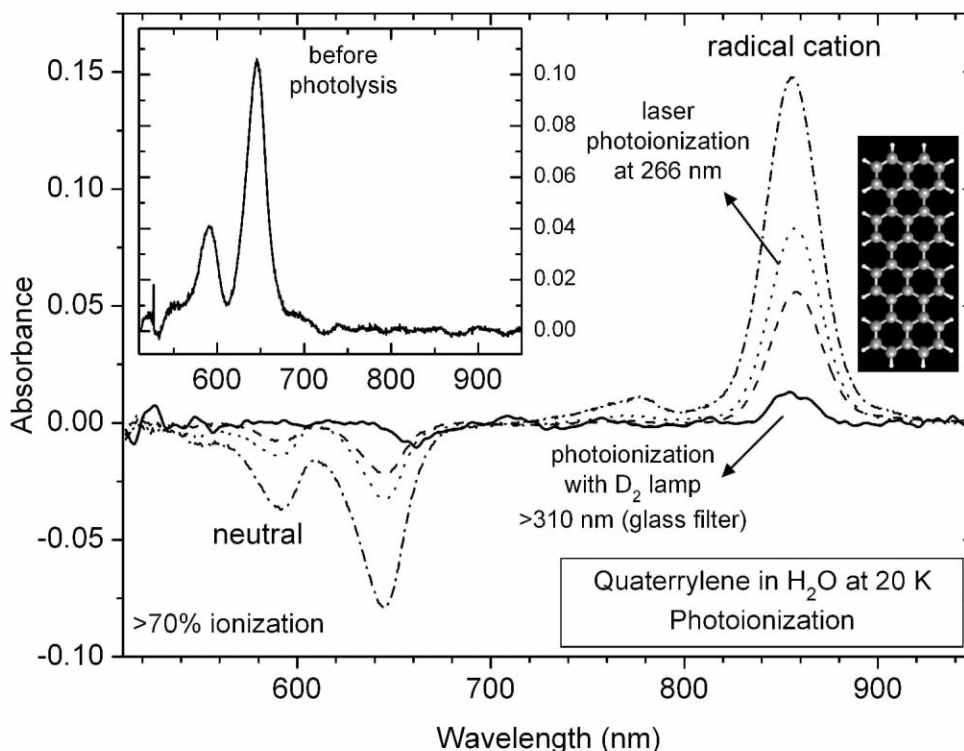
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FIG. 1.—Low-energy photoionization of QTR in H_2O ice at 20 K. The absorption spectrum of a freshly deposited neutral QTR/H_2O ice is shown in the insert. The spectrum of the corresponding radical cation (QTR$^+$), generated through low-energy photon photoionization in H_2O ice at 20 K, is shown in the full figure. Negative bands represent depletion of the parent species (neutral molecules), and positive bands represent generation of new species (radical cation molecules). *Insert*: The solid line spectrum with positive bands between 500 and 750 nm with no corresponding peak at 850 nm is the spectrum of neutral QTR in a freshly prepared H_2O ice. *Full figure*: The thick solid line spectrum, labeled "photoionization with D_2 lamp," is obtained after a 30 minute irradiation of the freshly prepared QTR/H_2O ice using a D_2 lamp filtered with glass. This combination permits only wavelengths above 310 nm (energy < 4 eV) to strike the sample. This spectrum is enlarged 10 times to show the details. The dashed line spectra, shown without enlargement, were obtained after subsequent photolysis at 5 minute (*dashed line*), 15 minute (*dotted line*), and 45 minute (*dot-dashed line*) photolysis times with 266 nm (energy ~4.66 eV) laser light. The ionization potential for gas-phase QTR is 6.11 eV.

(4.66 eV) with the fourth harmonic of a Nd-YAG laser. A 30 W ozone-free deuterium lamp (Oriel Instruments), with quartz focusing objective, delivers UV-enhanced light from 200 nm to longer wavelengths (<6.2 eV). The approximate flux of the lamp at 300 nm is 14 μW nm^{-1} or ~2 × 10^{13} photons s^{-1} cm^{-2} nm^{-1}. A 2 inch crown-glass plano-convex lens ($f = 500$ mm) was used to filter the UV component of the deuterium lamp (<10% transmission at 310 nm). The 266 nm photons were generated as follows. A Nd-YAG laser (Quanta Ray DCR-1A), with a frequency doubling unit, was used to generate 532 nm laser pulses at a 10 Hz repetition rate and a pulse width of 5 ns. These were again frequency-doubled to 266 nm using a BBO crystal in an Inrad autotracker unit. The UV laser line at 266 nm was separated from the green line (532 nm) and the remnants of the IR fundamental using a 4 prism harmonic separator (Inrad 752-104). To avoid multiphoton processes occurring in the ice, the 266 nm laser spot size of approximately 3 × 3 mm was defocused to approximately 15 × 15 mm at the sample by using a quartz lens. Furthermore, the Nd-YAG laser was operated at close to minimum energy, delivering ~30 mJ pulse^{-1} at 532 nm by using only the oscillator part of the laser. After frequency doubling and separating the UV from green and IR laser light, the energy of the 266 nm laser was 1 mJ pulse^{-1}, which corresponds to ~10^{15} photons per pulse.

