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Positive and negative ion formation via slow electron collisions with 5-bromouridine

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Abstract. Cation and anion formation is studied experimentally upon inelastic low energy electron interactions with 5-bromouridine (BrUrd) using a crossed electron/neutral beams set-up combined with a quadrupole mass spectrometer. The BrUrd molecule belongs to the class of radiosensitizers that increase the sensitivity of DNA (or RNA) to ionizing radiation. In the case of positive ion formation the ionization efficiency curves are measured near the threshold and the corresponding appearance energies are determined using a non-linear least square fitting procedure. The anion yields are investigated in the electron energy range from about 0 to 14 eV. From the comparison of the present results for negative and positive ions information concerning the underlying mechanism of radiosensitizers is deduced.

PACS. 34.80.Ht Dissociation and dissociative attachment by electron impact – 87.14.Gg DNA, RNA – 87.50.-a Effects of radiation and external fields on biomolecules, cells and higher organisms

1 Introduction

Halouracils can substitute thymine in the genetic sequence of cellular DNA without changing the normal gene expression in non irradiated cells [1]. Thereby, the sensitivity of living cells to X-rays is increased by a factor of four [2]. Radiation therapy following the incorporation of 5-halouridines (a halouracil attached to the sugar moiety, such as 5-bromouridine), acting as radio-sensitizers, has been suggested as a promising means in cancer treatment [3,4]. However, the molecular processes by which such radio sensitizers operate have not been unraveled so far. In general the damage to the living genome can be characterized as direct or indirect processes [5]. Direct damage occurs by immediate energy deposition to the DNA or RNA and its closely bound water molecules of the irradiated cells. Indirect damage is ascribed to the highly reactive hydroxyl radicals formed by the interaction of the primary radiation with the aqueous surrounding. Two third of the damage to the genome is expected to be indirect damage and one third direct [5].

Since the discovery that low energy electrons [6,7] and photons [8] with energies as low as 7 eV can efficiently induce single and double strand breaks in plasmid DNA the contribution of especially low energy electrons for DNA damage has been considered to be particularly significant. The number of low energy (<20 eV) secondary electrons per 1 MeV deposited primary quantum is 10^4 [9]. Within the last years theoretical and experimental studies were performed to investigate the specific action of low energy electrons with isolated and condensed biomolecules including DNA/RNA-bases [10–13], amino acids [14,15], sugar [16] and nucleosides [17]. Moreover, isolated gas phase halogenated bases were also investigated extensively [18–25] with respect to the interaction with low energy electrons. The most studied halouracils are 5-chlorouracil and 5-bromouracil where the hydrogen at the C5 position is replaced by a halogen atom (Cl and Br, respectively). The electron interaction with 5-bromouracil (BrUra) was studied for the isolated gas phase molecule [21–24], in the condensed phase [26] and even for BrUra paired with adenine [27]. In contrast to isolated nucleobases which possess a negative vertical electron affinity, for halogenated nucleobases a stable parent anion was observed in the gas phase. This result is consistent with the positive electron affinity reported for halouracils [25]. Compared with non-halogenated pyrimidine bases the cross-sections for dissociative electron attachment (DEA) of the halogenated molecules were more than two orders of magnitude higher [18,22,23]. However, for 5- and 6-chlorouracil the positive ion mass spectra revealed just the opposite tendency, i.e., higher yield of fragment ions in the case of the non halogenated species [19].

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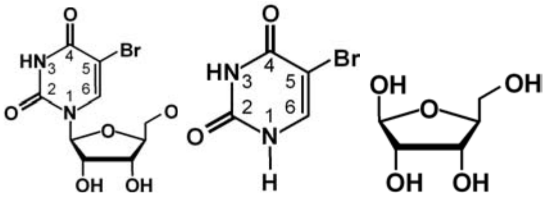

Fig. 1. Molecular structure of 5-bromouridine and its building blocks 5-bromouracil and ribose.

Thus, the mechanism of radio sensitization by halouracils has been ascribed to the enhanced dissociative electron attachment cross-section [19].

