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Negative ions in thymine and 5-bromouracil produced by low energy electrons

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Abstract

We have compared the negative ion production processes in thymine (T) and 5-bromouracil (BrU) after impact of low energy electrons (0–2 eV). In agreement with earlier studies we have observed in BrU a long lived parent ion BrU^- and fragment ions Br^- and Uyl^- with cross sections in the 10^{-14} cm^2 range. In contrast with other observations in thymine, the most intense ions are found to be $(T–H)^-$ fragment ions and not the parent ion T^-. For the fragment ions Br^-/BrU, Uyl^-/BrU and $(T–H)^-$/T the shape of the cross section vs. electron energy reveals a complex nature. Close to zero energy, several peaks separated by a few hundreds of meV appear in these cross sections, instead of only one peak reported in earlier works. Our observations are understood as vibrational structures due to predissociation of rather long lived anion states, possibly dipole bound states, by valence Π^* resonant states, close to zero energy.

Keywords: Electron molecule scattering; Negative ions in molecules of biological interest

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1. Introduction

Interaction of ionising radiations with biological material induces, after several cascades, the occurrence of numerous low energy secondary electrons. It has been recently demonstrated that these electrons (0–20 eV) can produce substantial damages to the biological material [1,2]. In this energy range, electron collisions with molecules are well known to be responsible of efficient dissociations, well below the positive ionisation potential, due to the dissociative attachment process. In this last process, the electron is captured by the target during a very short time, giving rise to a transitory negative ion (“resonance”). The decay of this resonance will occur either by rejection of the captured electron, generally leaving the molecule vibrationally excited, or by dissociation of the molecule, one of the fragment being a thermodynamically stable negative ion.

Studies of negative ion productions after low energy electron interaction with DNA bases have already been recently published ([3] and references therein). It shows the occurence of numerous anionic fragments or long lived parent ions. Evidence of the existence of several resonances has also been demonstrated in DNA bases and uracil in a derivated transmission experiment [4]. In a recent experiment on 5-bromouracil (BrU), Abdoul-Carime et al. [5] have also observed a

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very efficient negative ion production at low electron energy.

However, the nature of the most intense ions in thymine (T) is still the object of discussions. Huels et al. [3] have observed a T^- ion indicating a long lived parent ion. The observation of this long lived parent ion, from 0 up to 15 eV, is really unusual in molecules of this size. The occurence of a $(T–H)^-$ ion produced by dissociative attachment has also been suggested by Desfrançois et al. [6,7], besides the T^- dipole bound produced by Rydberg electron transfer, and could certainly be more likely in such a large energy range.

It is known that 5-bromouracil can act as a radiosensitiser after replacement of thymine in DNA, enhancing the damage to biological material submitted to ionising radiations [8,9]. A possible process involves the formation of the uracil radical after dissociative attachment of BrU^- anions formed by capture of thermalised electrons [10]. It would therefore be interesting to see if the situation concerning the ions produced at zero in BrU is the same as in T.

In the present work we have studied, in more detail, the negative ion production at low electron energy in these two molecules for comparison, to try to bring some new elements of answer to these questions.

2. Experimental

The device used for the present experiment is essentially an electrostatic electron spectrometer using hemispherical energy analysers in tandem. The optics and magnetic shielding have been carefully designed to allow both the electron gun and the electron analyser to go down to zero energy, preserving close to zero energy, an electron resolution of about 0.05 eV FWHM. Mass analysis of the ions is achieved with a time of flight system based on a Mac-Laren geometry. For studies of negative ions, the incident electron beam is pulsed to avoid perturbations due to electron collection on the channel plates. Thymine and bromouracil vapors are produced by heating commercial products (Merck) in a double stage oven around 150 °C, that is well below their decomposition temperature [5]. The whole electron spectrometer and the time of flight system are heated at the same temperature to reduce insulating deposits which forbid any experiment after 1 or 2 h. In these conditions runs of a few days could be performed before a full cleaning of the device.

The energy scale has been calibrated using $SF_6{}^-$ anions recorded in the same experimental conditions. The checking of the transmission of the device in the very critical 0–0.5 eV range is achieved by comparison of the shape of the cross section of $SF_5{}^-$ anion in this energy range, with the results of Chen and Chantry [11] at 150 °C.

3. Results and discussion

As mentioned in Section 1, detailed studies on negative ions production in these molecules have already been performed [3,5], and therefore we have focussed the present paper only on a few ions (the most intense) found in thymine and bromouracil at low electron energy (0–2 eV).

3.1. Bromouracil

We have revisited in BrU the fragment anions Br^- and Uyl^- produced by dissociative attachment and the long lived BrU^- parent ion produced by capture of low energy electron (Uyl^- stands for an anion originating from an uracil radical U).

