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VUV Study of Electron Impact Dissociative Excitation of Thymine

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Abstract:

A crossed electron-gas beam system coupled to a VUV spectrometer has been used to investigate the dissociation of thymine into excited atomic fragments in the impact energy range from threshold to 400 eV. The main features in the spectrum are the H Lyman series lines. The relative emission cross section of Lyman-α has a broad maximum at an energy of 160 eV. The probability of extracting excited C, N or O atoms from the parent molecule is shown to be very small. Possible dissociation channels and excitation mechanisms in the parent molecule are discussed.

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Introduction.

As one of the DNA base molecules, thymine ($C_5H_6N_2O_2$) and its interactions with charged particles have been widely studied in recent years. Ever since it was demonstrated [1] that dissociative electron attachment (DEA) at low energies provided a mechanism for double and single strand breaking within the DNA structure, there has been a need for quantitative electron scattering data for this molecule. This is to enable accurate modelling of damage produced by the entry of high-energy radiation into biological media and the subsequent low energy electron cascade which is released. Recent work by van der Burgt et al [2] references a large body of relevant work on ionization, dissociative ionization and DEA. A number of review articles are also available [3-7]. Elastic scattering from thymine at 100 and 500 eV has been reported by Colyer et al [8] while Abouaf et al (27) and Chernyshova et al (28) have studied low energy energy-loss spectroscopy. Calculations of low-energy, elastic and inelastic scattering from thymine and cytosine, have been reported by Winstead *et al* [9] and Dora et al [10].

Photon impact studies on isolated nucleobases such as thymine are also numerous [e.g.11-13 and included references]. These are relevant as they provide information on the dipole allowed channels for exciting and dissociating the molecule.

A more limited number of studies is available where photon emission following electron collisions with DNA bases was investigated. To date the only spectral information following such electron bombardment consists of observations in the visible and near-UV spectral regions where the data are dominated by radiation from molecular fragments. Target molecules studied include uracil, cytosine adenine and thymine [14-18]. In the present work we investigate the break-up of the thymine molecule into excited atomic fragments. By working in the VUV spectral region where atomic radiation dominates the spectrum we were able to gain useful data on which bonds are most likely to be broken in such electron collisions. Because of the close relationship between thymine and pyrimidine we will draw comparisons with our previous study [19] of this latter molecule. Preliminary results from this study were presented at recent conferences [20, 21]

Experimental Details:

The experimental set-up and techniques are very similar to those used in earlier work [19, 22-24, and references therein] on molecular dissociative excitation in this laboratory and so only a brief summary is given here together with details pertinent to thymine. Reagent grade thymine was contained in a stainless steel oven with a capillary output nozzle. On heating, to around 150°C, the oven projected a beam of thymine vapour vertically upwards where it was intersected at right angles by a magnetically collimated electron beam. The capillary nozzle was kept at a temperature some 40-50°C higher than the main oven to prevent clogging. Radiation from the interaction region was observed in a direction orthogonal to both the electron and gas beams by a ½ metre Seya-Namioka VUV spectrometer coupled to a CsI coated channel electron multiplier. The energy resolution of the electron beam was approximately 1 eV full width at half maximum (FWHM) and beam currents were typically 50 μA. Electron beam currents were recorded synchronously with measurements of photon emission rates so that photon rates could be properly normalized. Photon fluxes were assumed to be unpolarized. This is a reasonable assumption given the size and complexity of the parent molecule. When required, He gas could be mixed with the thymine vapour so that energy calibration of the system could be carried out using the known 21.21 eV threshold of the 58.4 nm He $(2^1P - 1^1S)$ transition

Two types of experimental data were collected. In the first, a constant electron beam energy (100 eV) was maintained and the photon emission spectrum was recorded over the wavelength range 90-160 nm. In the second, a particular spectral feature (wavelength) was selected and the photon emission rate (relative excitation cross section or probability) was measured as the electron beam energy was scanned. This produced a so-called "excitation function" for the line under consideration.

