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The radiolysis of poly(4-vinylpyridine) quaternary salt ion exchange resins

Kazuyuki Enomoto [a], Jay A. LaVerne [a,b,*], Lav Tandon [c], Alejandro E. Enriquez [d], John H. Matonic [d]

[a] Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA
[b] Department of Physics, University of Notre Dame, Notre Dame, IN 46556, USA
[c] Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA
[d] PMT-5 Pu-238 Science and Engineering Group, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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Abstract

The radiation chemical yields of gaseous products, especially molecular hydrogen (H_2), have been determined in the radiolysis of different poly(4-vinylpyridine) quaternary salt ion exchange resins with up to about 30 wt% of absorbed water. Irradiations were performed with 5 MeV ^{4}He ions to simulate α-particle radiolysis and with γ-rays for comparison. The resins were quaternary salts of chloride and nitrate that are commonly used as matrixes in anion exchange and in plutonium recovery processes. An increase in H_2 yields with increasing water loading was observed for both types of ionizing radiation in all of the resins. The yield of H_2 for the nitrate-form was lower than that for the chloride and the yield of H_2 was lower when the pyridinium nitrogen atom is coordinated to a methyl group rather than to atomic hydrogen. Spectroscopic studies included UV/vis, IR, and Raman and suggested that all the resins exhibit a high radiolytic stability.

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1. Introduction

Ion exchange resins used in the reprocessing of radioactive materials are a vital link in the nuclear fuel cycle [1]. Even though some resins have been engineered for their selectivity and efficiency, their characteristics will constantly be changing as they undergo radiolysis in the separation of radioactive materials. Poly(4-vinylpyridine) quaternary salts under various forms have been used in nitric acid plutonium recovery processes [2]. Plutonium in the positive four charge state is stable in nitric acid, forming the divalent hexanitrate complex $Pu(NO_3)_6^{2-}$ [3–5]. The plutonium can be removed selectively from the nitric acid by Reillex™ HPQ and Reillex™ 402 anion-exchange resins (Reillex™ HPQ and Reillex™ 402 are registered trademarks of Reilley Industries, Inc.), which are based on poly(4-vinylpyridine) quaternary salts [6]. Reillex™ HPQ is a poly(4-vinylpyridine) resin cross-linked with divinyl benzene, which consists of a 1-methylpyridinium cation and chloride, Cl^-, or nitrate, NO_3^-, counterions. Reillex™ 402 is similar, except that a hydrogen atom is attached to the nitrogen. Fig. 1 shows the structures of the series of Reillex™ resins employed here. These resins are packed into a column through which the nitric acid solution of plutonium is flowed. The plutonium hexanitrate is retained by complexing with two positively charged nitrogen sites of the resin [2]. Radiolysis of the resin and associated water by emitted α-particles can lead to concerns in the management of the exchange columns. The production of molecular hydrogen, H_2, is especially important because its

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[*] Corresponding author. Address: Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA.
E-mail address: laverne.l@nd.edu (J.A. LaVerne).

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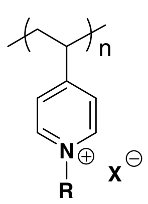

	R	X
HPQ	CH_3	Cl NO_3
402	H	Cl NO_3

Fig. 1. Structures of the pyridinium salts.

flammability and explosion potential can cause serious engineering and maintenance problems [7–10]. Molecular oxygen, O_2, formation from the water or nitrate radiolysis can exasperate the problem considerably.

The radiolysis of organic polymer materials leads to the production of gases, especially H_2, depending on the nature of polymers or the type of ionizing radiation [11–17]. The production of H_2 can be explained from simple radical chemistry (e.g., H atom–H atom combination, H atom abstraction, and disproportionation) following C–H bond breakage due to the energy deposited by the passage of ionizing radiation or from the unimolecular decomposition of excited singlet states [13,16]. In general, H_2 yields are found to increase with increasing LET (linear energy transfer $= -dE/dx$) of the incident radiation because of changes in the track geometry as defined by the local region where the energy is deposited. For instance, the yield of H_2 is fourfold greater with 5 MeV ^{4}He ions than with γ-rays for both liquid benzene and polystyrene [13]. Reillex™ resins carry a repeated unit of a pyridine analogue and the radiation chemistry is expected to correlate closely with the radiolysis of liquid pyridine, which also exhibits an increase in the yield of H_2 with increasing LET [13,18–20].

Since separation processes include an aqueous phase, the radiolytic decay of water must also be considered. The hydrated electron, e^-_{aq}, and its precursors are major contributors to the production of H_2 in the radiolysis of liquid water [21–25]. H atoms are also expected to play an important role, especially in acidic solutions [26]. The yield of H_2 in water is 0.45 molecule/100 eV with γ-rays and a strong LET dependence is observed [21,26]. Water radiolysis may be different when it is present in the adsorbed state on the resin surface than in the bulk, but water is still expected to contribute to the overall decomposition mechanism. Experimental studies on the radiolytic decomposition of these systems may lead to models for predicting radiation damage allowing for the better management of nuclear waste materials and reprocessing systems.

In this work, the radiation chemical yields of gaseous products, especially H_2, have been determined in the radiolysis of poly(4-vinylpyridine) and various Reillex™ resins with different amounts of adsorbed water. Irradiations were performed with 5 MeV ^{4}He ions to simulate α-particle radiolysis and with γ-rays for comparison. Optical analysis included obtaining IR, Raman, and UV/vis spectra of the irradiated resins to determine bulk degradation and to identify product formation.

2. Experimental section

2.1. Materials

Poly(4-vinylpyridine) (P4VP), poly(4-vinylpyridine) methylammonium chloride (Reillex™ HPQ), and poly(4-vinylpyridine) ammonium chloride (Reillex™ 402) resins were purchased from Aldrich and used without further purification. (Reillex™ HPQ and Reillex™ 402 are registered trademarks of Reilley Industries, Inc.) The latter two compounds are referred to in this work as Reillex™ HPQ and Reillex™ 402, respectively. The manufacturing lots were 04719PC, 04411PC, and 08227PI, respectively. Reillex™ HPQ chloride-form, lot no. 80302MA, was obtained directly from Reilley Industries and is referred to in this work as LANL HPQ. These resins are in the form of beads with diameters of about 100–1000 μm.

