Double Ionization of Quaterrylene (C_{40}H_{20}) in Water-Ice at 20 K with Ly_{α} (121.6 nm) Radiation

Murthy S. Gudipati*†,‡ and Louis J. Allamandola†§

NASA Ames Research Center, Mail Stop 245-6, Moffett Field, California 94035, and Institute for Physical Sciences and Technology, University of Maryland, College Park, Maryland 20742

Received: March 7, 2006; In Final Form: May 16, 2006

Polycyclic aromatic hydrocarbon (PAH) molecules undergo facile ionization in cryogenic water-ices resulting in near quantitative conversions of neutral molecules to the corresponding singly charged radical cations. Here we report, for the first time, the production and stabilization of a doubly ionized, closed shell PAH in water-ice. The large PAH quaterrylene (QTR, C_{40}H_{20}) is readily photoionized and stabilized as QTR^{2+} in a water-ice matrix at 20 K. The kinetic analysis of photolysis shows that the QTR^{2+} is formed at the expense of QTR\(^{+}\), not directly from QTR. The long-axis polarized S_{1}→S_{0} (1^1B_{3g}→1^1A_{g}) transition for QTR^{2+} falls at 1.59 eV (782 nm). TD-DFT calculations at the B3LYP level predict that this transition falls at 1.85 eV (670 nm) for free gas-phase QTR^{2+}, within the 0.3 eV uncertainty associated with these calculations. This red shift of 0.26 eV is quite similar to the 0.24 eV red shift between the TD-DFT computational prediction for the lowest energy transition for QTR^{+} (1.68 eV) and its value in a water matrix (1.44 eV). These results suggest that multiple photoionization of such large PAHs in water-ice can be an efficient process in general.

Introduction

The chemistry and physics of low-temperature water-ices and impurities trapped within are undergoing a revival of interest due to recent advances in astrophysics and atmospheric science. Water-rich, mixed molecular ices are common throughout interstellar molecular clouds,\(^{1}\) the Solar System,\(^{2,3}\) and atmospheric aerosols.\(^{4}\) Laboratory analogue experiments have shown vacuum ultraviolet (VUV) irradiation and particle bombardment of water dominated mixed molecular ices containing impurities such as CH_{3}OH, NH_{3}, CO and PAHs (polycyclic aromatic hydrocarbons) produce complex organic species, including important biogenic molecules such as amino acids and functionalized PAHs which may have played a role in the origin of life.\(^{5-10}\)

In an attempt to understand the fundamental processes that occur during VUV photolysis of water dominated mixed molecular ices containing PAHs, several counterintuitive phenomena were recently discovered. PAHs embedded in cryogenic water-ice are easily and efficiently ionized (>80%, i.e., near quantitative ion yields) to the cation form by VUV photons.\(^{11,12}\) PAH ionization energy is lowered by up to 2 eV compared to that in the gas phase.\(^{13}\) in agreement with recent theoretical predictions;\(^{14,15}\) and PAH cations are stabilized to temperatures as high as 120 K.\(^{16}\) Here we report, for the first time, that closed-shell PAH dications can also be produced and stabilized in water-ice.

The results presented here show that the PAH quaterrylene (QTR), when trapped in water-ice at a low temperature, can be doubly ionized to the QTR dication (QTR^{2+}) through a sequential ionization process, QTR to QTR^{+} to QTR^{2+}, with Ly_{α} photons (121.6 nm, 10.2 eV). Up to now, multiple ionization of aromatic molecules is known only in the gas phase and detection is typically via mass spectrometry.\(^{17,18}\) Direct double photoionization of aromatic molecules needs high-energy photons, as illustrated in the case of naphthalene. The first ionization threshold of naphthalene is at 8.12 eV, whereas double photoionization requires photons with energies greater than 21 eV.\(^{19}\)

Other recent work on energetic processing of water-ices includes the study of molecular dissociation through photolysis and radiolysis,\(^{20,21}\) and the chemistry of anthropogenic aromatic pollutants in arctic ice.\(^{22}\) Electron bombardment of water-ice surfaces has recently been shown to produce protons and hydrogen molecular cations as a result of dissociative ionization of water molecules on the surface.\(^{23}\) To the best of our knowledge, there are no reports of sequential double ionization of aromatic molecules with photons as low in energy as Ly_{α}.