The relative spectral sensitivity of the detection system was established using a refinement of the so-called "molecular branching-ratio" technique. Essentially this involved taking a spectrum of the well-known H_2 emissions in the relevant

wavelength region (90−160 nm) and then comparing this with the theoretical H_2 spectrum. This method is fully discussed in [22]. Having established the relative sensitivity of the system with wavelength, the entire observed thymine spectrum could be scaled to show the correct relative strengths of the different features. Unfortunately the data could not be put on an absolute basis because, as yet, we have no accurate method of determining the target number density in our thymine beam. Background spectra taken under identical experimental conditions except with the thymine oven cold revealed a small nitrogen contamination in the system. This has been subtracted from the data.

To determine the relative cross sections, we fitted Gaussian line shapes to obtain the areas under the peaks. This procedure enabled the relative individual emission line intensities to be extracted even when it was not possible to fully resolve the spectral features
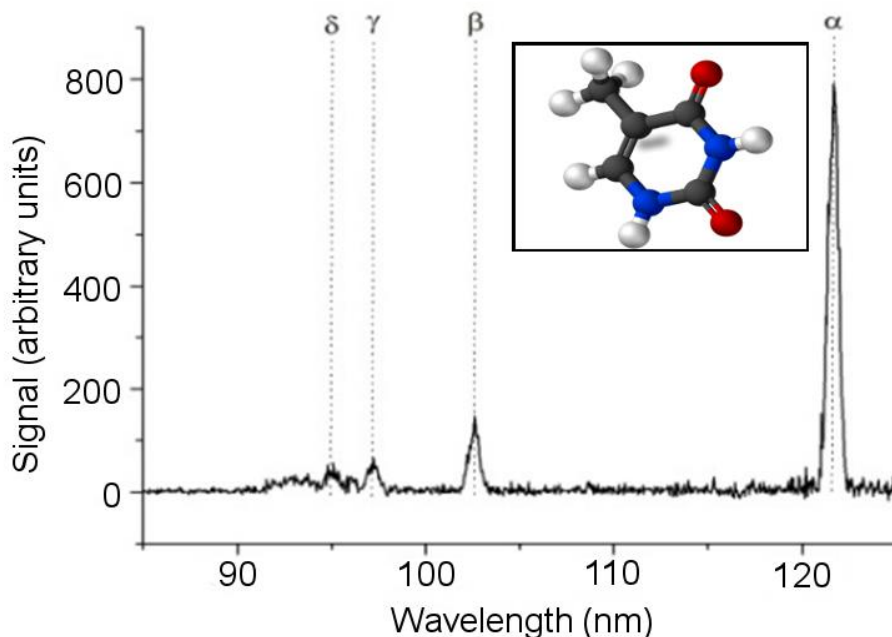
Results and Discussion:

A. Spectra:

Figure 1. Thymine VUV spectrum excited by 100 eV electrons. The features are identified in Table 1 where their relative emission cross sections are given. Data have been corrected for variation of the detection sensitivity with wavelength. A small nitrogen background component has been subtracted off as mentioned in the text. The insert shows the geometry of the thymine molecule.

As can be seen from Fig 1, the dominant spectral features constitute the hydrogen Lyman series. There are a number of reasons why this might be expected. First, the structure of the molecule, (see insert, Figure 1), suggests that it should be much easier to break a C-H or N-H bond with excitation of the resultant H atom than

extract an excited C or N atom from the ring. The double-bonded O atoms should similarly be more difficult to release and excite. This is discussed more quantitatively later. Secondly, comparison with the electron impact mass spectroscopy work [25] indicates that C^+, N^+ and O^+ ions are very minor (1% or less) components in the overall mass spectrum whereas both H^+ and H_2^+ are more prominent. Thus excited H species are expected to be more significant than excited C, N or O.

The relative emission cross sections of the first two members of the Lyman series, α:β, are 1.00:0.16 (see Table 1). This may be compared with the equivalent value obtained with pyrimidine targets, namely 1.00:0.19. The uncertainties listed in Table 1 were computed using standard mathematical techniques and were a combination of statistical and spectral calibration errors.

Feature	Wavelength (nm)	Relative Cross-section
α	121.6	1.00
β	102.6	0.16 ± 0.01
γ	97.3	0.08 ± 0.01
δ	95.0	0.05 ± 0.01

Table 1.   100 eV relative emission cross section data for the individual lines of the Lyman series.