2.2. Anion exchange

Reillex™ resins in the chloride-form were anion exchanged using aluminum nitrate (Aldrich), $Al(NO_3)_3$, to give the nitrate-form. Two slightly different methods were used at the two laboratories to check for nitrating effects. At Notre Dame, the chloride-form resin from Aldrich (5.0 g) immersed in high purity water was transferred to a column of Pyrex ($\phi \sim 1$ cm, $L \sim 50$ cm) containing a plug of glass wool to support the resin bed. An aqueous solution 100 mL of 0.1 M $Al(NO_3)_3$ was allowed to flow through the column at a rate of 1 mL/min. The treatment was repeated three times, a total of 300 mL solution, until the column effluent showed no traces of chloride ion using an ion chromatography (Dionex Ion Chromatograph). The resin was then rinsed with water, filtered, and dried under vacuum. The apparatus is more of a commercial scale at Los Alamos where the Reillex™ HPQ resin was placed in a Pyrex column and covered with 0.6 M $Al(NO_3)_3$ for 24 h. The resin was then rinsed twice with 0.2 M HNO_3 followed by four rinses of deionized water and transferred using a peristaltic pump for storage under water in a carboy. Part of the resin was removed and dried under vacuum. A portion of the LANL HPQ nitrate-form was further heat treated to give LANL HPQ LTE according to a procedure reported by Crooks et al. [27]. This latter treatment is meant to remove any residual ethylbenzene pendant groups from the polystyrene copolymer.

2.3. Water loading

Prior to radiolysis, the resins were dried under vacuum, weighed, and placed in constant humidity chambers at room temperature. Three different relative humidity chambers were used. One chamber with drierite (calcium sulfate) was used to simulate “dry” conditions. Another chamber contained $Mg(NO_3)_2$ salt slush to obtain a relative humidity of 53% [28,29]. The final chamber contained water alone to obtain a relative humidity of about 95%. The resins were periodically removed from the constant relative humidity chambers and weighed to determine total water adsorbed. Equilibrium was attained in about 4 days for 1 g of material.

2.4. Five MeV helium ion radiolysis

The heavy ion radiolysis experiments were performed using the facilities of the Nuclear Structure Laboratory in the University of Notre Dame Physics Department. The 10 MV FN Tandem Van de Graaff in this facility was used to accelerate ^{4}He ions to an energy of about 10 MeV resulting in an energy of 5 MeV incident to the sample of resin after passing through all windows. The window assembly was the same as reported earlier and gave a beam diameter of 6.4 mm with a uniform flux across the sample surface [30,31]. Energy loss of the helium ions in passing through all windows was determined from a standard stopping power compilation [32]. The samples were irradiated with completely stripped ions at a charge beam current of about 2 nA. Total energy deposition was obtained from the product of the integrated beam current and the ion energy incident to the resin sample. The ranges of the helium ions are about 34 μm in the resins, which is smaller than the sample thickness. Dosimetry was calculated from the total energy deposition in the local volume exposed to the beam and varied up to 20 MGy. The sample cell ($\phi \sim 1$ cm, $L \sim 0.013$ mm) was made of quartz with a mica window of about 5.0 mg/cm^2 epoxied to the front for the beam entrance. Inlet and outlet ports allowed the cell to be purged before and after the irradiation. Irradiations were performed at room temperature and the dose rate was sufficiently small so that no significant macroscopic heating was observed.

2.5. γ-Radiolysis

Radiolysis with γ-rays was performed using a Shepherd 109–68 60Co source at the Radiation Laboratory of the University of Notre Dame. The dose rate was 100 Gy/min as determined using the Fricke dosimeter [33]. The sample cell and dosimetric technique are the same as in a previous study [34]. The Fricke dosimeter gives the amount of energy deposited of each target material relative to that for water. Energy absorption by the total sample was estimated from the weight of both the resin and water. Total sample weights were typically ~1 g. The ambient temperature of the irradiation chamber was about 30 °C, and samples would rise to this temperature during long irradiations.

2.6. Gas analysis

Molecular hydrogen was determined using an inline technique as previously reported [33]. Gas chromatographic, GC, analysis was carried out using an SRI 8610 equipped with a thermal conductivity detector. The column was a 6.4 mm diameter 13× molecular sieve 3 m long, maintained at 40 °C. The sample cell was made from a quartz cuvette. The sample was purged with ultra-high-purity argon for 10 min at room temperature and the cell was sealed with a four-way valve during the radiolysis. A prebubbler was used with the samples at a relative humidity of 53% and 95% in order to prevent sample drying. Dose dependent studies were performed with 10–50 kGy of γ-rays. Following irradiation, the sample cell was opened to the column gas stream using the four-way valve. Calibration was performed by injection of pure hydrogen gas.

Other gases were analyzed with a quadrupole mass spectrometer coupled to the GC and operated in a multiple-ion-detection mode. The sample for γ-radiolysis was placed in Pyrex tubes ($\phi \sim 1$ cm, $L \sim 10$ cm), purged with helium, degassed, and heat-sealed. Total sample weights were typically ~1 g. Following irradiation the tube was broken using an inline technique and the generated gases were determined by the mass spectrometer operating at $m/z =$ 16, 28, 30, 32, 44, and 46. Molecular nitrogen was monitored at mass 28 and nitrous oxide at mass 44. The limit of the sensitivity of the measurements of molecular nitrogen and nitrous oxide was determined experimentally to be about 1 μL at room temperature and atmospheric pressure. Ultra-high-purity helium was used as the carrier gas with flow rates of about 50 mL/min. The estimated error in gas measurement is about 5%.

2.7. Spectroscopic analysis

The resins were placed in the recessed center of an aluminum button, covered, secured with a mica window, and exposed to the ^{4}He ion beam. The resin beads are not very mobile so removal of the mica window following irradiation allows reflective spectroscopic analysis of the surface. Diffuse infrared Fourier transform spectroscopy (DRIFT) was performed using a Bruker Vertex 70 FT-IR spectrometer with a resolution 4 cm^{-1} and 512 scans in the range of 400–4000 cm^{-1}. Diffuse Raman spectroscopy was performed with a Renishaw Raman microscope using a 12 mW 514 nm laser source with a 1200 grooves/mm grating. Diffuse reflection UV/vis analysis was performed with an ocean optics USB2000 spectrometer, LS-1 tungsten–halogen lamp, and a R400-7 reflection/backscattering probe.