Experimental Section

The experimental setup, consisting of a cryogenic sample holder, a spectrophotograph and detector has been described elsewhere.\(^{13,24}\) 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 QTR was carried out using a microwave-powered, flowing hydrogen-discharge lamp which produces Ly_{α} radiation at 121.6 nm and a roughly 20 nm wide band of molecular hydrogen emission lines centered near 160 nm, with a flux of approximately 2 \times 10^{11} photons/s.

QTR (molecular structure shown in Figure 1) was obtained from Dr. W. Schmidt (PAH Forschungs Institut, Greifenberg, Germany) and used without further purification. High-purity deionized water (18 MΩ) was deposited at an approximate rate of 0.02 mmol h^{-1} onto a LiF cryogenic optical window kept at 30 K. Quaterrylene vapor was simultaneously deposited onto...
The absorption spectrum of a freshly deposited neutral quaterrylene compromise was made to maintain the window at 30 K during deposition of QTR and H$_2$O vapor onto the LiF window, is shown in the top-frame of Figure 1. This spectrum, which consists of a strong band peaking at 650 nm and two vibronic components at 595 and 550 nm, is due to the $S_1 \rightarrow S_0$ ($\text{I}^1\text{B}_3 \leftarrow \text{I}^1\text{A}_2$) transition in QTR, which has an oscillator strength of 1.08. $^{2,5}$ The lower frame of Figure 1 shows the absorption spectra that were obtained at different VUV-photolysis doses, by taking the preirradiation spectrum (upper frame) as the reference. Between 0 and 600 s of photolysis, the simultaneous growth of a strong absorption band around 860 nm with a very weak satellite feature at 780 nm can be clearly seen. Both are due to the QTR radical cation (QTR$^+$) generated upon photoionization. These bands are assigned to the D$_2$ $\rightarrow$ D$_0$ ($2^3\text{B}_g \leftarrow 1^2\text{A}_u$) transition in QTR$^+$, which has an oscillator strength of 1.03.$^{2,5}$

The corresponding loss of the neutral parent QTR is about 50% after 600 s of photoionization. Upon prolonged photolysis, absorption overlapping the weak satellite feature at 780 nm grows more rapidly, whereas the dominant QTR$^+$ absorption band at 860 nm diminishes in intensity. After 2400 s of irradiation, close to 80% of the neutral QTR has become ionized. These photochemical reactions are modeled with Scheme 1 below. Reaction rates ($k$) are determined by manually changing the variable parameters in a manner similar to the procedure used to obtain the relative photoionization reaction rates of 4-methylpyrene in a water matrix.$^{12}$ The results are plotted as dashed lines in Figure 2. All the parameters are expressed in terms of $k_2$, which is determined to be $2.5 \times 10^{-3}$ absorbance units per second ($k_1 = k_3 = 0.02k_2$, $k_{-2} = 0.45k_2$).

**Results and Discussion**

Section 1: Identification of QTR$^{2+}$. Throughout the following we use water-ice and water matrix interchangeably to represent the cryogenic H$_2$O solid, in either the amorphous or crystalline phases as specified. The absorption spectrum of a QTR/H$_2$O ($\sim$1/500) ice at 20 K, prepared by 4 h of co-deposition of QTR and H$_2$O vapor onto the LiF window, is shown in the top-frame of Figure 1. This spectrum, which consists of a strong band peaking at 650 nm and two vibronic components at 595 and 550 nm, is due to the $S_1 \rightarrow S_0$ ($\text{I}^1\text{B}_3 \leftarrow \text{I}^1\text{A}_2$) transition in QTR, which has an oscillator strength of 1.08.$^{2,5}$ The lower frame of Figure 1 shows the absorption spectra that were obtained at different VUV-photolysis doses, by taking the preirradiation spectrum (upper frame) as the reference. Between 0 and 600 s of photolysis, the simultaneous growth of a strong absorption band around 860 nm with a very weak satellite feature at 780 nm can be clearly seen. Both are due to the QTR radical cation (QTR$^+$) generated upon photoionization. These bands are assigned to the D$_2$ $\rightarrow$ D$_0$ ($2^3\text{B}_g \leftarrow 1^2\text{A}_u$) transition in QTR$^+$, which has an oscillator strength of 1.03.$^{2,5}$

