Low-Energy (3−24 eV) Electron Damage to the Peptide Backbone

P. Cloutier,[†] C. Sicard-Roselli,[‡] E. Escher,[§] and L. Sanche*[,†]

Groupe en Sciences des Radiations, Département de Médecine Nucléaire et Radiobiologie, Faculté de Médecine, Université de Sherbrooke, Sherbrooke, Québec J1H 5N4, Canada, Laboratoire de Chimie Physique, Université Paris-Sud, CNRS UMR 8000 CNRS, 91405 Orsay Cedex, France, and Département de Pharmacologie, Faculté de Médecine, Université de Sherbrooke, Sherbrooke, Québec J1H 5N4, Canada

Received: October 23, 2006; In Final Form: December 18, 2006

We report the mass spectrometric measurement of anions desorbed by 3−24 eV electron impact on thin films of formamide-1-d ($DCONH_2$) and on the self-assembled monolayer (SAM) of two different Lys amide molecules used as a molecular model of the peptide backbone. In the present SAM configuration, the amides are elevated from a gold substrate by hydrocarbon chains to remove the effects of the metal substrate. Electron irradiation produces H^- and D^- from the formamide-1-d film and H^-, CH_3^-, O^-, and OH^- from the SAM Lys amides. Below 13 eV, the dependence of the anion yields on the incident electron energy exhibits structures indicative of the dissociative electron attachment process, which is responsible for molecular fragmentation via the initial formation of core-excited anions. Above 13 eV, anion desorption is dominated principally by non-resonant dipolar dissociation. Our results suggest that the sensitivity of the peptide backbone to secondary electrons produced by ionizing radiation depends on the chemical environment (i.e., the amino acids sequence).

Introduction

To provide information on the phenomena induced by ionizing radiation in living tissues, many studies have dealt with radiation damage in cells and DNA.[1−5] Whereas the mechanisms of high-energy processes leading to such damage are well-understood,[6,7] those produced by low-energy (<30 eV) secondary electrons are not so well characterized in biomolecules. When high-energy radiation penetrates a biological cell, it produces along its ionization track a large amount ($\sim 3 \times 10^4$/MeV) of these secondary low-energy electrons (LEE)[8,9] that interact with the surrounding medium and may afterward irreversibly modify and damage the cellular medium. Recently, Boudaiffa et al.[10] showed the important DNA damages caused by electrons, whose energy lies below 20 eV. In biological cells, nucleic acids interact with proteins such as histones and transcription factors to regulate gene expression for example. Proteins can be intercalated or complexed within DNA grooves and interact directly with DNA bases.[11,12] Thus, DNA degradation could be highly dependent on the sensitivity of proteins to ionizing radiation. Therefore, a more complete understanding of radiation damage to the genome requires information on radiolytical processes on peptides and proteins induced by LEE.

Amino acids are linked together to form peptides and proteins. The protein backbone is made of covalent amide bonds between the carbon atom of the carboxylic acid group ($-CO_2H$) of an amino acid and the nitrogen atom of the amino group ($-NH_2$) of another amino acid. In the present work, we focus on the damages induced by LEE on the peptidic backbone. Because the complexity of protein structure would not allow a detailed interpretation of the mechanisms underlying the fragmentation process induced by electron impact, we propose to identify first the contribution of the peptide backbone to the anion desorbing yield induced by LEE bombardment. In this first LEE impact investigation of the backbone, we report measurements of the desorption of anions from two self-assembled monolayer (SAM) samples (Lys amide 1 and Lys amide 2), stimulated by 3−24 eV electrons. To determine the origin of anion signal within the SAM samples, we also discuss anion electron stimulated desorption yields from acetamide and formamide-1-d molecules in thin films condensed on a platinum substrate.