Radiation chemical yields, *G*-values, are given in units of molecules formed per 100 eV of total energy absorption to the resin and any adsorbed water (1 molecule/100 eV = 1.04×10^{-7} mol/J). Errors in the yields are estimated to be better than 10%.

3. Results and discussion

3.1. Water loading

A considerable amount of water can be associated with humid resins. Fig. 2 shows that at about 100% relative

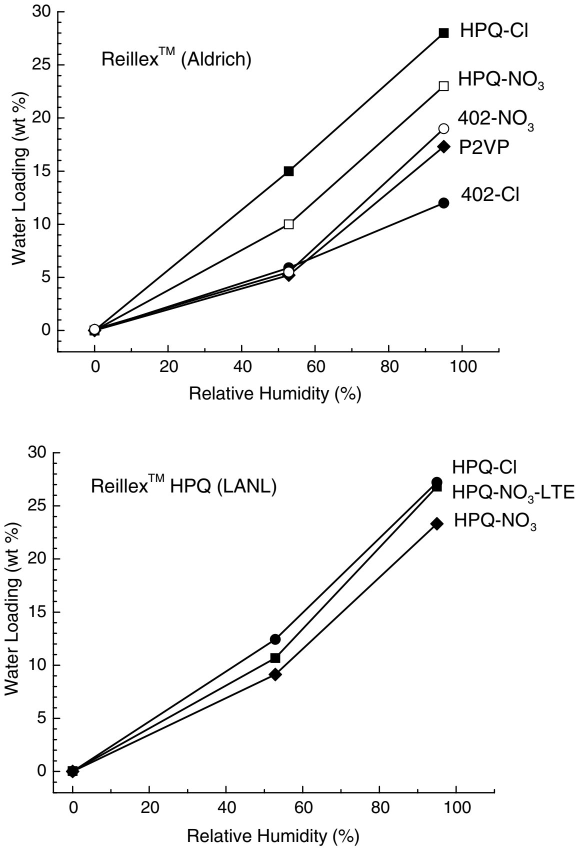

Fig. 2. Relative water loading (wt %) as a function of relative humidity (%): (a) (■) Reillex™ HPQ chloride, (□), Reillex™ HPQ nitrate; (●), Reillex™ 402 chloride; (○), Reillex™ 402 nitrate; (◆), P4VP, (b) (■), LANL HPQ chloride; (□), LANL HPQ nitrate; (◆), LANL HPQ LTE.

humidity water accounts for almost 25% of the weight of the Reillex™ HPQ salts. The wide variations in water loading for the Aldrich samples would seem to indicate that different efficiencies exist for the various forms. The presence of hydrogen on the pyridinium nitrogen gives a lower water loading than with a methyl group. Conversion of the neutral P4VP to the ammonium salts has little effect on water loading capacity. Variation in water loading with the LANL HPQ compounds is much smaller that with those samples from Aldrich. The LANL HPQ samples were sized, e.g. several water washings were used to remove small particulates. The result is a more uniform resin bead size distribution. Water is probably adsorbed in a finite number of layers, so the total weight fraction will depend on the bead size. The results indicate that resins in confined containers with any residual water will not be completely dry. Also, a significant amount of the radiation chemistry of these systems can be attributed to the water.

3.2. Dose dependence

Resins used in plutonium processing must be relatively radiation inert to high doses to avoid costly and potentially dangerous reloading of the exchange columns. Most hydrocarbons are sensitive to total dose because the buildup of products can significantly alter the radiolytic mechanism [35]. Previous studies examined the degradation of Reillex™ HPQ to 10 MGy doses of γ-rays [36]. The γ-ray dose rates available for this study are about 100 Gy/min and would require prohibitively long times to reach 10 MGy. Further studies to be completed later will explore the effects of high dose γ-radiolysis on Reillex™ resins. Nevertheless, experiments with γ-rays were performed at low doses for comparison with conventional hydrocarbon radiolysis. The dose response for the production of H_2 with γ-rays is shown in Fig. 3(a) for Reillex™ HPQ with different amounts of water loading. The dose dependencies are linear to the maximum of 50 kGy used in this study. The slopes of the straight lines are proportional to the radiation chemical yields, *G*-values. Standard units for radiation chemical yields are molecules per 100 eV of total energy absorbed. Energy is initially absorbed in both the resin and water in amounts proportional to the fraction of electron density. A distinction between the two compounds is not made in this study and *G*-values are reported relative to the total energy deposited in the system, i.e. resin and water. The H_2 *G*-values for the γ-rays shown in Fig. 3(a)

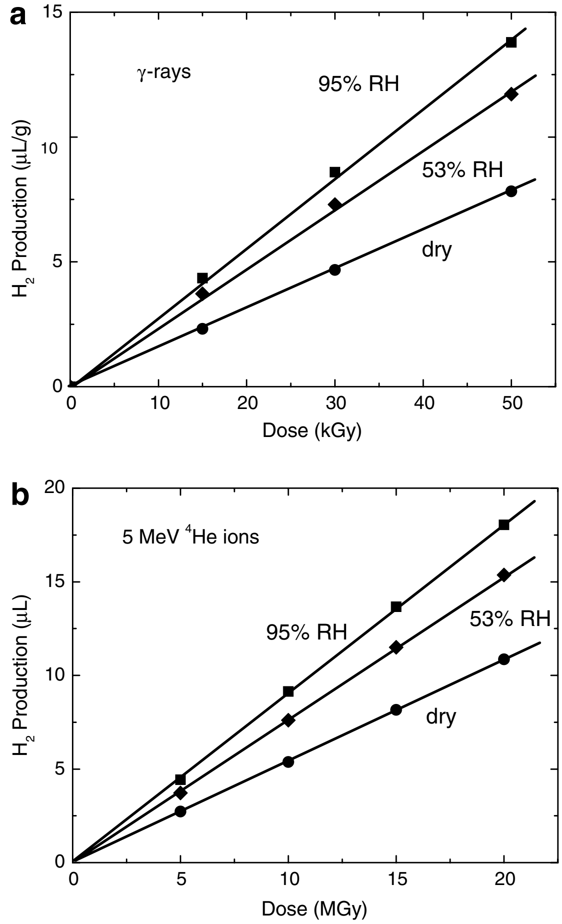

Fig. 3. Dose dependence of H_2 produced in the γ-ray (a) and 5 MeV ^{4}He ion (b) radiolysis of Aldrich Reillex™ HPQ chloride-form prepared with different relative humidity: (●), dry; (◆), 53% RH; (■), 95% RH.

are 0.062, 0.095, and 0.11 molecules/100 eV for dry, 53%, and 95% relative humidity, respectively.

