

# Identification of ion fragments produced from thymine and deuterated thymine by low energy ion impact in films and electron impact in the gas phase

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## Abstract

The chemical composition of charged fragments desorbing from thymine-methyl-d<sub>3</sub>-6-d (T<sub>d</sub>) films during 10–200 eV Ar<sup>+</sup> ion irradiation is studied by mass spectrometry of positive and negative ions. The resulting mass spectra are compared to those obtained from similar films of thymine (T), and from 70 eV electron impact on both T and T<sub>d</sub> in the gas phase. Ion impact on T and T<sub>d</sub> films produces numerous positive and negative ion fragments via endocyclic and exocyclic bond cleavage, even at ion energies well below 60 eV. The major cations desorbing from T films are identified as HNCH<sup>+</sup>, HN(CH)CCH<sub>3</sub><sup>+</sup>, [T–OCN]<sup>+</sup>, OCNH<sub>2</sub><sup>+</sup>, C<sub>x</sub>H<sub>y</sub><sup>+</sup> (x = 1–3 and y = 0–4), and [T + H]<sup>+</sup>. While ion impact on T and T<sub>d</sub> films produces a new fragment [T–O]<sup>+</sup>, [T<sub>d</sub>–O]<sup>+</sup>, not seen in gas phase electron impact, the latter yields CO<sup>+</sup> fragments that are not observed during ion impact on the films. Anion desorption is dominated by H<sup>–</sup>, O<sup>–</sup>, CN<sup>–</sup>, OCN<sup>–</sup>, and [T–H]<sup>–</sup> formation, with lesser dissociation channels leading to desorption of C<sub>2</sub><sup>–</sup>, C<sub>2</sub>H<sup>–</sup>, C<sub>2</sub>CN<sup>–</sup>, NC<sub>3</sub>H<sub>2</sub><sup>–</sup>, HNC<sub>3</sub>H<sub>3</sub><sup>–</sup>, OC<sub>3</sub>H<sub>3</sub><sup>–</sup>, C<sub>2</sub>OCN<sup>–</sup>, and C<sub>3</sub>H<sub>x</sub><sup>–</sup> (x = 2 and 3). Measurements of the primary ion energy dependence of the fragment desorption yields show that positive ion fragments appear at energies near 15–20 eV, while generally the endocyclic fragments appear at lower energies than the exocyclic (anion and cation) fragments. Our results show that even at very low ion energies, thymine is sensitive to complete fragmentation, whereby the loss of the HNCH (or HNCD from T<sub>d</sub>) fragment, i.e., ring cleavage involving the N1 and C6 atoms, dominates; in cellular DNA, this would correspond to complete loss of the base. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

Ionizing radiation (protons, heavy ions, electron, X- and γ-rays) treatment of biological media causes severe damage to DNA mainly by producing single and double strand breaks of DNA and complex clustered lesions [1]. This damage is associated with abundant secondary particles produced along the radiation tracks, which include low-energy ions, radicals, and ballistic secondary electrons [2,3]. Traditionally, DNA damage has been linked to thermal, or solvated, secondary electrons, and the formation of reactive radicals [4]. Hence,

in the past decades, most experimental studies have focused on DNA damage by free radicals and solvated electrons.

However, most of the secondary electrons created along ionizing radiation tracks in solids and liquids have non-thermal initial energy distributions below 100 eV, with a most probable energy below 10 eV. Some secondary electrons such as Auger electrons may have energies up to several 100 eV, or a few kilo electron volts for “delta rays”. Non-thermal secondary electrons can also produce secondary ions, by either ionization, excitation, or dissociative electron attachment (resonances). Recently, this has been shown to cause severe damage to DNA and its components at electron energies as low as 3 eV via resonant mechanism [5–11].

Simultaneously, hyperthermal ( $E < 100$  eV) secondary ions are created along any radiation track as a result of dis-

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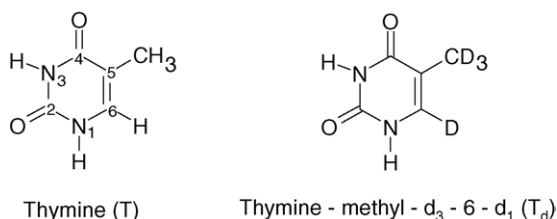


Fig. 1. Molecular structures of thymine (T) and thymine-methyl-d<sub>3</sub>-6-d (T<sub>d</sub>).

sociative ionizations. High energy electrons or photon tracks usually produce secondary ions with low kinetic energies (typically below 10 eV), but with different chemical reactivities. Some of the ions formed via Auger-decay of specific core excitations can have energies of several tens of electron volts. More important for the present studies, during heavy ion therapy [12,13], secondary atomic ions with energies of several hundred electron volts and multiple charge states can be produced [14]. Furthermore, while heavy ion therapy relies on the ion's highly localized relative dose distribution (Bragg peak), the primary ion's linear energy transfer is highest at the ion track ends where the ionization density is highest, and where the primary ion energy is reduced below a few kilo electron volts. Thus, the chemical and kinetic damage produced by either track-end primary ions, or hyperthermal secondary ions in subsequent scattering events, is of great biological relevance in heavy ion therapy, since it will occur over short distances (a few nanometers) and result in complex DNA damage clusters that cannot be easily repaired by the cell.