Much of our fundamental understanding of LEE impact on biomolecules arises from gas-phase experiments[13−18] by which the interaction of a single molecule with an electron can be studied. Information on the electron energy dependence of this interaction is unfortunately not available for large molecules such as peptides, proteins, oligonucleotides, and DNA, so that our present knowledge is derived from condensed phase studies.[13] The latter have considerably contributed to our understanding of biomolecules−electron interaction, but it is often desirable to obtain data from an isolated electron−biomolecule pair to fully understand the modifications induced by the presence of neighboring molecules in the condensed phase.[19]

In solid-phase studies, molecules are deposited on a metal substrate.[19] Thus, the yield of LEE-induced anion desorption is modified by the polarization forces induced by the anion in the metal and within the solid.[20,21] Furthermore, transient anions leading to dissociative electron attachment (DEA) and hence anion desorption may have their fundamental properties modified by the surrounding medium.[21] We propose here a technique to study isolated solid-phase molecules, where the backbone of the peptide chain is isolated from a gold substrate with long saturated carbon chains having a terminal thiol group. The latter is used to form the chemical bond with the gold surface (i.e., the SAM technique) as shown in Figure 1.

* Corresponding author. E-mail: leon.sanche@usherbrooke.ca.
[†] Département de Médecine Nucléaire et Radiobiologie, Université de Sherbrooke.
[‡] Université Paris-Sud.
[§] Département de Pharmacologie, Université de Sherbrooke.

10.1021/jp066947q CCC: $37.00
Published on Web 01/26/2007

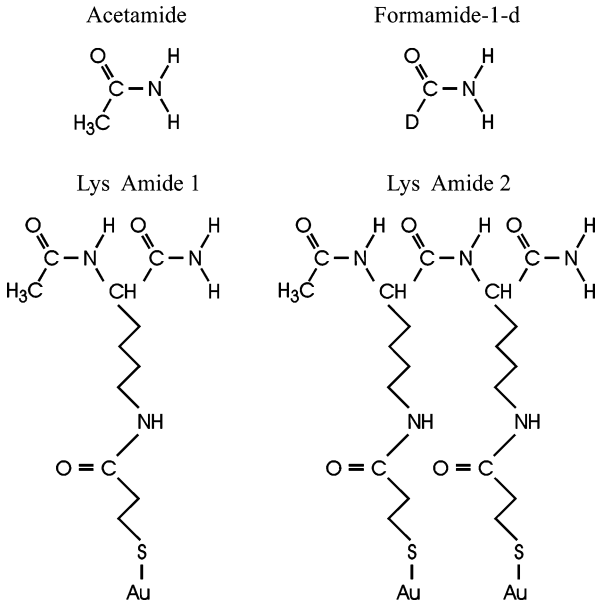


Figure 1. Nomenclature of acetamide, formamide-1-d, and SAM of Lys amide 1 and Lys amide 2. The horizontal chains of the two last molecules have the same structure as that of the peptide backbone.

Experimental Methods

Apparatus. The apparatus used in the present investigation has been described in detail elsewhere.[22,23] Only a brief description of the procedure and experimental arrangement is provided here. The electron-stimulated desorption of anions is measured in an ultrahigh vacuum (UHV) chamber held at a base pressure of $\sim 10^{-10}$ Torr. The different samples are bombarded at an incident angle of 70° from the surface normal by an electron beam from a commercial electron gun (Kimball Physics Inc.). It provides a beam of 1−100 nA, focused on a 3-mm-diameter spot, with an energy resolution of 0.5 eV full width at half-maximum. The incident electron energy is calibrated by measuring the onset of the current transmitted through the film.[24] Desorbing anions are collected by an ion lens and detected by a mass spectrometer (Extrel 150-QC). It is then possible to measure the magnitude of a single anion yield as a function of the incident electron energy, defined as the yield function. Assuming that the efficiency for detection (i.e., ion desorption, ion extraction conditions, transmission of the quadrupole mass analyzer) of negative species, other than H^-, is similar for CH_3^-, O^-, and OH^-, we can tentatively compare the yields of these anions.

Sample Preparation and Irradiation. All yield functions from acetamide and formamide-1-d were obtained by irradiating 3-monolayer-thick physisorbed molecular films deposited and kept under UHV on a clean polycrystalline platinum foil. In the case of the acetamide films, H^- desorption was measured with a 6.5-nA electron beam, and the heavier negative anions were recorded at a current of 200 nA. For the formamide-1-d films and the SAM Lys amides, data were acquired with a current of 30 nA. The acetamide results have been obtained by our group 4 years ago, and the description of the films preparation method is given in ref 25. In the present paper, the electron energy scale of these results has been down-shifted by 0.6 eV to account for the more accurate calibration of the incident electron energy.