The corresponding loss of the neutral parent QTR is about 50% after 600 s of photoionization. Upon prolonged photolysis, absorption overlapping the weak satellite feature at 780 nm grows more rapidly, whereas the dominant QTR$^+$ absorption band at 860 nm diminishes in intensity. After 2400 s of irradiation, close to 80% of the neutral QTR has become ionized.

**Photokinetics.** These photochemical reactions are modeled with Scheme 1 below. Reaction rates ($k$) are determined by manually changing the variable parameters in a manner similar to the procedure used to obtain the relative photoionization reaction rates of 4-methylpyrene in a water matrix.$^{12}$ The results are plotted as dashed lines in Figure 2. All the parameters are expressed in terms of $k_2$, which is determined to be $2.5 \times 10^{-3}$ absorbance units per second ($k_1 = k_3 = 0.02k_2$, $k_{-2} = 0.45k_2$).
defined, work by several investigators indicates that photolytic production of the 782 nm band as these species are not expected to the host ice matrix,26 even if this energy is localized on one photoproduct, or to doubly ionize QTR\(^+\) to QTR\(^{2+}\), a process that needs 6–7 eV to occur efficiently. Thus the role of secondary ionization reactions caused by ionized or dissociated host photoproducts through energy transfer can be neglected. The second possibility is the direct reaction of QTR\(^+\) with the host photoproducts H or H\(^+\) to produce the 782 nm band carriers. Such reactions may be possible, leading to the formation of QTR\(^+\) from QTR and QTR\(^{2+}\) from QTR\(^+\), when H\(^+\) reacts with the QTR or QTR\(^+\), respectively. Similarly, it should be possible for H atoms to react with QTR to generate QTR\(^+\), and with QTR\(^+\) to generate QTR\(^{2+}\). We can rule out the possibility that a reaction product of neutral QTR with H or H\(^+\) produces the 782 nm band because the behavior shown in Figure 2 and the kinetic analysis indicates that the species responsible for the 782 nm absorption is generated from QTR\(^+\), not QTR. Protonation of QTR\(^+\) seems less likely than protonation of neutral QTR due to Coulomb repulsion. This leaves QTR\(^+\), formed through H atom addition to QTR\(^+\), as the possible alternative to QTR\(^{2+}\) as the carrier of the 782 nm band.

QTR\(^+\) is ruled out as the carrier of the 782 nm band as follows. After 2400 s of in-situ VUV photolysis, the QTR/H\(_2\)O ice was warmed to 50 K. As shown in Figure 3, the initial warm-up from 20 to 50 K resulted in slight depletion of the 782 nm band (assigned to QTR\(^{2+}\)) and growth of the 860 nm QTR\(^2\) band. This is possible only if the species responsible for the 782 nm band absorption is something that readily reverts to QTR\(^+\) in a water matrix at 50 K. It is highly unlikely that protonated QTR (QTR\(^+\)) or a fragment of QTR\(^+\) is the carrier of the 782 nm band as these species are not expected to of the PAH to PAH\(^+\). However, these reactions are considered here in light of the greater size of QTR. We exclude these reaction products as potential carriers of the 782 nm feature as described below. Keeping in mind that the carrier of the 782 nm absorption band is created at the expense of QTR\(^+\), reactions that are pertinent to QTR\(^+\) are only considered.