Recently a new line of research was started by the investigation of the (low) energy interaction with a nucleoside [17], i.e. the nucleobase is combined with a sugar molecule via the N-glycosidic (1N–C) bond. Dissociative electron attachment to the nucleoside thymidine (thymine + deoxyribose) was studied by Illenberger and co-workers [17]. They observed, analogous to isolated nucleobases [10,11], no stable parent anion but the dehydrogenated parent anion as the heaviest fragment anion. Moreover, the most abundant anion turned out to be the thymine moiety of the thymidine molecule. Abdoul-Carime et al. [28] carried out recently first experiments about the interaction of low energy electrons with a halogenated nucleoside, i.e. DEA to 5-bromouridine in the gas phase by using a trochoidal electron monochromator combined with a quadrupole mass spectrometer. The 5-bromouridine consists of the 5-bromouracil molecule connected to the ribose sugar moiety (see Fig. 1 for the molecular structure). Abdoul-Carime et al. [28] observed strong fragmentation of the 5-bromouridine molecule upon electron attachment with two main fragmentation channels, i.e. the formation of Br^- and $(BrUra–H)^-$. Both anions were formed effectively at very low electron energies (close to 0 eV). In addition several minor fragment anions were identified, however, with at least an order of magnitude lower intensity. Except for O^- and H^- all other fragment anions exhibited a well pronounced resonance at about zero eV [28].

In the present investigation we measure the ionization efficiency curves near the threshold for cations formed via electron impact ionization of 5-bromouridine (BrUrd). From the measured data sets the corresponding appearance energies (*AE*s) are determined by a fitting procedure. To our best knowledge the present work is the first experiment determining appearance energies of BrUrd.

The present results for positive ions are compared with the isolated components of the BrUrd-molecule studied previously. Moreover, we investigate negative ion formation upon electron attachment to BrUrd. Our more extensive measurements are compared with the earlier study by Abdoul-Carime et al. [28] where exclusively dissociative electron attachment to this molecule was investigated. A comparison of positive and negative ion formation shows again a strong effect of radiosensitization for DEA.

2 Experimental

Positive and negative ions are formed via a collision of free electrons with gas phase molecules of 5-bromouridine (BrUrd). A neutral beam of BrUrd is generated by heating a powder (purity > 99%, obtained from Sigma-Aldrich) in an electrically heated oven optimized for the vaporization of biomolecules. The temperature of the oven during the present experiments is kept at 400 K, measured with a Pt100 resistance temperature sensor mounted at the top of the oven. At this temperature the thermal decomposition due to the heating process can be excluded (which was extensively discussed in [28]). The neutral molecules are guided from the oven to the ionization region by an 8 cm long capillary and enter the collision chamber through a hole with a diameter of 1 mm. Ions formed in the collision chamber after the interaction with low energy electrons are then extracted by a weak electrostatic field into the entrance of a quadrupole mass spectrometer (mass range from 2 to 2048 Da). The mass analyzed ions are detected by a channeltron type SEM operated in a pulse counting mode and recorded by a computer. In the present work ion efficiency curves, i.e., ion yields as a function of the electron energy, are reported. For positive ions the electron energy covers a range from about 5 eV below to 5 eV above the threshold and the energy scale is calibrated with the well-known ionization energy of krypton [29], measured under the same conditions. For negative ions the electron energy is scanned from about zero to 14 eV and the energy scale is calibrated with the 0 eV resonance of Cl^-, formed via DEA to CCl_4 and measured under the same conditions [30]. In order to avoid possible anion molecule reactions [11] between Cl^- and BrUrd all spectra shown below are recorded without the presence of CCl_4. The heart of the presently utilized apparatus is a hemispherical electron monochromator. Electrons are emitted from a hairpin filament with a typical resolution of 1 eV and focussed with a lens system to the focal point of a custom made 178° hemispherical analyzer. After passing the hemispheres the spread of the kinetic energy of the electron beam reaches a best value of 35 meV (with an electron current of about 1 nA) [31]. In the present studies a FWHM of the electron energy distribution of approximately 120 meV is used, resulting in a substantially higher sensitivity of the instrument (electron current typically 8 nA). The low energy spread electrons are focussed and accelerated from the exit aperture of the hemispheres with a second lens system into the collision chamber, where the interaction with the neutral beam takes places. The standard electron energy range is from about 0 to 100 eV and with additional power supplies electron energies up to 600 eV are possible. After the collision chamber the electron beam is collected at a final plate, where the electron current is measured. A detailed description of the apparatus is given elsewhere [32]. The corresponding appearance energy (*AE*) for cations from a measured data set is derived by a non linear least square fitting routine using the Marquart-Levenberg algorithm. Briefly, the *AE* values are obtained by fitting the ion efficiency curves with a