The formamide-1-d films were grown by condensation of the vapor on the polycrystalline platinum foil held at a temperature of 87 K. The liquid sample (99 atom % D) was supplied by Sigma-Aldrich Canada Ltd. The film thickness (3 monolayers) is estimated to have a ±30% accuracy, from the calibrated amount of gas needed to deposit a monolayer, assuming no change in the sticking coefficient for the adlayers, as previously described.[24,26]

The compounds Lys-amide 1 and Lys-amide 2 were synthesized by solid-phase peptide synthesis on 0.5 g of MBHA resin (0.57 mequiv/g).[27] In brief, N^{α}-Boc-N^{ϵ}-Fmoc-L-Lys was coupled, using HOBT/DCC as reagents and a 4−8-fold excess of acylating agent.[28] The resin was then separated in 0.1 g portions. To a first portion, Boc-protected β-mercaptopropionic acid was coupled after removal of the Fmoc protection by piperidine. The remaining Boc protection was removed with 40% TFA in CH_2Cl_2, and the resin was per-acetylated with acetic anhydride. Lys-amide 1 was released from the resin with liquid HF, lyophilized, redissolved in water, purified on a SEP-PAK-C_{18} column with a gradient of 0−50% CH_3CN in 0.05% aqueous TFA, and lyophilized again. Purity was assessed by HPLC (>95%); the total yield of pure product was 45% with respect to the initial resin load (gravimetry). Mass spectrometry (MS) and nuclear magnetic resonance (NMR) provided data in accordance with the theoretical structure. On a second portion of resin, the Boc protection was removed, and a second N^{α}-Boc-N^{ϵ}-Fmoc-L-Lys was coupled to the first residue. Coupling of mercaptopropionic acid, subsequent acetylation, resin cleavage, and purification of Lys-amide 2 were carried out as described above for Lys-amide 1; analytical data (MS and NMR) were in accordance with the theoretical structure.

Lys amides were chemisorbed on gold substrates supplied by Arrandee, Werther, Germany. The substrates were successively cleaned by rinsing in ethanol and pure water, exposing to ozone for 30 min, rinsing with pure water to remove the impurities due to reaction with ozone, exposing to ozone for another 30 min, and, finally, rinsing in pure water. The samples were then prepared by immersing the cleaned gold substrates (1.44 cm^2) in an aqueous solution (2 mL) for at least 20 h. The Lys amide concentrations were 0.01 mg/mL. Under these conditions, the chemisorbed molecules are expected to form a densely packed layer with the carbon chains standing parallel to each other at a fixed angle from the normal of the gold surface.[29] Once removed from the solution, the samples were rinsed thoroughly with pure water and dried under a stream of N_2 gas. Afterward, the samples were immediately placed in a load lock vacuum system, which was evacuated for 12 h ($\sim 10^{-8}$ Torr). From the load lock, the samples were transferred to the UHV chamber where the ion desorption measurements were performed with the gold substrate held at room temperature.

Results and Discussion

The dependence of the desorbed anion yields on incident electron energy shown in Figures 2, 3, 5, and 6 exhibits pronounced maxima superimposed on an increasing monotonic background. This behavior can be attributed to a contribution from the formation of dissociative transient anions, which produces the peaks, and another contribution from dipolar dissociation (DD), which grows monotonically with increasing electron energy.[19,20] Because a dissociative anion state occurs at specific resonance energy, corresponding to that of an unoccupied orbital configuration, it produces an energy-localized maximum or peak in the anion yield function. DD results from the dissociation of a neutral excited state into a positive and a negative ion, the latter being detected in the anion yield function.[19,30] Unless electron resonances (i.e., transient anions) decay in the DD channel, the anion signal arising from DD does not exhibit any structure, because it is governed by direct