Under our experimental conditions in which Ly\(_\alpha\) radiation (10.2 eV) is used, the maximum amount of energy that is available to the photoproducts H or H\(^+\) is 3.4 eV because ion-pair and autoionization processes require 6.8 eV to occur in water ice.\(^{26}\) Even if this energy is localized on one photoproduct, it is not sufficient to ionize QTR to QTR\(^+\), or to doubly ionize QTR\(^+\) to QTR\(^{2+}\), a process that requires around 4.6 eV, or to doubly ionize QTR\(^+\) to QTR\(^{2+}\), a process that needs 6–7 eV to occur efficiently. Thus the role of secondary ionization reactions caused by ionized or dissociated host photoproducts through energy transfer can be neglected. The second possibility is the direct reaction of QTR\(^+\) with the host photoproducts H or H\(^+\) to produce the 782 nm band carriers. Such reactions may be possible, leading to the formation of QTR\(^+\) from QTR and QTR\(^{2+}\) from QTR\(^+\), when H\(^+\) reacts with the QTR or QTR\(^+\), respectively. Similarly, it should be possible for H atoms to react with QTR to generate QTR\(^+\), and with QTR\(^+\) to generate QTR\(^{2+}\). We can rule out the possibility that a reaction product of neutral QTR with H or H\(^+\) produces the 782 nm band because the behavior shown in Figure 2 and the kinetic analysis indicates that the species responsible for the 782 nm absorption is generated from QTR\(^+\), not QTR. Protonation of QTR\(^+\) seems less likely than protonation of neutral QTR due to Coulomb repulsion. This leaves QTR\(^+\), formed through H atom addition to QTR\(^+\), as the possible alternative to QTR\(^{2+}\) as the carrier of the 782 nm band.

QTR\(^+\) is ruled out as the carrier of the 782 nm band as follows. After 2400 s of in-situ VUV photolysis, the QTR/H\(_2\)O ice was warmed to 50 K. As shown in Figure 3, the initial warm-up from 20 to 50 K resulted in slight depletion of the 782 nm band (assigned to QTR\(^{2+}\)) and growth of the 860 nm QTR\(^2\) band. This is possible only if the species responsible for the 782 nm band absorption is something that readily reverts to QTR\(^+\) in a water matrix at 50 K. It is highly unlikely that protonated QTR (QTR\(^+\)) or a fragment of QTR\(^+\) is the carrier of the 782 nm band as these species are not expected to of the PAH to PAH\(^+\). However, these reactions are considered here in light of the greater size of QTR. We exclude these reaction products as potential carriers of the 782 nm feature as described below. Keeping in mind that the carrier of the 782 nm absorption band is created at the expense of QTR\(^+\), reactions that are pertinent to QTR\(^+\) are only considered.

Under our experimental conditions in which Ly\(_\alpha\) radiation (10.2 eV) is used, the maximum amount of energy that is available to the photoproducts H or H\(^+\) is 3.4 eV because ion-pair and autoionization processes require 6.8 eV to occur in water ice.\(^{26}\) Even if this energy is localized on one photoproduct, it is not sufficient to ionize QTR to QTR\(^+\), or to doubly ionize QTR\(^+\) to QTR\(^{2+}\), a process that requires around 4.6 eV, or to doubly ionize QTR\(^+\) to QTR\(^{2+}\), a process that needs 6–7 eV to occur efficiently. Thus the role of secondary ionization reactions caused by ionized or dissociated host photoproducts through energy transfer can be neglected. The second possibility is the direct reaction of QTR\(^+\) with the host photoproducts H or H\(^+\) to produce the 782 nm band carriers. Such reactions may be possible, leading to the formation of QTR\(^+\) from QTR and QTR\(^{2+}\) from QTR\(^+\), when H\(^+\) reacts with the QTR or QTR\(^+\), respectively. Similarly, it should be possible for H atoms to react with QTR to generate QTR\(^+\), and with QTR\(^+\) to generate QTR\(^{2+}\). We can rule out the possibility that a reaction product of neutral QTR with H or H\(^+\) produces the 782 nm band because the behavior shown in Figure 2 and the kinetic analysis indicates that the species responsible for the 782 nm absorption is generated from QTR\(^+\), not QTR. Protonation of QTR\(^+\) seems less likely than protonation of neutral QTR due to Coulomb repulsion. This leaves QTR\(^+\), formed through H atom addition to QTR\(^+\), as the possible alternative to QTR\(^{2+}\) as the carrier of the 782 nm band.