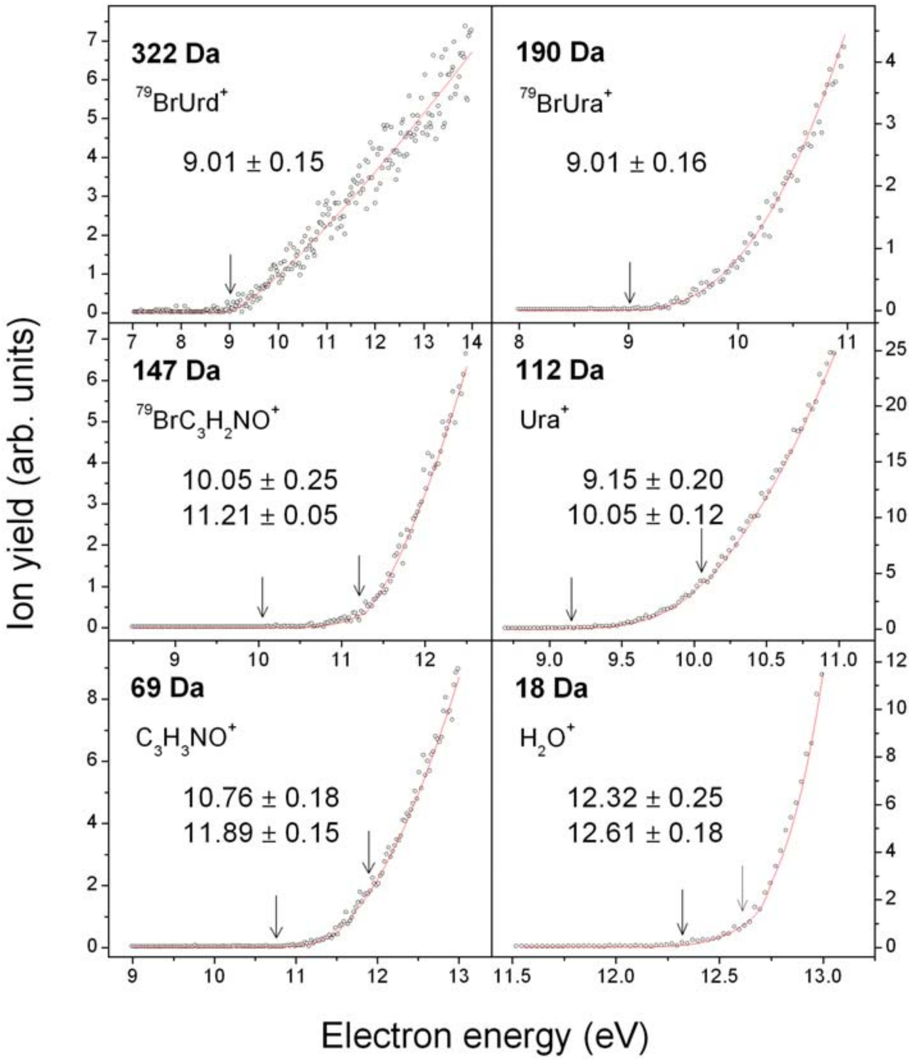

Fig. 2. Ion efficiency curves of cations formed upon electron impact ionization of 5-BrUrd. The measured data sets are shown as open circles. The solid lines represent the best fit of equation (1) to the data. Also included in the figure are the appearance energies for the measured cations deduced from the fit. The arrows indicate the positions of the appearance energies.

modified Wannier type threshold [33] law of the type:

$$f(E) = b + c_1\,(E - AE_1)^{p_1} + c_2\,(E - AE_2)^{p_2} \qquad (1)$$

where b is a possible constant background signal, c_1 and c_2 are two scaling constants that become zero for electron energies E lower than the respective threshold energies AE_1 and AE_2 and p_1 and p_2 are exponential Wannier factors. In the case of a single threshold c_2 is zero at all energies. The program ORIGIN 7.0 is used to fit equation (1) to the measured data by variation of the seven parameters. A more detailed description of the used fitting routine is given in [34]. With the present experimental set-up and the fitting method, a reliable and accurate determination of appearance energies is possible which has been demonstrated in previous experiments with rare gases and simple molecules [35].