B. Excitation functions:

Figure 2 shows the relative excitation function (emission cross section) of the dominant Lyman-α feature. As can be seen, it is devoid of sharp features and displays a broad maximum near 160 eV. Analysis of more detailed near threshold data reveals a rather gradual threshold at 23 ± 1.0 eV followed by a steeper rise in the excitation probability function some 6 eV higher in energy. This suggests that at least two different processes are active in the near threshold region. Progression to higher impact energies sees a further steepening of the cross section curve indicating the presence of more contributing processes.
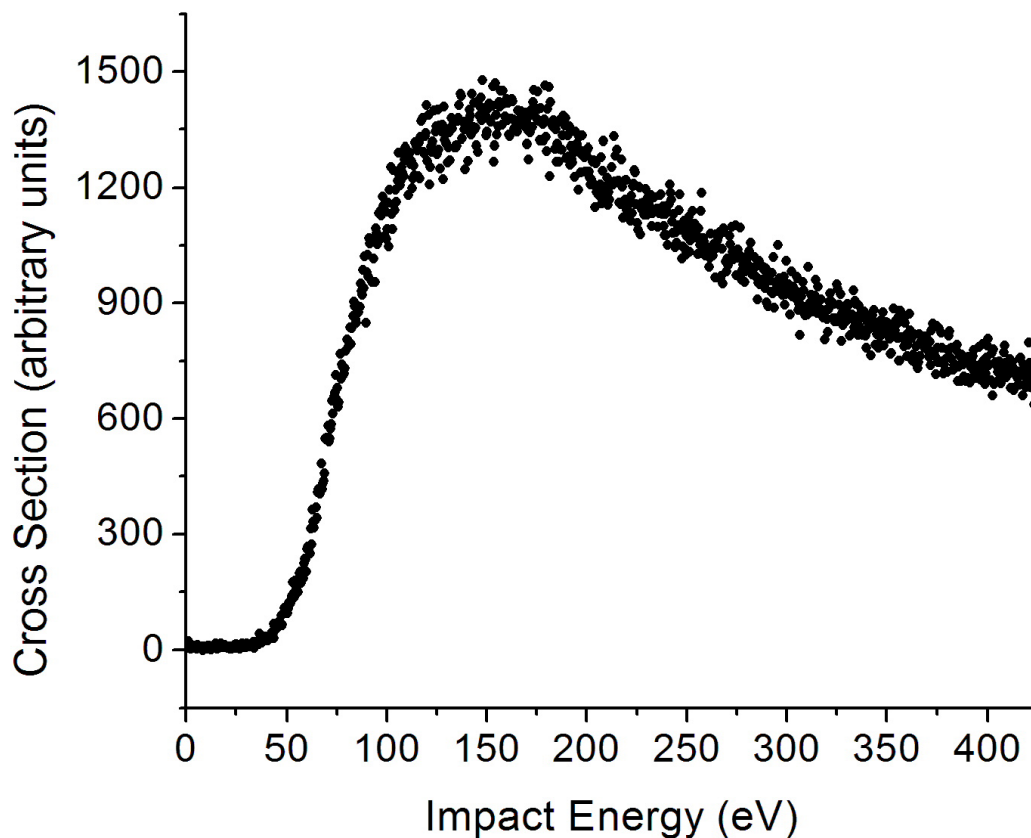
Figure 2. Relative emission cross section for the 121.6 nm H[2p-1s] transition in the electron-impact energy range from 0-435 eV

Removal of an excited hydrogen atom involves the breaking of a single C-H or N-H bond in the molecule. Schneider et al [12] indicate that the minimum energy required with production of ground state H is that to fracture the $C_{(7)}$-H bond in the methyl group, namely 3.72 eV. For the $C_{(6)}$-H bond cleavage 4.77 eV is required. The $N_{(1)}$-H and $N_{(3)}$-H bonds require energy inputs of 4.08 and 5.19 eV respectively. Excitation of the H atom to the 2p state requires a further 10.2 eV and hence the lowest possible thresholds for Lyman-α emission would occur between 13.92 and 15.39 eV. We measure a gradual onset of excitation starting at approximately 23 eV followed by a rapid rise in the excitation function some 6 eV higher. Even assuming that some kinetic energy release accompanied the dissociation, it is very unlikely that this would be sufficient to account for the large difference between the observed and calculated thresholds for simple extraction with excitation of a hydrogen atom.