QTR\(^+\) is ruled out as the carrier of the 782 nm band as follows. After 2400 s of in-situ VUV photolysis, the QTR/H\(_2\)O ice was warmed to 50 K. As shown in Figure 3, the initial warm-up from 20 to 50 K resulted in slight depletion of the 782 nm band (assigned to QTR\(^{2+}\)) and growth of the 860 nm QTR\(^2\) band. This is possible only if the species responsible for the 782 nm band absorption is something that readily reverts to QTR\(^+\) in a water matrix at 50 K. It is highly unlikely that protonated QTR (QTR\(^+\)) or a fragment of QTR\(^+\) is the carrier of the 782 nm band as these species are not expected to
regenerate QTR\(^{+}\) upon warm-up over this temperature domain in which the ice matrix does not undergo any major phase transitions.\(^{28}\) On the other hand, we have found thermally promoted electron migration and electron–ion recombination over this temperature range in water ice, work which will be described elsewhere.

**Theoretical Computations.** To better understand the nature of the transition and the ionization energetics, time dependent-density functional theory (TD-DFT) computations were carried out on QTR\(^{2+}\). The B3LYP method and 6-31G(d) basis sets using the GAUSSIAN03 program package\(^{29}\) were used to determine the 0\textendash{}0 transition energies for various ground-to-excited state transitions. Such calculations have already been reported for neutral and singly ionized QTR at the BLYP/6-31G* level.\(^{29}\) The results of these calculations and the experimental values available are summarized in Table 1. The electronic states for the mono- and dications show similar matrix shifts (\(0.25 \text{ eV}\)) between the gas-phase theory predictions and the values measured in a water matrix. All of the calculated values fall within 0.3 \text{ eV}\) of the experimental values, the uncertainty normally associated with this level of calculation. Systematic studies show that indeed TD-DFT maintains uniform accuracy for open-shell (multiplets) and closed-shell (singlets) systems.\(^{30}\) Interestingly, the matrix red shift in going from a Ne to \(\text{H}_2\text{O}\) matrix is smaller for QTR\(^{+}\) (0.04 \text{ eV}) than it is for neutral QTR (0.13 \text{ eV}).

On the basis of the kinetic behavior shown in Figures 1 and 2, taken together with these calculations, we assign the absorption band at 782 nm to QTR\(^{2+}\). These results suggest that the photoelectron is ejected from the site (cage) in which QTR\(^{2+}\) is generated and is subsequently stabilized at another “site” in the water matrix (cage-exit of the photoelectron). Given the greater electron affinity of \(\text{H}_2\text{O}\) matrix over Ne matrix, it is likely that electrons diffuse far more slowly and travel much smaller distances in a \(\text{H}_2\text{O}\) matrix compared to a Ne matrix.

The low first ionization energies of the neutral and singly charged QTR in \(\text{H}_2\text{O}\) matrix, combined with the ability of the \(\text{H}_2\text{O}\) matrix to stabilize the ionized molecules and the corresponding electrons, allows the significant single and double photoionization processes observed here with relatively mild photon energies (\(\leq 10.2 \text{ eV}\)) and mild photon flux.

To have sequential photoionization of QTR with Ly\(_{\alpha}\) photons, ionization threshold energies for both neutral QTR and QTR\(^{+}\) below 10.2 eV are implied. To test this, the vertical ionization energies using the B3LYP method with 6-31G(d) basis sets were computed. For neutral QTR the computed ionization energy is 5.43 eV, in reasonably good agreement with the experimental value of 6.11 eV.\(^{31}\) For the second ionization step, namely, QTR\(^{+}\) to QTR\(^{2+}\), the ionization energy is computed to be 8.3 eV. Thus, Ly\(_{\alpha}\) radiation is sufficient to drive both steps of the sequential ionization processes.