3 Results and discussion

3.1 Positive ions

In the present work the formation of the following cations formed via electron impact ionization of gas phase molecules of 5-bromouridine (BrUrd) is studied:

$$e^- + \mathrm{BrUrd} \rightarrow \mathrm{BrUrd}^+ + 2e \qquad (2)$$

$$\mathrm{BrUra}^+ + 2e + \text{neutral fragments} \qquad (3)$$

$$(\mathrm{BrC_3H_2NO})^+ + 2e + \text{neutral fragments} \qquad (4)$$

$$\mathrm{Ura}^+ + 2e + \text{neutral fragments} \qquad (5)$$

$$(\mathrm{C_3H_3NO})^+ + 2e + \text{neutral fragments} \qquad (6)$$

$$(\mathrm{H_2O})^+ + 2e + \text{neutral fragments}. \qquad (7)$$

Figure 2 shows the ion efficiency curves close to the threshold region of the positively charged parent ion

Table 1. The appearance energies (*AE*s) of common product ions for the molecules bromouridine, uridine, uracil, deoxyribose and water.

	AE (in eV)				
	molecule				
cation	bromouridine present	uridine [36]	uracil [37]	deoxyribose [16]	water [29]
Ura^+	9.15 ± 0.2 10.05 ± 0.12	9.90 ± 0.15	9.59 ± 0.08		
$(C_3H_3NO)^+$	10.76 ± 0.18 11.89 ± 0.15	11.12 ± 0.15	10.89 ± 0.07		
$(H_2O)^+$	12.32 ± 0.25 12.61 ± 0.18			13.54 ± 0.02	12.65 ± 0.05

(reaction (2)) and the most abundant fragment cations (reactions (3–7)) formed upon electron impact ionization of gas phase BrUrd. The measured data are shown as open circles. The solid lines represent best fits of equation (1) to the experimental data. The corresponding *AE* values are also included in Figure 2. The parent cation with the mass of 322 Da ($^{79}BrUrd^+$) has a threshold energy of 9.01 ± 0.15 eV which is within the error bars the same as the ionization energy of normal uridine measured recently with the same instrument, i.e., 9.05 ± 0.15 eV [36]. In contrast, a recently calculated *AE* value for the parent cation of 5-BrUra (5-$BrUra^+$) of 9.07 eV [25] is much lower than the experimental *AE* of the parent cation of uracil (Ura^+) which was determined to be 9.59 ± 0.15 eV [37] (calculated value: 9.47 eV [25]).

From the masses of the observed fragment cations and taking into account the molecular structure of BrUrd we tentatively assign the fragment cations to certain preferential dissociation pathways. Thus we conclude that all fragment cations with the exception of H_2O^+ originate from the halo-nucleobase moiety. However, the second tendency observed from such an assignment is that hydrogen is apparently rather efficiently transferred from the sugar moiety. Such hydrogen transfer is also observed in chemical ionization mass spectra of nucleosides [36]. For example the fragment cation at the mass of 190 Da ($^{79}BrUra^+$) requires one hydrogen transfer from the sugar prior to their separation. The cation has exactly the same threshold energy as the parent cation. At a mass of 112 Da we observe the parent cation of uracil which requires the transfer of two hydrogen atoms from the sugar. The ion efficiency curve at this mass shows clearly two onsets, one at 9.15 eV and a second at 10.05 eV. As already mentioned the appearance energy of the gas phase uracil cation is about 9.6 eV [37] which is between the presently determined onsets of the fragment cation Ura^+ from 5BrUrd. In the case of normal uridine the fragment ion with a mass of 112 Da has a single threshold energy of 9.9 eV [36]. The two fragments with mass 69 Da and 147 Da have essentially the same structure, i.e., $C_3H_2NOX^+$ with X = H for the light ion and X = ^{79}Br for the heavier fragment, respectively. Both cations exhibit two thresholds that are separated by about 1.15 eV. In addition, the contribution to the ion yield from the low energy process is significantly lower in both cases. A case similar to the formation of $C_3H_2NOX^+$/BrUrd was reported for 6-chlorouracil [19] where the fragment cations $(C_3H_2NO)^+$ and $(C_3H_2NOCl)^+$ were observed upon electron impact ionization of 6-chlorouracil. The difference in the *AE* of the latter two cations was ∼0.75 eV which is close to the presently observed difference (∼0.7 eV) in the *AE* of both cations. The cation $(C_3H_3NO)^+$ was also the most abundant fragment cation formed upon electron impact ionization of the isolated nucleobase uracil with an *AE* value of 10.89 ± 0.07 eV [37] which is slightly above the presently determined *AE* $(C_3H_3NO)^+$/BrUrd.