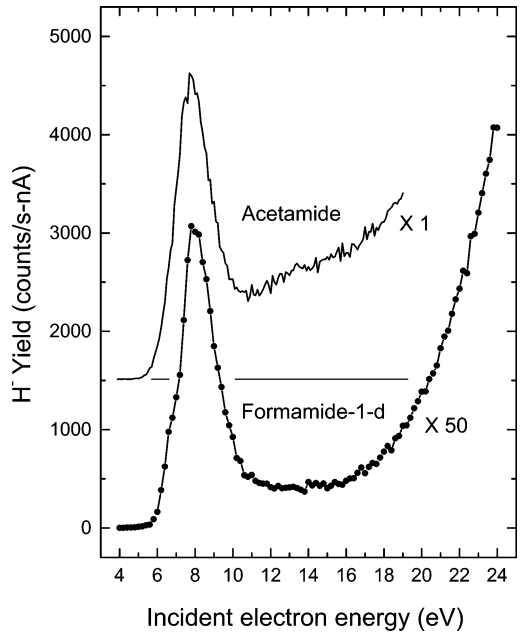


Figure 2. Electron energy dependence of the H^- ion yield desorbed by electron impact on 3-monolayer-thick formamide-1-d (lower curve) and acetamide (upper curve) films deposited on platinum substrate at 87 and 300 K, respectively. The signal of the lower curve has been amplified by a factor of 50. The acetamide data have been taken from ref 20.

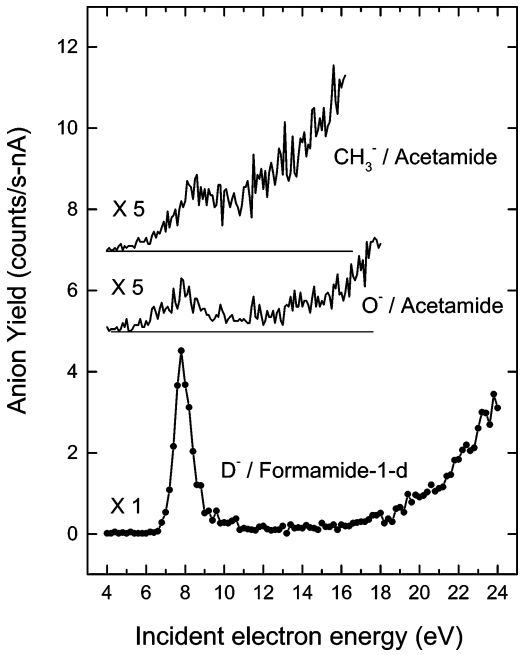


Figure 3. Electron energy dependence of anion yields desorbed by electron impact on 3-monolayer-thick formamide-1-d (lower curve) and acetamide (upper curve) films deposited on platinum substrate at 87 and 300 K, respectively. The acetamide data have been taken from ref 20.

(nonresonant) electronic excitation from inelastic scattering of the incoming electron.[19] There exist two major types of transient anions: (1) shape or single-particle resonances, in which the additional electron temporarily occupies a usually unfilled orbital of the target molecule, and (2) core-excited resonances or two-particle one-hole states, which are composed of two electrons in electronically excited orbitals and a positive ion core. Core-excited anions may be seen as an electron captured by the positive electron affinity of an electronically excited state of the molecule. These latter anionic states have relatively long lifetimes close and above the energy of the first electronically excited state, whereas shape resonances are usually too short-lived at those energies to cause molecular dissociation.[31] The resonance observed in the DEA channel in the present work lies above the first electronically excited state of the studied molecules. They are therefore interpreted as core-excited anion states.

Acetamide and Formamide-1-d. To better understand and interpret the results obtained from SAM Lys amide samples, we first present the data obtained with formamide-1-d and acetamide thin films (see nomenclature in Figure 1). For both molecules, H^- is the most important desorbed anion. The yield functions for H^- desorption from acetamide (upper curve) and formamide-1-d (lower curve) are shown in Figure 2. As seen from Figure 1, the only difference between the molecular structures of acetamide and formamide-1-d is the methyl group of acetamide, which is substituted by a deuterium atom for the formamide-1-d. Nevertheless, the magnitude of the anion signals desorption is very different. The number of H^- desorbed per incident electron from the acetamide film can be seen from Figure 2 to be 50 times higher than the one from formamide-1-d film. So, we propose that the methyl group of acetamide produces the major portion of the H^- detected. However, we cannot conclude that only 2% of the H^- yield arises from the amino group, because the chemical environment of the molecule is modified by replacement of CH_3 by deuterium. Such a change could modify the resonance parameters, which, in turn, could modify H^- yields from the amino group. In any case, the yield function for H^- desorption from the formamide-1-d film shows that the amino group can effectively dissociate and produce H^- desorption.