The range of 5 MeV ^{4}He ions is only about 34 μm in theses resins so a large amount of energy is deposited in a relatively small volume resulting in very large dose rates. A 5 MeV $^4He^{2+}$ beam at 2 nA (charge current) of diameter 6.35 mm as used in these studies results in a dose rate of about 4.4 kGy/s. The dose response for the production of H_2 with 5 MeV ^{4}He ions is shown in Fig. 3b for Reillex™ HPQ with different amounts of adsorbed water. The production of H_2 was found to be linear with 5 MeV ^{4}He ions to doses of 20 MGy for all the systems examined here. As with γ-rays, *G*-values were determined from straight line fits to plots similar to those in Fig. 3.

The use of accelerated beams as a mimic for α-particle radiolysis can be questioned because of the potential of a dose rate effect. Accelerated ion beams may deposit energy at a dose rate that is considerably larger than encountered in some applications using low level waste materials. Radiolytic responses are independent of the dose rate if the chemistry associated with the track of each individual incident ion is complete before another ion can deposit energy within that track, i.e. ion tracks are isolated within the time frame of the formation of radiation chemical products. Of course, the geometry defined by ion tracks will eventually overlap, but if the chemistry of the first track has been completed the result is a dose effect, not a dose rate effect. For a dose rate effect to occur one must essentially irradiate the reactive species, i.e. radicals, excited states, etc., and for a dose effect to occur one must irradiate the final products to give a different distribution of products than would be found for a single ion irradiation. The irradiations in this work were performed at fluxes of about 2×10^{14} He ions/m^2 s. Calculations coupled with experimental observations in the 2 MeV ^{4}He ion radiolysis of polystyrene and polysilanes suggest a track radius of about 10 nm [37]. For any given portion of the sample surface that has been previously exposed to a He ion, there is an average of 1 He ion every 16 s $(\pi \times (10^{-8}\,\mathrm{m})^2 \times 2 \times 10^{14}$ He ions/m^2 s$)^{-1}$. The time to form H_2 is typically on the order of less than a μs which is much shorter that the average time for the passage of a He ion. Therefore, no dose rate effects for the formation of H_2 are expected under the conditions used in these experiments [38]. The linearities of the dose responses shown in Fig. 3 are another good indication of the lack of a dose rate effect.

3.3. Gas production

Since the resins examined here contain a mixture of water and an organic matrix, an understanding of the radiolysis must consider both types of compounds. The γ-radiolysis of liquid water leads to the production of H_2 with a yield of 0.45 molecule/100 eV [26]. Scavenging experiments show that the hydrated electron, e^-_{aq}, and especially its precursors, e^-_{pre}, have a dominant role in the formation of H_2 [34,38]. The addition of e^-_{aq} or e^-_{pre} scavengers decreases the yield of H_2 by removing them from the system so they cannot react with each other. H atoms are also expected to play an important role, especially in acidic solutions since the e^-_{aq} readily reacts with hydrated protons to give H atoms [26]. On the increase in LET from γ-rays (LET = 0.2 eV/nm) to 5 MeV ^{4}He ions (LET = 160 eV/nm), the energy deposition density and thereby the local concentration of reactive species increase in the ion track [39,40]. Intratrack reactions are importance in high LET tracks resulting in an increase in molecular yields such as H_2. The yield of H_2 in the 5 MeV ^{4}He ion radiolysis of water is 1.2 molecules/100 eV [38].

H_2 production in organic materials can be complicated and its yield depends on the type of compound. No published values exist for the yield of H_2 with P4VP. The yields of H_2 with γ-rays and with 5 MeV ^{4}He ions in liquid pyridine radiolysis are 0.027 and 0.12 molecule/100 eV, respectively [18]. H_2 yields are found to be similar for liquid benzene and solid polystyrene and a similar relationship is expected for pyridine and P4VP [13]. The precursor of H_2 in liquid pyridine radiolysis is thought to be a high-energy singlet excited state above the S1 state [18,41]. This phenomenon is called the ‘channel three’ process [42]. The yield of high-energy singlet states increases with increasing LET through triplet–triplet annihilation reactions [43,44]. A similar process may lead to an increase in the yield of H_2 with increasing LET in the radiolysis of P4VP and the Reillex™ resins.

The production of H_2 by γ-rays is shown in Fig. 4 as a function of the water loading on P4VP, and Reillex™ HPQ chloride and nitrate-form resins, the yields for the corresponding LANL HPQ resins are given in Table 1. Dry P4VP has an H_2 yield of 0.058 molecule/100 eV, which is on the same order as observed with liquid pyridine (0.027 molecule/100 eV). This result was expected from studies on the relative yields of benzene and polystyrene. An increase in the yield of H_2 with increasing water loading

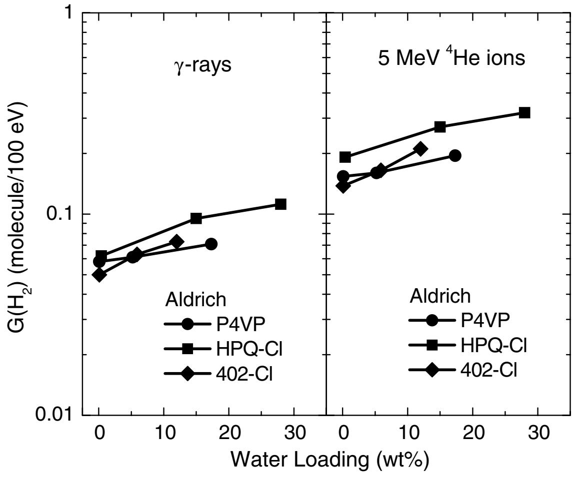

Fig. 4. Production of H_2 with γ-rays and with 5 MeV ^{4}He ions as a function of the water loading on: (●), P4VP; (■), Reillex™ HPQ chloride-form; (◆), Reillex™ 402 chloride-form resins.