As the lightest fragment ion of 5BrUrd we analyze H_2O^+ with the first threshold energy of 12.32 eV. Water is known to be efficiently formed as a fragment from sugar molecules like deoxyribose. However, in the case of deoxyribose we determined recently the threshold energy for H_2O^+ to be 13.5 eV which is just 0.9 eV higher than the ionization energy of single isolated water [29]. In the present case the second onset is very close to the *AE* of H_2O^+ from water. Thus it is not possible to exclude that water is present in the effusive beam, most likely as moisture in the sample. Table 1 summarizes the appearance energies of common product ions formed upon electron impact ionization of gas phase 5BrUrd, uridine, uracil, deoxyribose and water. In all the cases where a Br atom is replacing H in a fragment ion the appearance energy of the halogenated molecule is lower. Additionally, the (first) onset of the ion efficiency curve for corresponding ions originating from 5BrUrd is consistently lower compared to normal uridine.

3.2 Negative ions

Figures 3 and 4 show the relative attachment cross-sections of the most abundant anions of 5BrUrd that are measured with the present apparatus. For many fragments the presence of the two bromine isotopes, i.e. ^{79}Br and ^{81}Br that have roughly the same natural abundance, makes the identification very easy. For several cases a short section of a mass spectrum is shown to demonstrate the identification of the fragment anions (see Fig. 5). The limited mass range of the quadrupole mass spectrometer utilized in the earlier study on negative ion formation upon low-energy electron attachment to 5BrUrd [28] did not

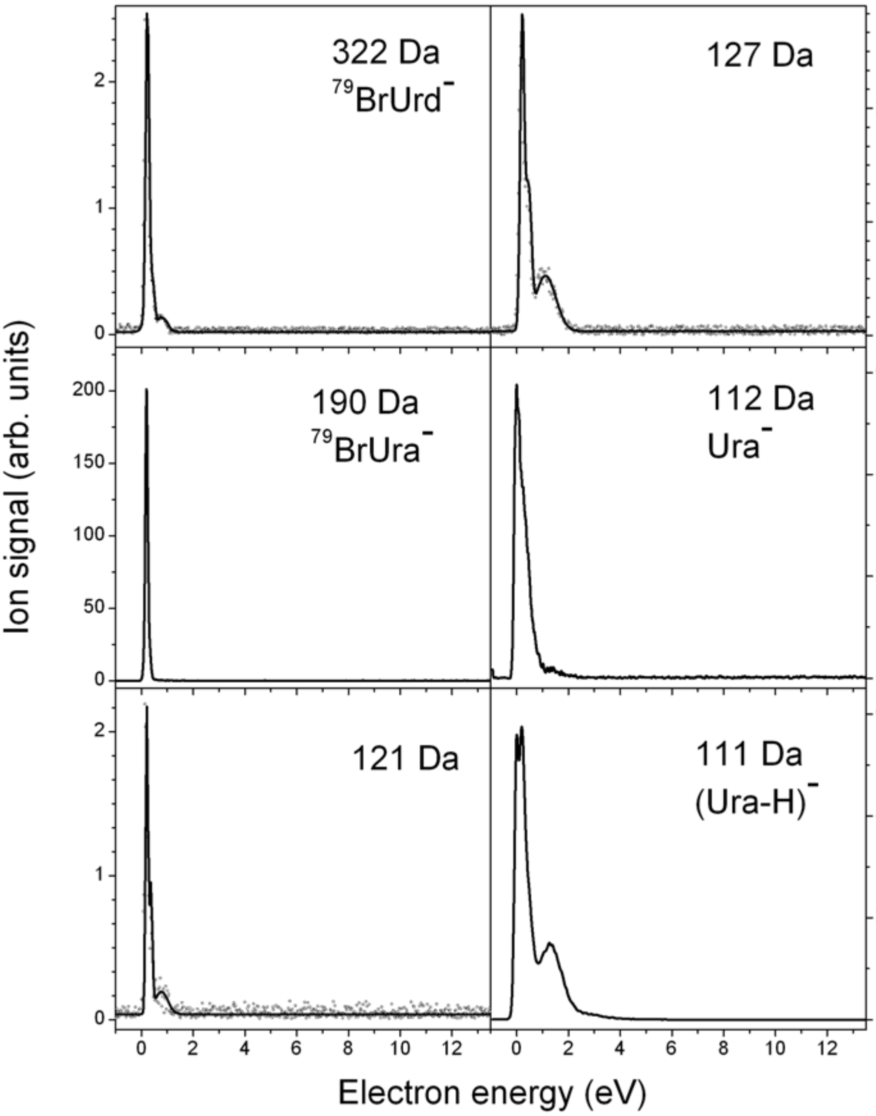

Fig. 3. Anion yields (for masses from 111 Da to 322 Da) as a function of the electron energy formed via electron attachment to 5BrUrd. The ion intensities are given in arbitrary units but proportional to the count rate so that the yields can be compared directly. For the masses 322 Da, 127 Da and 121 Da the data are shown as open symbols and the line represents a smoothening of these data. In all other cases the data are shown directly as line graphs.