Figure 3 exhibits the energy dependence of the D^- desorption signal from formamide-1-d and CH_3^- and O^- desorption yield functions from acetamide. The 16-nucleon anions that are desorbed from acetamide films can be ascribed, a priori, to O^- or NH_2^-, but in several previous experiments on the impact of electrons on molecules containing only amino group,[23,25,30,32−34] no production of NH_2^- anions or NH_2 was detected. We therefore ascribe the 16-nucleon fragment to the O^- anion as proposed in ref 25 (i.e., NH_2^- species are not produced).

From the results of Figures 2 and 3, we suggest that, between 6 and 10 eV, incoming electrons can be captured by both formamide-1-d and acetamide molecules to form a one-hole-two-electron state (i.e., a core-excited resonance).[19,25] The transient anion thereafter undergoes unimolecular fragmentation into a stable anion and its neutral counterpart. In the case of acetamide, the methyl group enhances the probability of H^- desorption with a factor of 50 as compared to H^- desorption from formamide-1-d. The position of the peaks in the yield function of the other desorbed anions (O^-, CH_3^- from acetamide and D^- from formamide-1-d) suggests competitive channels for dissociation. The absence of O^- desorption for formamide-1-d further suggests that its desorption highly depends on the chemical environment (i.e., in this case, the presence of the methyl group). Figure 4 shows the different fragments desorbing from acetamide and formamide-1-d films and their measured relative magnitudes. Because of the different mass sensitivity of the quadrupole and the different escape probabilities of each anion produced, the relative value given in Figure 4 provides only a rough estimate of the relative yields.

Lys Amides 1 and 2. The yield functions for anion desorption from Lys amide 1 and Lys amide 2 are shown in Figures 5 and 6, respectively. The mean free path of ions in a molecular film is only a few angstroms.[35] In the following interpretation, we

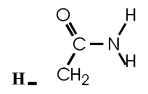
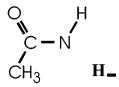
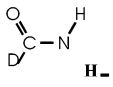
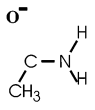
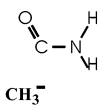
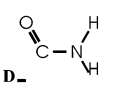
Acetamide	Formamide-1-d	Magnitude
		500
		10
 		1

Figure 4. Nomenclature of the fragments desorbed by 6−24 eV electron impact on thin films of acetamide and formamide-1-d. The relative magnitude of the anion fragment signal is shown on the right.

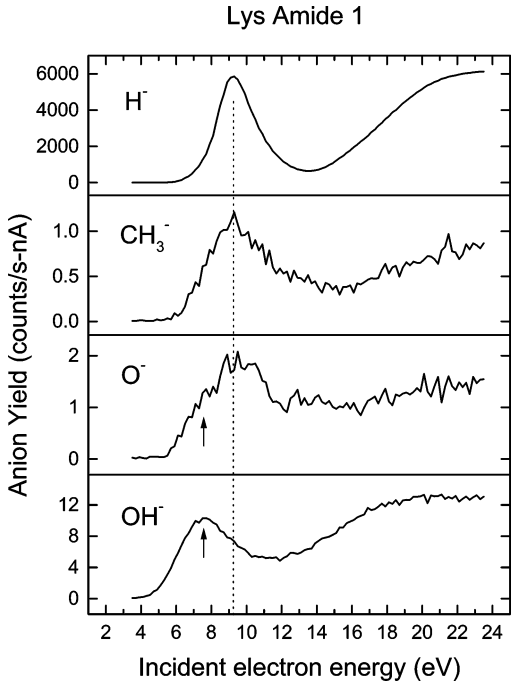


Figure 5. Energy dependence of the H^-, CH_3^-, O^-, and OH^- ion yields desorbed by electron impact on a Lys amide 1 self-assembled monolayer (SAM) chemisorbed on a gold substrate held at 300 K.

therefore assume that the long chains of CH_2 units used as spacer between the Lys amide molecules and the gold substrate do not produce an appreciable amount of detectable anions. However, even in their dry state, under UHV conditions, SAM samples could still contain water molecules, which could contribute to the H^-, O^-, and OH^- yields. However, the line shapes of the H^- yield function seen in Figures 5 and 6 bear no resemblance to those obtained from H_2O and D_2O films.[36] We therefore exclude any substantial contribution to the H^- signal arising from H_2O. Furthermore, Pan et al.[36] have shown that the weak O^- and OH^- anion signals induced by LEE impact on water ice increase as a function of time. Such a behavior is usually due to DEA to new products synthesized during electron bombardment. We therefore consider that the present O^- and OH^- signals emanate from the Lys amide molecules because they are constant as a function of bombardment time.