QTR (molecular structure shown in Fig. 1) was obtained from W. Schmidt (PAH Forschungs Institut, Greifenberg, Ger-

many) and used without further purification. High-purity deionized water (18 MΩ) was deposited at an approximate rate of 0.02 mmol hr^{-1} onto a LiF cryogenic optical window kept at 30 K. QTR vapor was simultaneously sublimed onto the LiF window from a glass-finger containing solid QTR heated to 300°C. The PAH and water vapor streams were codeposited for about 4 hr during which time transmission spectra were measured to monitor the optical depth of the absorption by QTR as well as the optical quality of the ice. Under the present experimental conditions the cryogenic water ices thus prepared had excellent optical properties showing no haze or cracks—comparable to rare gas matrices, as detailed in an earlier publication (Gudipati 2004). The ratio of QTR to H_2O is estimated to be ~1 : 500 for the results presented here.

Single-beam transmission spectra were recorded and stored in the 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 (GA03). This procedure ensures removal of artifacts due to long-term instrumental instabilities and changes in the optical properties of the ices due to photolysis. Using this procedure, negative absorbances indicate depletion of the molecular species, whereas positive absorbance results from the creation of new molecular species. To simultaneously monitor the absorption bands of both the neutral and the radical

cation forms of QTR within the same frame of the spectrum, the limits of the spectrometer were set at 510 and 950 nm. All spectra were baseline-corrected with broad smooth continua.

We have attempted to get an approximate estimate of the ionization yields for QTR at 266 nm as follows. The extinction coefficient (ϵ) for the absorption around 650 nm of the neutral QTR is 1.4×10^5 liters mol^{-1} cm^{-1} (Meyer et al. 1997) or an absorption cross section (σ_a) of 5×10^{-16} cm^2 molecule^{-1}. From the absorbance shown in Figure 1, the number of neutral QTR molecules in the ice matrix is estimated to be around 5×10^{14}. About 80% of the neutral QTR molecules were ionized in 45 minutes of laser photolysis (10 Hz, 1.3×10^{15} photons pulse^{-1}, and a total of ~3.5×10^{19} photons). Thus, the ionization yields at 266 nm are ~10^{-5} ions photon^{-1}. However, the actual number of photons involved in the ionization of neutral QTR molecules may be a couple of orders of magnitude smaller because of scattering from ice grains and the much weaker absorption cross section of neutral QTR at 266 nm. In this case, the ionization yields could even be higher by a couple of orders of magnitude. Further studies are planned to look into photoionization yields with tunable laser excitation between 200 and 400 nm.

3. RESULTS AND DISCUSSION

The absorption spectrum of a QTR/H$_2$O (~1/500) ice at 30 K, prepared by 4 hr of codeposition onto the LiF window, is shown in the insert of the Figure 1. This spectrum, which consists of a maximum at 645 nm and two vibronic components at 590 and 550 nm, is due to the $S_1 \leftarrow S_0$ transition in QTR, which has an oscillator strength of 1.08 (Halasinski et al. 2003). The full figure spectrum shows the growth of a strong absorption band around 855 nm with a very weak satellite feature at 775 nm, both of which are due to the QTR radical cation generated upon photoionization. This arises from the $S_2 \leftarrow S_0$ transition in QTR$^+$, which has an oscillator strength of 1.03 (Halasinski et al. 2003). The full spectrum also shows the corresponding loss of the neutral parent QTR upon photolysis.

These data were obtained as follows. The freshly prepared QTR/H$_2$O ice was irradiated with the light from a 30 W deuterium lamp after it passed through a glass-filter. This combination ensured that only photons with wavelengths longer than 310 nm (energy < 4 eV) struck the sample. The sample was photolyzed for 30 minutes and a difference absorption spectrum taken. This spectrum revealed a clear new absorption feature at 855 nm, accompanying a decrease in absorbance by neutral QTR around 660 nm. This spectrum, enlarged 10 times, is shown as the solid line labeled "photoionization with D$_2$ lamp" in Figure 1. The absorption feature at 855 nm, although faint, was well above the signal-to-noise ratio limits and is due to the ionized QTR molecule (QTR$^+$), demonstrating that the ionization energy of QTR is reduced by at least 2 eV. This assignment is further substantiated by subsequent photoionization using 266 nm (energy ~4.66 eV) laser light. Full spectra measured after 5, 15, and 45 minutes of photolysis with the 266 nm laser line are shown as dashed curves in Figure 1. The growth of QTR$^+$ after each photolysis step is tightly correlated with the loss of neutral QTR. After 45 minutes of 266 nm laser photolysis, more than 70% of the neutral QTR has been nearly quantitatively converted to QTR$^+$ behavior, which is very similar to that found for other PAHs (GA03).