allow the identification of the parent anion or the dehydrogenated fragment anion. In contrast, the presently used quadrupole mass spectrometer has a mass range of 2048 Da and thus enables the experimental observation of these ions with masses of 324 and 323 Da, respectively. Indeed the present experiments confirm the existence of a parent anion. These ions are at least stable within the time window of the present experimental set-up (the flight time of the parent anion from the collision chamber to the channeltron is about 400 μs). From the presence of the parent anion it is also possible to conclude a positive electron affinity of the 5BrUrd molecule. Such a positive electron affinity was also observed for 5BrUra (and other halouracils) whereas the electron affinity for the isolated sugar moiety is not known yet (although for isolated deoxyribose no parent anion can be observed [16]). We have analyzed the negative-ion mass spectrum at about zero eV in the mass range close to the parent anion. By fitting calculated isotopic patterns of the parent anion BrUrd$^-$ and the fragment anion (BrUrd-H)$^-$ to the measured mass spectrum the ratio of 7:3 is obtained for the parent to fragment anion yield (see Fig. 5).

In the present study no cross-section values are estimated for the most abundant anions formed via DEA to 5BrUrd. However, Abdoul-Carime et al. [28] reported the highest absolute partial cross-section for Br$^-$/5BrUrd to be of the order of 10^{-18} m^2, which has the same magnitude like Br$^-$/5BrUra. We observe in agreement with [28] the formation of Br$^-$ as the most abundant anion formed via DEA to 5BrUrd. This high relative abundance of the Br$^-$ anion when going from 5BrUra to the halogenated nucleoside is probably preserved due the