Further support for the QTR\(^{2+}\) assignment is derived from the absence of the 782 nm absorption band when neutral QTR is irradiated in a water matrix with 266 nm laser photons under identical experimental conditions (dotted spectrum in Figure 1).\(^{13}\) The energy of the 266 nm photons at 4.66 eV is sufficient only for the first ionization of QTR to QTR\(^{+}\) in a water matrix.

Given the ability of a water matrix to lower the ionization energy of PAH molecules by about 2 eV,\(^{12\text{–}14}\) it may be possible that even lower energy photons could doubly ionize such large PAHs in these matrices. As only single photoionization of QTR occurs in water matrices with 266 nm photons,\(^{13}\) double ionization of QTR is expected to occur in such matrices at threshold photon energies of 6\textendash{}7 eV. This range is deduced on the basis of the observed lowering of QTR ionization energy by 2 eV in water matrices and the computed second ionization threshold for gas-phase QTR to be 8\textendash{}9 eV. When a hydrogen flow-discharge lamp is used, in addition to Ly\(_{\alpha}\) photons at 121.6 nm (10.2 eV) due to atomic hydrogen, photons are also emitted from the molecular hydrogen around 160 nm. The energy of these lines centered around 7.75 eV, is sufficient to ionize QTR to QTR\(^{+}\) and QTR\(^{+}\) to QTR\(^{2+}\) in water ice (after taking lowering of the ionization energy of 2 eV in ice compared to that in the gas phase into account). Further work is underway to obtain threshold ionization energies for both QTR and QTR\(^{+}\) in water-ices. We also plan to investigate if quaterrylene can be triply ionized to QTR\(^{3+}\) and stabilized in water-ices and extend these studies to PAHs of various sizes to understand how far these molecules can be ionized before they spontaneously break apart due to Coulomb repulsion.

**Section 2: Comparison between QTR Photochemistry in \(\text{H}_2\text{O}\) and Neon Matrices.** The absorption spectra of QTR, its monocation QTR\(^{+}\), and its monoanion QTR\(^{-}\) have been measured by Halasinski et al. in Ne matrices.\(^{25}\) The ions have been formed by in-situ irradiation of QTR isolated in a neon matrix in a manner similar to that described here. The detection of QTR\(^{-}\) in a neon matrix raises the possibility of its formation and stabilization in an \(\text{H}_2\text{O}\) matrix as well.

As one would expect, the vibronic bands of QTR trapped in a Ne matrix show more structure and are narrower than those of QTR in a water matrix. The 650 nm band of neutral QTR shown in Figure 1 has a FWHH of nearly 35 nm whereas the fwhh for the same transition in Ne at 608 nm is about 9 nm. Furthermore, the vibronic bands of QTR in a neon matrix show substructure that is not evident in the spectra in the ice matrix shown in Figure 1. At our resolution of 0.44 nm, the neon matrix substructure would be resolvable. The lack of such structure indicates that, in amorphous water ice, inhomogeneous line broadening due to sites is far more dominant than in neon matrices.

Although they did not report the double ionization of QTR to QTR\(^{2+}\) in a neon matrix, Halasinski et al. observed formation of the radical anion QTR\(^{-}\) via electron capture by neutral QTR.\(^{23}\)

Upon in-situ photolysis, these authors detected absorption by the radical cation (QTR\(^{+}\)) at 835 nm when matrices contained NO\(_2\), an electron trap. In the absence of NO\(_2\), absorption bands

---

**TABLE 1: Time Dependent, Density Functional Theory (TD-DFT) Energies (eV) for the Lowest Level Transitions of QTR, QTR\(^{+}\), and QTR\(^{2+}\) Compared with the Values Measured in a Neon Matrix at 4 K and in Water-Ice at 20 K (Computed Oscillator Strengths \(\beta\) in Parentheses)**