Table 1
Radiolytic yields (molecules/100 eV) of gaseous products with γ-rays and 5 MeV ^{4}He ions

Gaseous product	Radiation	RH%	LANL HPQ		
			Cl	NO_3	NO_3 (LTE)
			G (molecules/100 eV)		
H_2	γ-rays	Dry	0.066	0.047	0.037
		53% RH	0.10	0.055	0.048
		95% RH	0.14	0.066	0.067
	5 MeV ^{4}He ions	Dry	0.19	0.12	0.11
		53% RH	0.29	0.14	0.12
		95% RH	0.35	0.18	0.16
N_2	γ-rays	Dry	–	0.036	0.098
N_2O	γ-rays	Dry	–	0.082	0.072
	5 MeV ^{4}He ions	Dry	–	0.097	0.092

is observed for all compounds because of the increased importance of the water radiolysis. H_2 yields show very little dependence on the organic component of the polymeric side chain. A neutral pyridine has about the same H_2 yield as the quaternary salts with hydrogen or a methyl group attached to the pyridinium nitrogen. This result is important because the degree of quaternarization can be different for different batches or various vendors. The yield of H_2 appears to be relatively unaffected by these variations in the case of the radiolysis of the chloride salts with γ-rays. The largest deviation is observed for dry resins irradiated with 5 MeV ^{4}He ions.

The yields of H_2 are found to be more dependent on the anion than with variations in the organic component. Fig. 5 shows the results for the radiolysis of Reillex™ HPQ in chloride and in nitrate-forms as a function of water loading. The yields of H_2 for the nitrate-form are about half that with the chloride-form. To a first approximation, the major precursors to H_2 are electrons. The electrons may be from the initial ionization of the resin in the case of dry samples or e^-_{pre} and e^-_{aq} from any water present. Very little is known about the kinetics of electrons in these resins, but considerable information is available for electrons in water. Nitrate is an especially good scavenger of e^-_{pre} and e^-_{aq} [34,45,46]. The rate coefficient for e^-_{aq} with nitrate is $9.7 \times 10^9\ M^{-1}\ s^{-1}$ in aqueous solutions. On the other hand, the reaction of e^-_{aq} with chloride has a rate coefficient of $< 1.0 \times 10^6\ M^{-1}\ s^{-1}$, which is negligible compared to its other reactions [47]. The rate coefficient for e^-_{pre} reaction with nitrate in water was determined from experimental C_{37} values to be $1 \times 10^{13}\ M^{-1}\ s^{-1}$ and one can expect scavenging of the electron to occur in the nitrate-form of the resins [46,48]. Scavenging of the electron in any form reduces the subsequent yield of H_2.

The resins from Los Alamos exhibited a more uniform water loading capacity because of their similarity in size so they will be compared directly to each other. Additionally, some of the resins from Los Alamos were thermally treated to remove any potential exotherms that may cause a runaway reaction in the exchange columns. H_2 production for these resins is shown in Fig. 6 as a function of water loading. As with the Reillex™ HPQ, the LANL HPQ resins show an increase in H_2 yield with increasing water loading due to the increased importance of water decomposition. A large decrease in H_2 yields is observed on conversion from the chloride to nitrate-form because of the increased scavenging capacity of the latter anion. Very little difference in the H_2 yields is observed between the LANL HPQ nitrate and HPQ LTE nitrate for both types of radiation. The latter result reconfirms evidence presented above that variations in the organic component have little effect on the yield of H_2, provided the total elec-

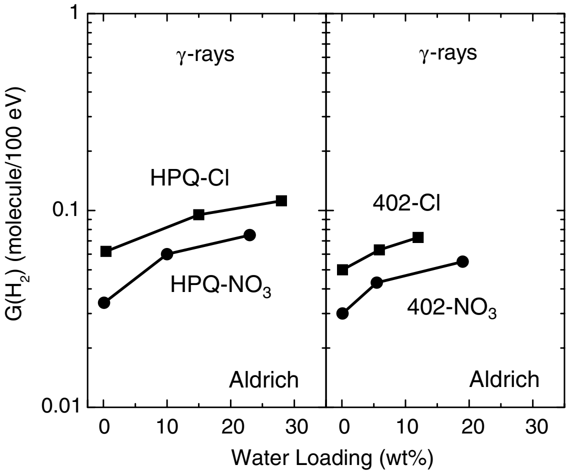

Fig. 5. Production of H_2 with γ-rays as a function of the water loading on (■), Reillex™ HPQ chloride-form; (●), Reillex™ HPQ nitrate-form resins.

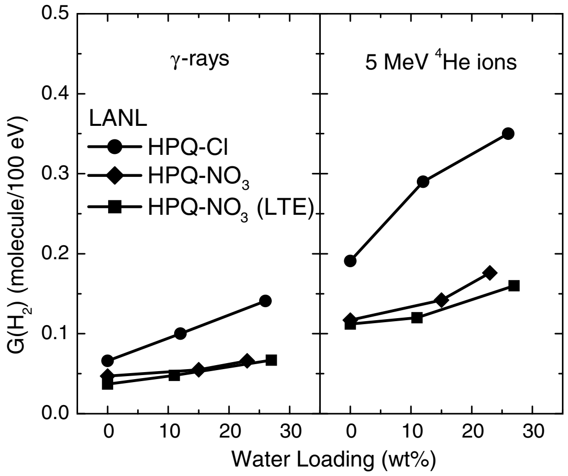

Fig. 6. Production of H_2 relative to the amount of total energy deposited by γ-rays and 5 MeV ^{4}He ions as a function of the water loading on the (●), LANL HPQ chloride-form; (◆), LANL HPQ nitrate-form; (■), LANL HPQ LTE nitrate-form.

tron fraction is small. A variety of experiments have shown that H_2 yields from aliphatic compounds are considerably greater that with aromatic compounds [35]. Significant addition of an aliphatic copolymer or other similar substitution could have a large influence on H_2 production.