In a recent preliminary study [15], we have found that ion impact on condensed phase thymine, at ion energies below 200 eV, results in significant film degradation via both kinetic and potential scattering (i.e., the primary ion's potential energy). However, to understand the sequence of events leading to DNA damage during irradiation requires a detailed knowledge of the initial fragmentation pathways and products, and the possible reactivity of the initial fragments. Thus, the identification of the chemical composition of the fragments produced by ion (or electron) irradiation is a prerequisite for the further study of their reactivity.

Here, we report detailed mass spectroscopy measurements of the energetic (1–5 eV) anion and cation fragments produced by 10–200 eV Ar<sup>+</sup> ion impact on condensed phase thymine-methyl-d<sub>3</sub>-6-d (T<sub>d</sub>) and thymine (T), with molecular structures shown in Fig. 1. The resulting ion stimulated desorption (ISD) mass spectra are compared to those produced in the same experimental set-up from gas phase T and T<sub>d</sub> by 70 eV electron impact, and the chemical identity of fragments produced by ISD is determined.

Our results show that the most abundant cation fragments produced by hyperthermal Ar<sup>+</sup> impact are HNCH<sup>+</sup>, HN(CH)CCH<sub>3</sub><sup>+</sup>, C<sub>3</sub>H<sub>3</sub><sup>+</sup>, OCNH<sub>2</sub><sup>+</sup>, [T-OCN]<sup>+</sup>, and [T-O]<sup>+</sup>, where the first two are found to result from specific ring

cleavage at, respectively, the C2–N1 and C6–C5, and C2–N1 and C5–C4. For [T+H]<sup>+</sup> formation, we find a strong 4:1 preference for abstraction of nitrogen-bound hydrogen from adjacent T, relative to carbon-bound hydrogen, opposed to the stoichiometric NH to CH ratio of 1:2. The most prevalent desorbing anions include H<sup>-</sup>, O<sup>-</sup>, CN<sup>-</sup>, OCN<sup>-</sup>, and [T-H]<sup>-</sup> formation; the latter involves deprotonation almost exclusively via NH bond cleavage, while H<sup>-</sup> formation occurs with stoichiometric ratio from NH and CH sites. Lesser dissociation channels also lead to desorption of OH<sup>-</sup>, C<sub>2</sub><sup>-</sup>, C<sub>2</sub>H<sup>-</sup>, C<sub>2</sub>CN<sup>-</sup>, NC<sub>3</sub>H<sub>2</sub><sup>-</sup>, HNC<sub>3</sub>H<sub>3</sub><sup>-</sup>, OC<sub>3</sub>H<sub>3</sub><sup>-</sup>, C<sub>2</sub>OCN<sup>-</sup>, and C<sub>3</sub>H<sub>x</sub><sup>-</sup> (x=2 and 3). Here, OH<sup>-</sup> (or OD<sup>-</sup> from T<sub>d</sub>) formation likely involves subsequent reactive scattering of O<sup>-</sup> prior to desorption, leading to H abstraction from NH and CH bonds. More importantly, both exocyclic and endocyclic fragmentation is observed for ion beam impact well below 1 eV/amu, and results in the formation of ions that still have sufficient kinetic energy (>1 eV) to overcome the charge induce polarization barrier at the film surface and desorb into the vacuum.

## 2. Experimental method

The experiments were carried out on an ion beam apparatus developed in-house [15], and which will be discussed in detail elsewhere. Here, we give only a brief description of the experimental method: a low energy ion beam system delivers a highly focused, mass- and energy-resolved positive or negative ion beam in the 1–500 eV energy range into a UHV (10<sup>-9</sup> Torr) reaction chamber for sample film irradiation. A high resolution quadrupole mass spectrometer (QMS) (Hidden Analytical Ltd.) is installed perpendicularly to the ion beam line to monitor desorbing positive and negative ions *during* ion impact. A large diameter lens is used at the mass spectrometer entrance to ensure a large solid angle of acceptance and thus a higher sensitivity. The QMS is optimized to detect ions of up to 5 eV kinetic energy.

In this work, we focus mainly on 10–200 eV Ar<sup>+</sup> ion irradiation of 200 ng/cm<sup>2</sup> thymine (T and T<sub>d</sub>) films on Pt substrates, corresponding roughly to four *nominal* monolayers of thymine assuming no clustering of the molecules [8]. For negative ion desorption, we use 20 ng/cm<sup>2</sup> films. Films are prepared by in vacuo evaporation onto an atomically clean polycrystalline Pt substrate held on a manipulator at room temperature (22–24 °C), while the thymine condensation rate is calibrated to within 0.5 ng/cm<sup>2</sup> by a quartz crystal microbalance. Prior to film deposition, the Pt substrate is cleaned by resistive heating to 800 °C, and/or 500 eV Ar<sup>+</sup> sputtering. The evaporation temperature of ≤100 °C is well below the thymine decomposition temperature of about 320 °C. X-ray photoelectron spectroscopy and thin film chromatography results show that the films consist of intact molecules [16,17]. The sample film is positioned in the center of the reaction chamber at 2 cm from both the exit of the ion beam line and the entrance of the mass spectrometer,

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