<table>
<thead>
<tr>
<th>species</th>
<th>transition</th>
<th>experiment (\text{Ne matrix}(^{a}))</th>
<th>(\text{H}_2\text{O matrix}(^{b}))</th>
<th>theory (\text{BLYP/6-31G}(^{d}) TD-DFT(^{c}))</th>
<th>(\text{B3LYP/6-31G}(^{d}) TD-DFT(^{c}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>neutral (QTR)</td>
<td>(1^{1}\text{B}<em>{3u} \rightarrow 1^{1}\text{A}</em>{g})</td>
<td>2.04</td>
<td>1.91</td>
<td>1.67 (1.08)</td>
<td>1.87 (1.23)</td>
</tr>
<tr>
<td>monocation (QTR(^{+}))</td>
<td>(2^{2}\text{B}<em>{3u} \rightarrow 2^{2}\text{A}</em>{g})</td>
<td>1.48</td>
<td>1.44</td>
<td>1.62 (1.03)</td>
<td>1.68 (1.29)</td>
</tr>
<tr>
<td>dication (QTR(^{2+}))</td>
<td>(1^{1}\text{B}<em>{3u} \rightarrow 1^{1}\text{A}</em>{g})</td>
<td>1.59</td>
<td></td>
<td>1.85 (1.4)</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) From ref 25. \(^{b}\) Present work, also from ref 13.
attributed to both the radical cation and radical anion (QTR$^-$) were detected, the anion absorbing at longer wavelengths at 880 nm compared to the cation at 835 nm. This raises questions regarding the possibility of QTR$^-$ formation in irradiated water ice. Though this cannot be ruled out on the basis of the experiments reported here, we do not observe any significant absorption at wavelengths longer than that of QTR at 860 nm. However, it is possible that a very broad shoulder evident in the spectra shown in Figure 1 may indeed be due to the radical anion of quaterrylene. This feature which peaks near 910 nm appears to grow in continuously with photolysis and is clearly evident after 600 s of photolysis time.

In a water matrix, the absorption of doubly ionized quaterrylene, QTR$^{2+}$, occurs at a shorter wavelength (782 nm) than does the absorption of the quaterrylene monocation, QTR$^+$ (850 nm). Because no corresponding absorption is detected in a Ne matrix, this we conclude that double ionization of QTR is not facilitated in a Ne matrix. This difference in behavior likely originates from the 2–3 eV electron affinity of a water matrix, versus the negative electron affinity for a neon matrix of −1.3 eV. In Ne matrices, electrons are not bound to the lattice. As a consequence, in Ne, electrons recombine efficiently with QTR$^+$ or are captured by neutral QTR molecules, generating the anion, QTR$^−$. Conversely, the electron is strongly solvated in water matrices and trapped locally by H$_2$O molecules, hindering its recombination with other QTR species.

**Conclusions**

The case has been made for the production and stabilization of QTR$^{2+}$, a closed shell dication, in a water matrix by the sequential photoionization: QTR → QTR$^+$ → QTR$^{2+}$. These findings, combined with recent theoretical and experimental results, show that ionization in water-ice is not unusual, but an important process. Cryogenic water matrices assist in-situ, stepwise, multiple photoionization processes and stabilize otherwise very reactive ionic products such as QTR$^{2+}$ reported here. The electron affinity of water lowers the ionization energy of trapped species and stabilizes the ionized products. Lower ionization energies of QTR and QTR$^+$ in water-ice and the ability of the water matrix to stabilize both ionized species and generated electrons allows the significant single and double photoionization processes observed here with relatively mild photon energies ($\leq$10.2 eV) and fluxes. These findings are important for our understanding of the chemistry and physics of low-temperature water-rich ices that are abundant in our Solar System and also in the interstellar medium. The water-assisted lowering of organic molecule ionization energies may also play a role in terrestrial chemistry. For example, related water assisted process involving charged species could be important in the chemistry of stratospheric aerosols and ices containing anthropogenic impurities in the Polar Regions of the earth.

**Acknowledgment.** This work was supported by grants from NASA’s Exobiology, Astrobiology, and Long Term Space Astrophysics Programs (Grants: 344-58-12, 344-53-92, and 399-20-40 respectively), NASA’s Planetary Geology and Geophysics Program (Grant: NNG05G101G) and a NASA—University of Maryland cooperative agreement (NCC 2-1303). We thank the referees, whose reviews helped to improve this publication significantly.

**References and Notes**