For both amides 1 and 2, the most important desorbed anion is H^-; at 3 orders of magnitude lower, we observe also CH_3^-, O^-, and OH^-. Considering that in acetamide, the methyl group

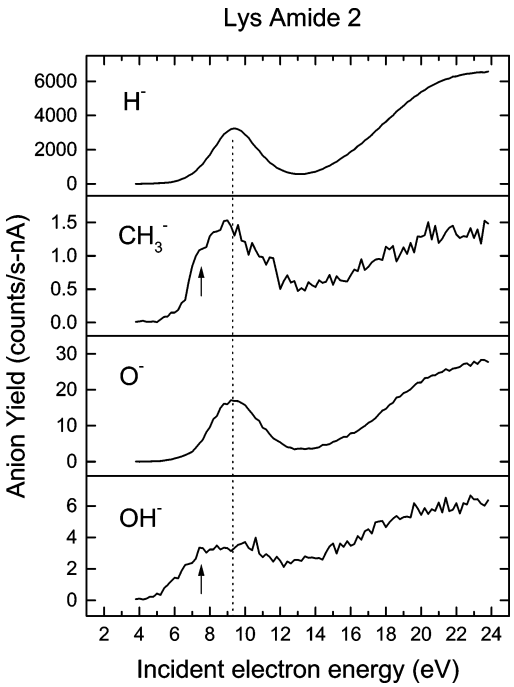


Figure 6. Energy dependence of the H^-, CH_3^-, O^-, and OH^- ion yields desorbed by electron impact on a Lys amide 2 SAM chemisorbed on a gold substrate held at 300 K.

is by far the most important source of desorbed H^-, we suggest that in both amides H^- emanates chiefly from that group. This interpretation is consistent with the fact that the Lys amide 1 produces more H^- than the Lys amide 2 due to its larger number of CH_3's per surface area (at least 1.5 times higher). We therefore ascribe the structure peaking at 9.2 eV in the H^- yield functions of Lys1 and Lys2 amides to the dissociation of a core-excited transient anion located on the amide unit containing CH_3. The appearance of a similar broad peak, also located at 9.2 eV, in the CH_3^- and O^- yield functions suggests that the same core-excited resonance may also be involved in the desorption of these anions. From further comparison of the yield functions for anion desorption from Lys amide 1 and Lys amide 2 (Figures 5 and 6) with those from acetamide and formamide-1-d, we note a shift (+1.2 eV) of the major H^- peak to higher energy. This shift is of the order of the polarization potential induced by anions at the surface of thin dielectric films condensed on a metal substrate.[19] In fact, it can be explained by the change in position of the molecule with respect to the substrate (platinum or gold). Because of the aliphatic chains, the Lys 1 and 2 amides are lying about 2.5 nm above the metal surface, whereas the acetamide and formamide-1-d molecules are physisorbed directly onto the Pt substrate. Thus, the polarization potential induced by the transient anion in the substrate is much larger for the latter molecules and lowers the energy of transient anions responsible for stable anion desorption in vacuum. Although the observed energy shift is close to that expected from induced polarization, the energy of anion desorption peaks may also be influenced by modification of the chemical environment in going from the molecular solid to the longer molecules in the SAM configuration.

Interestingly, when acetamide molecules are linked together to form a chain, a new anion, OH^-, appears in the mass spectrum. This anion signal is the second most intense originating from Lys amide 1. As shown by the arrows in Figures 5 and 6, the OH^- yield function exhibits a structure near 7.6 eV with an energy threshold around 4 eV. Thus, a large portion of the OH^- signal arises from dissociation of a different core-

excited resonance, located at a lower energy. However, the shoulder at 7.6 eV in the O^- yield function indicates that this resonance may also decay into the O^- DEA channel. Thus, another competitive channel may also exist for dissociation of the 7.6 eV transient anion state. Curiously, in the case of the Lys amide 2 molecule (Figure 6), this latter resonance seems lower in intensity in the OH^- yield function, but decays into the CH_3^- dissociative channel instead of the O^- channel. For Lys2, the O^- anion is the second most intense signal after the H^- signal.