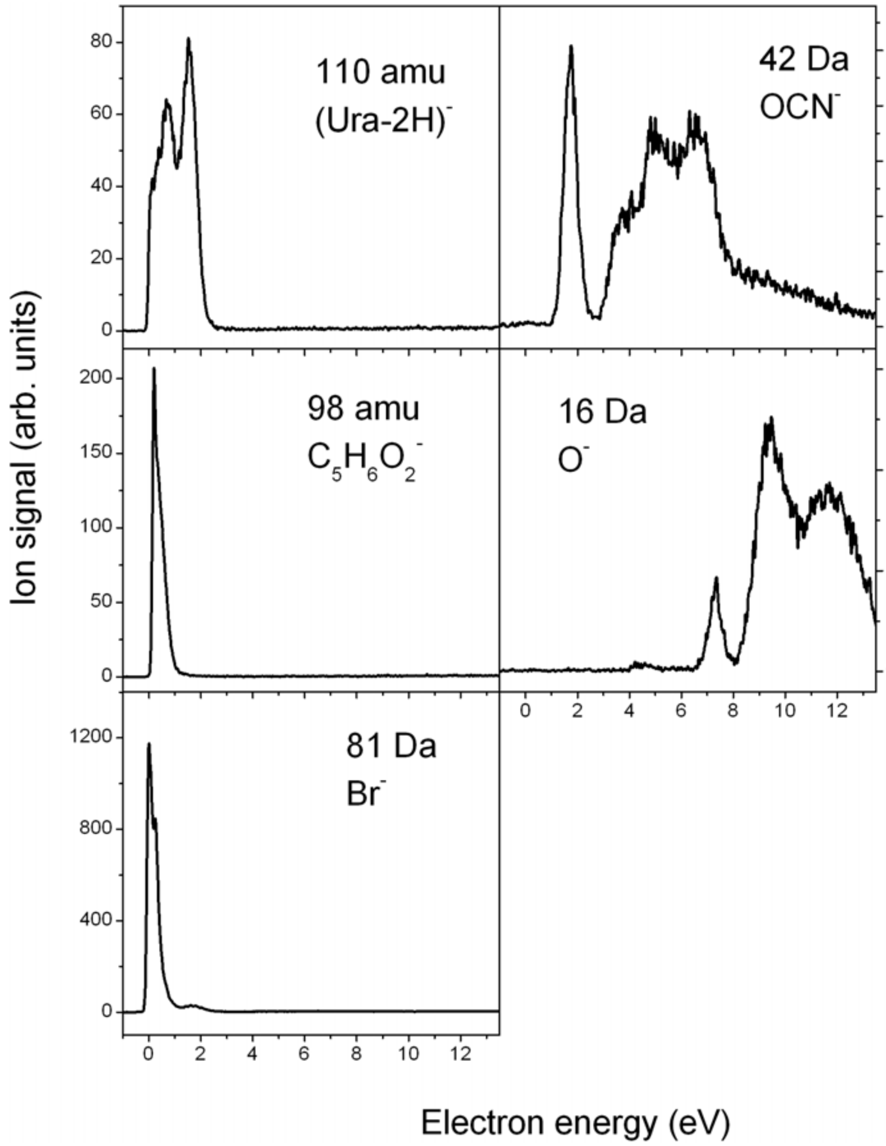

Fig. 4. Anion yields (for masses from 16 Da to 110 Da) as a function of the electron energy formed via DEA to 5BrUrd. The ion intensities are given in arbitrary units but proportional to the count rate so that the yields can be compared directly.

high electron affinity of the bromine atom (3.36 eV) [38]. The complementary reaction channel with the formation of (5BrUrd–Br)$^-$ with the neutral Br radical cannot be observed in the present experiment. The absence of (5BrUrd–Br)$^-$ may be explained by the weak glycosidic 1N–C bond between the sugar moiety and the base which favors a breakage of this bond prior to the loss of the halogen atom. In 5-BrUra the cleavage of the 5C–Br bond, forming the anion (Ura–H)$^-$, was as probable as the Br$^-$ formation upon low electron attachment. This result has also consequences for the detection of the anion at mass 190 Da, i.e. the anion (^{79}BrUra)$^-$. It can be excluded that BrUra is present in considerable amounts as an impurity of the BrUrd sample. Surprisingly, the formation of (^{79}BrUra)$^-$ via DEA to 5BrUrd requires the transfer of a hydrogen atom from the sugar moiety, which has also been observed for the cation formation.

The anion at mass 110 Da can be assigned to the (Ura-2H)$^-$/5BrUrd anion formed via dissociation of the N-glycosidic bond and the C–Br bond. The anions at masses 111 Da and 112 Da may follow the same dissociation pathway but in addition hydrogen transfer(s) from the sugar moiety is (are) required to form these anions. Moreover, we observe a fragment anion at mass 98 Da. This anion may be formed by the loss of one water molecule and one OH radical from the sugar moiety leading to the anion ($C_5H_6O_2$)$^-$. The negative ion at mass 98 Da was also the most abundant anion formed in DEA to isolated deoxyribose [16] formed by the attachment of ~0 eV electrons. Thus we may conclude that this anion is formed from the sugar moiety. The low abundant anions appearing at masses 127 Da and 121 Da cannot be assigned tentatively to some certain dissociation pathway.