Of the many other gases that can potentially be formed in the radiolysis of these resins, O_2 is the most important product because of its ability to support combustion or explosion. Gases other than H_2 in the radiolysis of dried LANL HPQ chloride and nitrate-forms and HPQ LTE nitrate-form with γ-rays and 5 MeV ^4He ions were measured by using a gas chromatograph followed by a quadrupole mass spectrometer in a multiple-ion-detection mode. The temporal separation with mass analysis gives an unambiguous assignment to the evolved gases. The targeted gases were nitrogen, nitric oxide, carbon monoxide, oxygen, carbon dioxide, nitrous oxide, and nitrogen dioxide. Fig. 7 shows the mass spectra observed for the γ-radiolysis of dried LANL HPQ nitrate-form with a dose of 200 kGy, as a typical response. There are two major peaks in the spectra. The peak at mass 28 is assigned to molecular nitrogen, N_2. Another peak is assigned to nitrous oxide, N_2O, on the basis of the base peak at mass 44 with other fragment ions at mass 30, 28, and 16. The measured mass fragments for N_2O agrees well with the expected mass

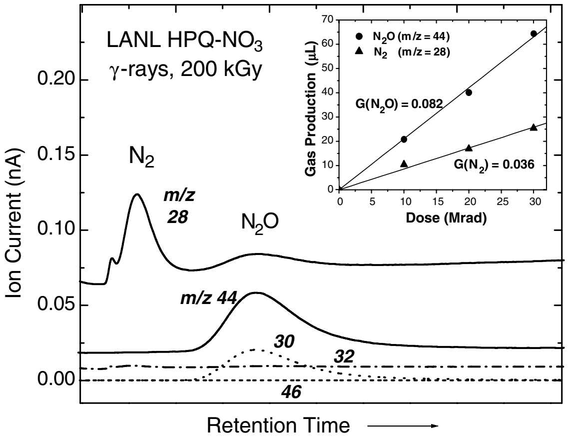

Fig. 7. Gas chromatographic–mass spectrometric spectra of the γ-radiolysis of LANL HPQ nitrate-form with a dose of 200 kGy. Inset shows the dose dependence of N_2 and N_2O production.

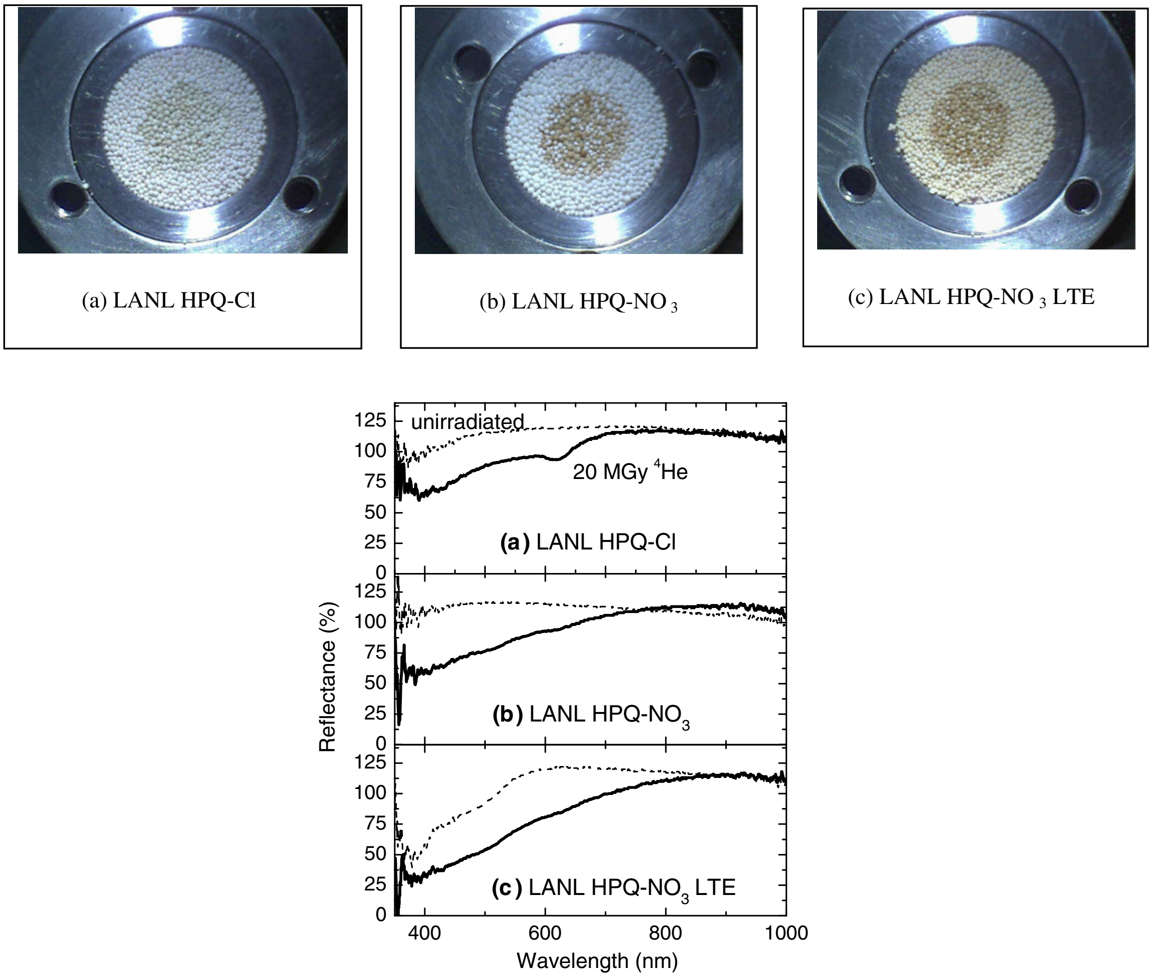

Fig. 8. Photographs and reflectance UV/vis spectra of 5 MeV ^4He ion irradiated (a) LANL HPQ chloride-form, (b) LANL HPQ nitrate-form, and (c) LANL HPQ –LTE nitrate-form resins to 20 MGy. The diameter of the beam spot is 6.35 mm and the sample diameter is 12.7 mm.

spectrum. Peaks corresponding to nitric oxide, carbon monoxide, oxygen, carbon dioxide, and nitrogen dioxide were not observed. The inset of Fig. 7 shows the a linear relationship for the dose dependence of N_2 and N_2O produced in the γ-radiolysis of dried LANL HPQ nitrate-form, which were monitored at mass 28 and 44, respectively. Linear dose responses are found for the radiolysis of dried LANL HPQ nitrate-form and HPQ LTE nitrate-form with γ-rays and 5 MeV ^{4}He ions. The yields of radiolytic N_2 and N_2O are listed in Table 1. Except for H_2, no gases were observed in the radiolysis of HPQ chloride-form with both types of radiation. The yields of N_2 produced in the γ-radiolysis of dried HPQ and HPQ LTE nitrate-forms are 0.036 and 0.098 molecule/100 eV, respectively. The large yield for the HPQ LTE nitrate-form suggest that a different functional group such as nitrogen dioxide might be formed in the LTE treatment with 8 M HNO_3 at 85 °C for 45 min [27]. The yields of N_2O produced in the γ-radiolysis of dried LANL HPQ and LANL HPQ LTE nitrate-forms are 0.082 and 0.072 molecule/100 eV, respectively. The yields of N_2O with 5 MeV ^{4}He ions are similar to those for γ-rays with both of these resins. The lack of an LET dependence shows that N_2O is formed in a first order process and the most likely sources is the direct degradation of nitrate anions.