We attribute the relatively high level of the O^- desorption from the Lys amide 2 molecule to arise essentially from the oxygen positioned between the two end groups of the molecule (see Figure 1). This oxygen atom is the only source that can explain the larger O^- desorption yields (i.e., by a factor of 8) for Lys amide 2 as compared to Lys amide 1. The increased efficiency of fragmentation is attributed to the considerably different chemical environment of the middle oxygen atom.

Second, we note that the resonance at 7.6 eV, which produces OH^- desorption, requires a rearrangement of the molecule. Thus, it seems that molecular rearrangement to produce OH^- can be realized more easily in the Lys amide 1 than in the Lys amide 2 molecule. The absence of a middle O═C−N−H−CH moiety in the Lys amide 1 molecule is a possible explanation and confirms the importance of the chemical environment for all of these fragmentation processes. The OH^- signal is stronger for the Lys amide 1 film, which contains a larger density of methyl groups. This suggests that CH_3 may play an important environmental role in OH^- desorption. Indeed, as seen from Figures 2 and 3, when the CH_3 group is replaced in acetamide by deuterium, no O^- is produced. Because O^- is likely to be involved in the molecular rearrangement forming OH^-, its absence in the anion desorption yield from formamide-1-d further supports the hypothesis that CH_3 plays a role in OH^- desorption. Finally, as seen from Figure 1, the CH_3^- signal can only arise from a single position in Lys amides 1 and 2. The environment of the CH_3 group being similar for both molecules, in this case the CH_3^- intensities are not expected to be too different. Indeed, we find that the maximum in the CH_3^- signal only varies by 33% in going from the curve in Figure 6 to that in Figure 5.

Conclusion

We have produced SAM chemisorbed on gold consisting of a short strand of the peptide backbone attached to long hydrocarbon chains, to isolate the peptide moiety from the metal substrate. Such a configuration allowed us to investigate the interaction of LEE with the peptide segments Lys amides 1 and 2 with minimal influence from the gold substrate. This was evidenced by the increase of about 1.2 eV in the position of the H^- resonances in going from physisorbed films of formamide-1-d and acetamide to the Lys amide 1 and 2 molecules in this particular SAM configuration. From comparison of the data obtained from all samples, we found the methyl group to be the major source of H^- in our model molecules of the peptide backbone. The presence of the CH_3 at the terminal group also appeared to favor OH^- desorption via molecular rearrangement. Most of the O^- signal arose from the amide functional group. All core-excited resonances decaying into the DEA channels were found to be influenced by the chemical environment of the bond, which leads to stable anion desorption. It is therefore probable that within proteins certain positions of the peptide backbone may be more vulnerable to LEE, which are produced in large quantities by ionizing radiation. A similar conclusion has been reached from electron capture dissociation investigations of charged peptides.[16,18,37]

Acknowledgment. This research is funded by the Canadian Institutes of Health Research.