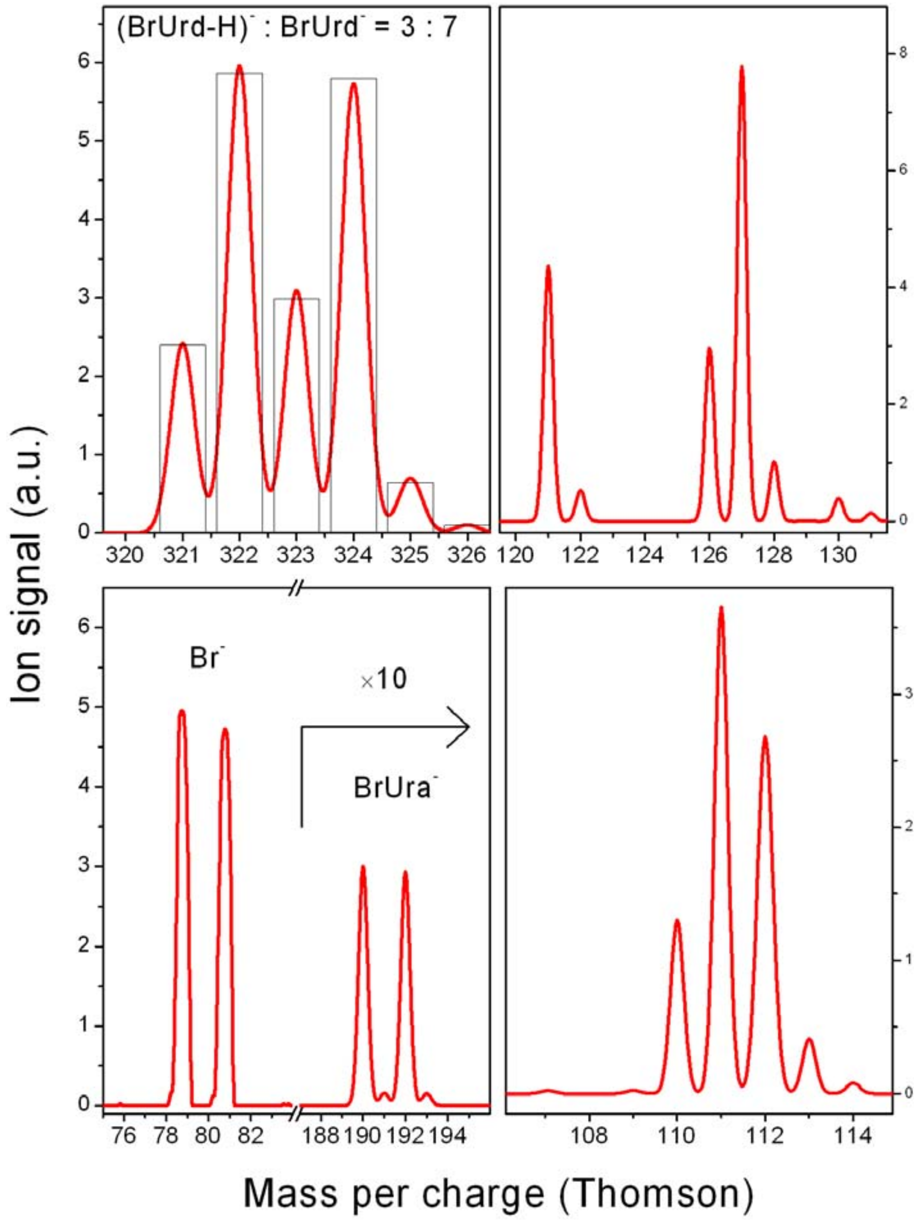

Fig. 5. Negative ion mass spectra of several product anions of 5BrUrd that are formed at the electron energy of about zero eV. In the case of the parent anion the histogram represents the best fit of calculated isotopic patterns of $BrUrd^-$ and $(BrUrd–H)^-$ to the measurement.

The negative mass spectrum at 0 eV clearly shows the absence of the bromine atom in these anions.

Nearly all observed anions are formed in a narrow zero eV resonance or in a rather broad structure from about 0 to 2 eV. Only the anions at mass 42 Da and 16 Da, which can be identified as OCN^- and O^-, respectively, are formed at higher electron energies. O^- formation was not observed for 5BrUra but this anion was observed in DEA to the sugar deoxyribose [16]. The peak positions of the resonances for O^- between 6 and 13 eV are close to the previously reported values for O^-/H_2O [39,40] and O^-/deoxyribose [16]. However, the relative height of the three resonances differs from the earlier measurements which may also result from discrimination effects due to initial kinetic energy of the O^- fragment anions. The present anion yield of O^- shows an additional weak resonance at about 4.2 eV which was not observed in the O^- yields of the previous experiments with water and deoxyribose. Like for H_2O^+ the O^- ion yield may originate from inelastic electron interactions with BrUrd and H_2O molecules present in the sample.

4 Conclusion

The present work is an extension of previous studies on isolated halouracils and sugars investigating free electron interactions (ionization/attachment) with gas phase

5BrUrd. For the first time appearance energies for cations upon electron impact ionization of BrUrd are determined experimentally. In earlier studies the appearance energy of the parent cation from the halogenated nucleobase BrUra was found to be ∼0.4 eV lower than the appearance energy of the nucleobase uracil which suggests an increased sensitivity towards low energy electrons for the halogenated species. However, for the corresponding nucleosides the present experiment yields for 5BrUrd and Urd nearly the same appearance energy values. Thus the present studies on halogenated uridine show even more clearly that the effect of radiosensitization is predominantly the result of an increased cross-section for negative ion formation. Moreover, it is interesting to note that several of the presently studied cations reveal two onsets in the ionization efficiency curve near the threshold which has not been observed for cations from isolated chlorouracil and deoxyribose. This result indicates that different reaction pathways to several product ions are possible in the case of the large halogenated molecular complex.

The present results for negative ion formation confirm that also the nucleoside 5BrUrd (like simple halouracils) is very sensitive upon low energy dissociative electron attachment with Br^- as the dominant reaction product. This large cross-section for DEA may be also preserved in the real DNA/RNA complex which explains the increased sensitivity of cells, treated with BrUrd, to ionizing radiation.

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