A significant feature of the mass spectrometry work is the revelation [26, 11, 2] that very often H atoms are released as a by-product of more complicated parent molecule break-up. For example ion mass 82 is produced in the reaction:

$$e + T \rightarrow C_4H_4NO^+ + HNCO + H + 2e^*$$ (1)
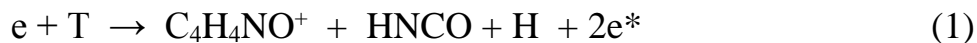
Similarly, appearance energy measurements [2] of ionic fragments with masses 53, 52 and 51 and also the mass sequences 40, 39, 38 and 37 together with 28, 27 26 and 15, 14, 13 were all shown to be consistent with the loss of H atoms from a heavier fragment. This means that H atoms are released in a number of fragmentation processes and hence excited H dissociation channels are likely available also. Significantly these groups of ions are among the most intense of the observed mass spectrum [25] following electron impact.

The appearance energy of the mass 82, $C_4H_4NO^+$ ion, Eq 1, was measured (2,11) to be close to 13 eV and so a channel similar to this could be producing H(2p) above an appearance energy of around 23 eV in rather close accord with our observations. A similar statement could be made about mass 54, $NC_3H_4^+$, where again a H atom is released in the fragmentation at a threshold energy close to 13 eV [2, 11]. We note that these ionization processes were observed using either photon or electron impact indicating that they were optically allowed.

Unfortunately although H^+ has been observed (25), its appearance energy does not appear to have been measured. Schneider et al (12) have studied the details of the dissociation dynamics of thymine following absorption of photons of insufficient energy to produce ionic fragmentation. They found that H atoms were released from the neutral molecule with kinetic energies in the range 0-2.5 eV. Two photons and an intermediate "dark" state were involved. Their minimum photon energy was 4.59 eV (270 nm). This channel is open in the electron impact case as well as demonstrated by Abouaf et al [27] and so, if additional excitation to H(2p) occurred, a minimum appearance energy around 19.4 eV would be expected. Again, our measured Lyman-α appearance energy of ~23 eV suggests that this channel is not an important contributor even if significant release of kinetic energy occurred. The rather sharp rise in the probability function at energies close to 30 eV suggests that a number of additional processes are contributing at these higher energies but it is not possible to quantify these channels. We note that similar effects were observed in the ionization channels [2].

The overall shape of the excitation function with its broad maximum at 160 eV suggests that spin-flip processes (which would demonstrate a sharp rise in the excitation function followed by a rapid decay) are unimportant. The fall off in the

excitation with energy (E) in the high energy region goes approximately as 1/E suggesting that spin-allowed but dipole forbidden processes play an important role.

Conclusions:

Dissociative excitation of thymine has been studied in the VUV spectral region. As when pyrimidine targets were considered [19], by far the dominant spectral features are the H Lyman lines. Their relative emission cross sections have been established using the emissions from H_2 in this spectral region to obtain the relative sensitivity of our detection system with wavelength. Significantly, we were not able to observe emissions from any other atomic species confirming that the probability of extracting excited C, O or N atoms from the molecule is very small. Clearly break-up into molecular fragments dominates. This is consistent with dissociative ionization measurements [2, 11, 25] which indicate that a very small (1% or less) fraction of total ionization results in C, O or N atomic ions. Simple removal with excitation of the H atom from the molecule, leaving the rest of the molecule intact, has been shown to be unimportant in the near threshold region. A more likely scenario is fragmentation of the target molecule with release of an excited hydrogen atom.

It will be interesting to study related bio-molecules, e.g. cytocine, adenine etc, to see if similar patterns occur. Rupturing of the hydrogen bonds for such molecules, when in the DNA context, could have serious harmful effects. Such experiments are currently underway in our laboratory.

Acknowledgements:

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