References and Notes

(1) Chaudry, M. A. *Mutat. Res.* **2006**, *597*, 98.
(2) Elshaikh, M.; Ljungman, M.; Ten Haken, R.; Lichter, A. S. *Annu. Rev. Med.* **2006**, *57*, 19.
(3) Pattison, D. I.; Davies, M. J. *EXS* **2006**, *96*, 131.
(4) Cadet, J.; Sage, E.; Douki, T. *Mutat. Res.* **2005**, *571*, 3.
(5) Nakabeppu, Y.; Sakumi, K.; Sakamoto, K.; Tsuchimoto, D.; Tsuzuki, T.; Nakatsu, Y. *Biol. Chem.* **2006**, *387*, 373.
(6) Inokuti, M. *Rev. Mod. Phys.* **1971**, *43*, 297.
(7) ICRU. *Average Energy Required to Produce an Ion Pair*; Report 31, International Commission on Radiation Units and Measurements, Bethesda, MD, 1979.
(8) Cobut, V.; Frongillo, Y.; Patau J.-P.; Goulet, T.; Fraser, M. J.; Jay-Gerin, J-P. *Radiat. Phys. Chem.* **1998**, *51*, 229.
(9) Pimblott, S. M.; Mozumder, A. *J. Phys. Chem.* **1991**, *95*, 7291.
(10) Boudaiffa, B.; Cloutier, P.; Hunting, D.; Huels, M. A.; Sanche, L. *Science* **2000**, *287*, 1658.
(11) Suzuki, M. *Nature* **1990**, *344*, 562.
(12) Werner, M. H.; Clore, G. M.; Fisher, C. L.; Fisher, R. J.; Trinh, L.; Shiloach, J.; Gronenborg, A. M. *Cell* **1995**, *83*, 761.
(13) For a review, see: Sanche, L. *Eur. Phys. J. D* **2005**, *35*, 367.
(14) Maeyama, T.; Mikami, N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2725.
(15) Seydou, M.; Modelli, A.; Lucas, B.; Konate, K.; Desfrancois, C.; Schermann, J. P. *Eur. Phys. J. D* **2005**, *35*, 199.
(16) Zubarev, R. A.; Haselmann, K. F.; Budnik, B.; Kjeldsen, F.; Jensen, F. *Eur. J. Mass Spectrom.* **2002**, *8*, 337.
(17) McLafferty, F. W.; Horn, D. M.; Breuker, K.; Ge, Y.; Lewis, M. A.; Cerda, B.; Zubarev, R. A.; Carpenter, B. K. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 245.
(18) Systrad, E. A.; Turecek, F. *J. Am. Soc. Mass Spectrom.* **2005**, *16*, 208.
(19) Sanche, L. *Scan. Microsc.* **1995**, *9*, 619.
(20) Bass, A. D.; Sanche, L. *Radiat. Phys. Chem.* **2003**, *68*, 3.
(21) Mozejko, P.; Bass, A. D.; Parenteau, L.; Sanche, L. *J. Chem. Phys.* **2004**, *121*, 10181.
(22) Hervé du Penhoat, M.-A.; Huels, M. A.; Cloutier, P.; Jay-Gerin, J.-P.; Sanche, L. *J. Chem. Phys*. **2001**, *114*, 5755.
(23) Abdoul-Carime, H.; Cloutier, P.; Sanche, L. *Radiat. Res*. **2001**, *155*, 625.
(24) Sanche, L. *J. Chem. Phys.* **1979**, *71*, 4860.
(25) Abdoul-Carime, H.; Cecchini, S.; Sanche, L. *Radiat. Res.* **2002**, *158*, 23.
(26) Leclerc, G.; Bass, A. D.; Mann, A.; Sanche, L. *Phys. Rev. B* **1992**, *46*, 4865.
(27) Matsueda, G. R.; Stewart, J. M. *Peptides* **1981**, *2*, 45.
(28) Maletinska, L.; Neugebauer, W.; Perodin, J.; Lefebvre, M.; Escher, E. *J. Med. Chem*. **1997**, *40*, 3271.
(29) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*; Academic Press: New York, 1991.
(30) Antic, D.; Parenteau, L.; Lepage, M.; Sanche, L. *J. Phys. Chem.* **1999**, *103*, 6611.
(31) Hotop, H.; Ruf, M.-W.; Allan, M.; Fabrikant, I. I. *Adv. At. Mol. Opt. Phys.* **2003**, *49*, 85.
(32) Dugal, P. C.; Huels, M. A.; Sanche, L. *Radiat. Res.* **1999**, *151*, 325.
(33) Abdoul-Carime, H.; Dugal, P. C.; Sanche, L. *Radiat. Res.* **2000**, *153*, 23.
(34) Huels, M. A.; Hahndorf, I.; Illenberger, E.; Sanche, L. *J. Chem. Phys.* **1998**, *108*, 1309.
(35) Akbulut, M.; Sack, N. J.; Madey, T. E. *Surf. Sci. Rep.* **1997**, *28*, 177.
(36) Pan, X.; Abdoul-Carime, H.; Cloutier, P.; Bass A. D.; Sanche, L. *Radiat. Phys. Chem.* **2005**, *72*, 193.
(37) Systrad, E. A.; Turecek, F. *J. Am. Soc. Mass Spectrom.* **2005**, *16*, 208.