An interesting aspect of the spectrum shown in Figure 1 is that soft-ionization with 310 nm lamp-light depletes the portion of the neutral QTR band that absorbs at 660 nm, on the long wavelength side of the main absorption peak at 645 nm. It is quite likely that these QTR molecules occupy "special sites" in the ice matrix, sites that have an environment that promotes ionization at $\lambda < 310$ nm, 2.1 eV below the gas-phase ionization energy of 6.11 eV.

Photoionization of PAH molecules leading to PAH radical cations has been known for some time (see, for example, de Boer & Weissman 1958). Similarly, ionization of impurities such as NH$_3$ in the presence of CO in CO or H$_2$O ices leading to the formation of the less reactive "close shell" ions NH$_4^+$ and OCN$^-$ is also well established in the astrophysical literature (see Hudson & Moore 2000 and references therein; Park & Woon 2004). However, our recent series of publications (GA03; Gudipati 2004) are the first reports of the direct observation of PAH radical ions—which are "open shell" and highly reactive species—in water-rich ices. Our present work highlights the first experimental observation of the lowering of ionization energy up to 2 eV and by using QTR also shows the generality of high conversions of neutral PAHs to PAH cations upon energetic processing and their indefinite stability in H$_2$O ices below 50 K. As detailed in a recent publication aimed at physical chemists (Gudipati 2004), the results presented here show again that H$_2$O ice is not as reactive a matrix as has been taken for granted in the literature.

Generation of short-lived electrons in pure liquid water, also known as "hydrated electrons" at 6.5 eV (6.1 eV below the gas-phase ionization energy of H$_2$O at 12.6 eV), has been known for some time (Boyle et al. 1969). However, more recent studies (Faubel et al. 1997) on electron ejection from liquid jet of water or ice surfaces put the threshold for detecting an ejected electron to be around 10.1 eV (2.5 eV below the ionization energy of H$_2$O in the gas phase). Thus, lowering the ionization energy of imbedded guest molecules in water-rich ices is a logical extension, as found in this present study.

PAH ionization energy reduction in low-temperature water ice substantially expands the astronomical regions in which trapped ions and electrons may be important to include regions of lower energy radiation fields than normally considered for ion-driven chemistry and physics. Consequently, while radiation from late-type A, early F, and G-type stars is generally not considered ionizing, if water ices containing PAHs are exposed to radiation from these types of stars, the ice will become charged with PAH cations and electrons and the ion-moderated ice processes considered in GA03 can be important. Also, since these longer near-UV wavelengths are more weakly scattered and absorbed than the shorter vacuum UV wavelengths, the volume of a dense molecular cloud surrounding early-type stars in which the ices can become ionized will be significantly increased. Similarly, aromatics trapped in the water-rich icy objects beyond the orbit of Jupiter in the solar system can also be ionized by the radiation from the Sun, a G star. For example, organics or other molecules that can be ionized at 12 eV in the gas phase in Earth's upper atmosphere can be ionized with approximately the same efficiency in water ices at around 10 eV (Lyα) in Saturn's rings. Approximately 100 times more solar radiation flux at Lyα compared to 12 eV compensates the 100 times weaker flux at Saturn (9.54 AU) compared to the flux at Earth (1 AU).

This reduction in ionization energy should also hold for other types of organics trapped in water ice. Furthermore, since more-saturated organic species such as alkanes and olefins typically have ionization energies higher than PAHs, it is quite likely

that this reduction also enables photoionization of these types of species in cosmic environments, in particular those experiencing radiation from A-type stars.

Cosmic water-rich ices at cryogenic temperatures are common throughout the cosmos and are among the most important constituents in star- and planet-forming regions. They are also important in comets and many solar system objects beyond the orbit of Jupiter. A substantial reduction of ionization energy of molecular species imbedded in water ice expands the cosmic regions in which ionization can be important from those with harsh high-energy radiation fields to those with relatively benign radiation fields. It is conceivable, therefore, that in these benign regions and within the same ice, not only can the crudest form of biochemistry be taking place alongside ion-driven ice chemistry and ice physics, but these two processes may be symbiotic.

The exact mechanisms that lead to lowering ionization energy in cryogenic water ices still need to be investigated. A thorough study of the roles of impurity concentration, as well as ice temperature, structure, and thermal history, on the ion formation and stabilization process are underway. The results of these studies and their application to specific astronomical environments will be presented in a future publication.

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