3.4. Spectroscopy

Various optical analyses were performed on the irradiated resins to determine the fate of the bulk material following radiolysis. Radiolysis of the LANL HPQ resins to doses of 20 MGy led to an observed discoloration as shown in Fig. 8. Small color differences were observed for the chloride and nitrateforms. Optical spectra in the UV/vis region show a general decrease in reflectance with irradiation to a dose of 20 MGy by 5 MeV ^{4}He ions, but formation of specific peaks is only observed in the case of the chloride-form. All of the samples appear to simply darken with irradiation. The IR spectra obtained by the 5 MeV ^{4}He ion radiolysis of LANL HPQ chloride and nitrate-forms and HPQ LTE nitrate-form with a dose of 20 MGy are shown in Fig. 9. The important bands of the chloride and nitrate-forms are at 2100 cm^{-1} and at 2400 cm^{-1}, which are respectively assigned to Cl^- and NO_3^- counterions. The IR spectra of all resins show very little difference before and after ^{4}He ion radiolysis. The Raman spectra shown in Fig. 10 are generally structureless for LANL HPQ resins. The ^{4}He ion radiolysis leads to a change in total absorption, with only a broad feature appearing in the chloride-form. A previous study using 752 nm excitation instead of the 541 nm used in this work came to the same conclusion that Reillex™ HPQ resins are poor Raman scatterers, but relatively insensitive to radiation [49]. Overall, little change is observed in any of the spectra following the 5 MeV ^{4}He radiolysis of the LANL HPQ resins suggesting that they are relatively radiation inert.

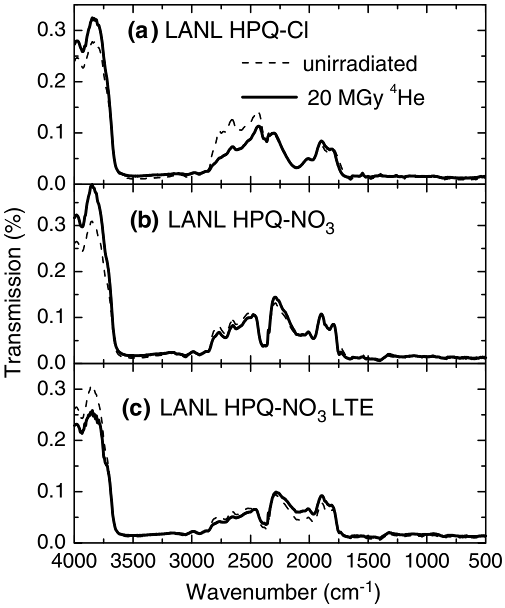

Fig. 9. Reflectance FT–IR spectra of 5 MeV ^{4}He ion irradiated (a) LANL HPQ chloride-form, (b) LANL HPQ nitrate-form, and (c) LANL HPQ – LTE nitrate-form resins to 20 MGy.

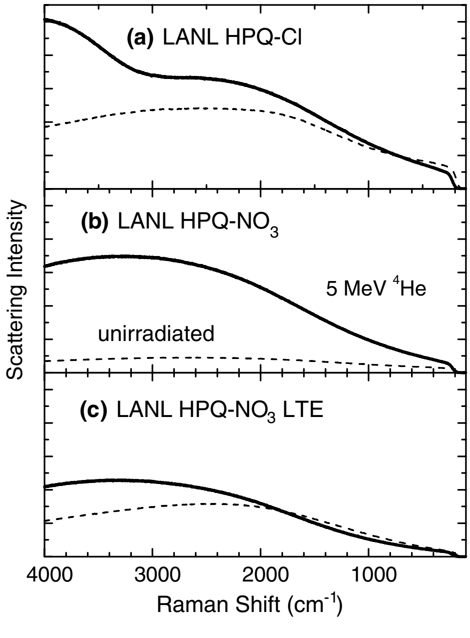

Fig. 10. Reflectance Raman spectra of 5 MeV ^{4}He ion irradiated (a) LANL HPQ chloride-form, (b) LANL HPQ nitrate-form, and (c) LANL HPQ –LTE nitrate-form resins to 20 MGy.

4. Conclusions

The radiation chemical yields of gaseous products, especially H_2, have been determined in the radiolysis of absorbed water on Reillex™ HPQ and Reillex™ 402 resins with 5 MeV ^{4}He ions to simulate α-particle radiolysis at high doses. The results are compared with lower dose γ-radiolysis studies. Both chloride and nitrate-forms were examined. An increase in H_2 yields with increasing water loading was observed for both types of ionizing radiation and with all of the resins because of the increased importance of water radiolysis. The yield of H_2 for the nitrate-form resin was lower than that for the chloride; in addition, the yield was lower when the pyridinium nitrogen atom is coordinated to the methyl group rather than to the hydrogen. Nitrate is expected to scavenge various forms of the electron before it can react to form H_2. The yield of H_2 with 5 MeV ^{4}He ions was higher than that observed with γ-rays because of the increased importance of both the 'channel three' processes through triplet–triplet annihilation in the pyridine component of the resin and intratrack processes in water. Gaseous N_2 and N_2O products were observed for the nitrate-form resin, but not for the chloride. No resin exhibited formation of O_2. Spectroscopic studies suggest that Reillex™ HPQ and Reillex™ 402 resins have a high radiolytic stability for both type γ-rays and 5 MeV ^{4}He ions (α-particles).

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References

[1] K.L. Nash, G.J. Lumetta, S.B. Clark, J.I. Friese, in: Separations for the Nuclear Fuel Cycle in the 21st Century, American Chemical Society, Washington, DC, ACS Symposium Series 933, 2006, p. 3.
[2] S.F. Marsh, D.K. Veirs, G.D. Jarvinen, M.E. Barr, E.W. Moody, Los Alamos Sci. 26 (2000) 454.
[3] P.G. Allen, D.K. Veirs, S.D. Conradson, C.A. Smith, S.F. Marsh, Inorg. Chem. 35 (1996) 2841.
[4] D.L. Clark, D.E. Hobart, M.P. Neu, Chem. Rev. 95 (1995) 25.
[5] J.L. Ryan, J. Phys. Chem. 64 (1960) 1375.
[6] S.F. Marsh, Solv. Ext. Ion Exch. 7 (1989) 889.
[7] J.M. Haschke, T.H. Allen, L.A. Morales, Science 287 (2000) 285.
[8] L.M. Stock, The Chemistry of Flammable Gas Generation, Richland, WA, RPP-6664, Rev. 1, CH2M HILL Hanford Group, Inc., 2001.
[9] R.E. Gephart, R.E. Lungren, Hanford Tank Clean Up: A Guide to Understanding the Technical Issues, Pacific Northwest National Laboratory, Richland, WA, 1995.
[10] C.D. Jonah, S. Kapoor, M.S. Matheson, W.A. Mulac, D. Meisel, Gas Generation from Hanford Grout Samples, 94-7, Argonne National Laboratory, Argonne, IL, 1994.
[11] R.L. Clough, S.W. Shalaby, Radiation Effects on Polymers, American Chemical Society, Washington, DC, ACS Symposium Series 475, 1991.
[12] Z. Chang, J.A. LaVerne, J. Phys. Chem. B 106 (2002) 508.
[13] J.A. LaVerne, Z. Chang, M.S. Araos, Radiat. Phys. Chem. 60 (2001) 253.
[14] Z. Chang, J.A. LaVerne, Radiat. Phys. Chem. 62 (2001) 19.
[15] Z. Chang, J.A. LaVerne, J. Polym. Sci., Part B: Polym. Phys. 39 (2001) 1449.
[16] Z. Chang, J.A. LaVerne, J. Phys. Chem. B 104 (2000) 10557.
[17] Z. Chang, J.A. LaVerne, J. Polym. Sci., Part A: Polym. Chem. 38 (2000) 1656.
[18] K. Enomoto, J.A. LaVerne, M.S. Araos, J. Phys. Chem. A 111 (2007) 9.
[19] K. Enomoto, J.A. LaVerne, S.M. Pimblott, J. Phys. Chem. A 110 (2006) 4124.
[20] J.A. LaVerne, M.S. Araos, J. Phys. Chem. A 106 (2002) 11408.
[21] B. Pastina, J.A. LaVerne, S.M. Pimblott, J. Phys. Chem. A 103 (1999) 5841.
[22] Z.D. Draganic, I.G. Draganic, J. Phys. Chem. 75 (1971) 3950.
[23] E. Peled, G. Czapski, J. Phys. Chem. 74 (1970) 2903.
[24] H.A. Schwarz, J. Phys. Chem. 73 (1969) 1928.
[25] H.A. Schwarz, J. Am. Chem. Soc. 77 (1955) 4960.
[26] A.O. Allen, The Radiation Chemistry of Water and Aqueous Solutions, Van Nostrand, New York, 1961.
[27] W.J. Crooks, E.A. Kyser, S.R. Walter, Solv. Ext. Ion Exch. 20 (2002) 543.
[28] American Society for Testing Materials, E104–85, Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions, 1996.
[29] CRC Handbook of Chemistry and Physics, 77th ed., Chemical Rubber Company, Boca Raton, FL, 1996–1997.
[30] J.A. LaVerne, R.H. Schuler, J. Phys. Chem. 91 (1987) 6560.
[31] J.A. LaVerne, R.H. Schuler, J. Phys. Chem. 88 (1984) 1200.
[32] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon, New York, 1985.
[33] J.A. LaVerne, L. Tandon, J. Phys. Chem. B 106 (2002) 380.
[34] B. Pastina, J.A. LaVerne, J. Phys. Chem. A 103 (1999) 1592.
[35] I. Gyorgy, L. Wojnarovits, In: Radiation Chemistry of Hydrocarbons, Akademiai Kiado, Budapest, 1981, p. 17.
[36] S.F. Marsh, The Effects of Ionizing Radiation on Reillex HPQ, A New Macroporous Polyvinylpyridine Resin and on Four Conventional Polystyrene Anion Exchange Resins, Los Alamos National Laboratory, LA-12655, 1991.
[37] S. Seki, S. Tsukuda, K. Maeda, et al., Phys. Rev. B 70 (2004) 144203.
[38] J.A. LaVerne, S.M. Pimblott, J. Phys. Chem. A 104 (2000) 9820.
[39] J.A. LaVerne, Radiat. Res. 153 (2000) 487.
[40] J.A. LaVerne, in: Charged Particle and Photon Interactions with Matter, Marcel Dekker Inc., New York, 2004, p. 403.
[41] J. LaVerne, I. Carmichael, M.S. Araos, J. Phys. Chem. A 109 (2005) 461.
[42] J.H. Callomon, J.E. Parkin, R. Lopez-Delgado, Chem. Phys. Lett. 13 (1972) 125.
[43] M. Klessinger, J. Michl, Excited States and Photochemistry of Organic Molecules, VCH Publishers, New York, 1995.
[44] E.C. Lim, Acc. Chem. Res. 20 (1987) 8.
[45] A. Hiroki, S.M. Pimblott, J.A. LaVerne, J. Phys. Chem. A 106 (2002) 9352.
[46] S.M. Pimblott and J.A. LaVerne, 102 (1998) 2967.
[47] J.K. Thomas, S. Gordon, E.J. Hart, J. Phys. Chem. 68 (1964) 1524.
[48] C.D. Jonah, J.R. Miller, M.S. Matheson, J. Phys. Chem. 81 (1977) 1618.
[49] C.T. Buscher, R.J. Donohoe, S.L. Mecklenburg, et al., Appl. Spect. 53 (1999) 943.