The present work is in general agreement with Abdoul-Carime et al. [5]. Concerning cross sections, even if we have not performed absolute measurements, qualitative arguments lead us to confirm the exceptionally large cross section reported by these authors for Br^- ions close to zero energy, this cross section being comparable to $SF_6{}^-$. Cross sections at the same energy for BrU^- and Uyl^-, even about one order of magnitude smaller, are still very large.

The shape of the cross section vs. electron energy for BrU^- is displayed on Fig. 1. It shows a peak located at 0.02 ± 0.02 eV followed by a smaller peak around 0.6 eV in good agreement with ref. [5]. The shift from zero of the main peak, being within the

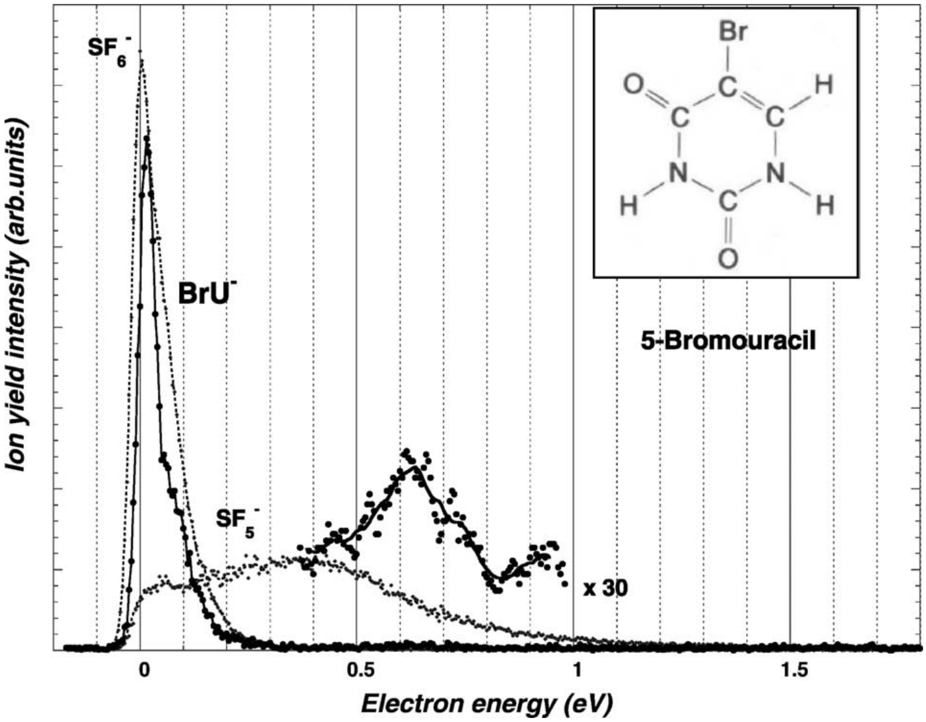

Fig. 1. Ion yield for BrU$^-$/BrU vs. incident electron energy. The peak is observed at 0.02 eV followed by a shoulder at 0.05 eV (values ± 0.02 eV) and a smaller wide bump around 0.6 eV. SF_6^- and SF_5^- yields recorded in the same experimental conditions are used respectively for energy scale calibration and to check the transmission behaviour of the device between 0 and 1 eV.

experimental uncertainties, could possibly not be meaningful. However, the shoulder observed around 0.05 eV, appearing in all the recordings is believed to be significant.

In contrast with ref. [5], we have not found any particular feature at 1.3 eV. However, it should be noted that this feature, certainly very weak, is not really obvious on the recording presented by these authors in their Fig. 1.

For Br$^-$ and Uyl$^-$ anions (Figs. 2 and 3), if our results present some general analogy with the results of Abdoul-Carime et al. [5], significant differences are observed close to zero energy. Concerning the analogy, we have also found two different processes, both for Br$^-$ and Uyl$^-$ ions, one close to 0 eV and the other one located around 1.45 eV, slightly weaker for Uyl$^-$ and clearly weaker for Br$^-$ (factor 20) than the main peak. However, close to zero, instead of one single peak, we have observed three peaks ranging from 0 to about 0.3 eV, located at 0.02, 0.09 and 0.28 eV (all values ± 0.02 eV).

The process around 1.45 eV is understood as dissociative attachment through a Π^* resonance, similar to the one reported at 1.58 eV by Aflatooni et al. [4] for uracil. The potential energy surface of the anion state reached around 1.5 eV has dissociation exit valleys leading both to Br$^-$ and Uyl$^-$ fragments with different cross sections.

The processes closer to zero are certainly more puzzling. Even if the possibility of three resonant states cannot totally be ruled out, it seems however unlikely in such a small energy range. The close spacings between the peaks observed is rather evocative of a vibrational structure. It is also remarkable that the three peaks observed in both Br$^-$ and Uyl$^-$ are located at the same energies. This suggest a structure due either

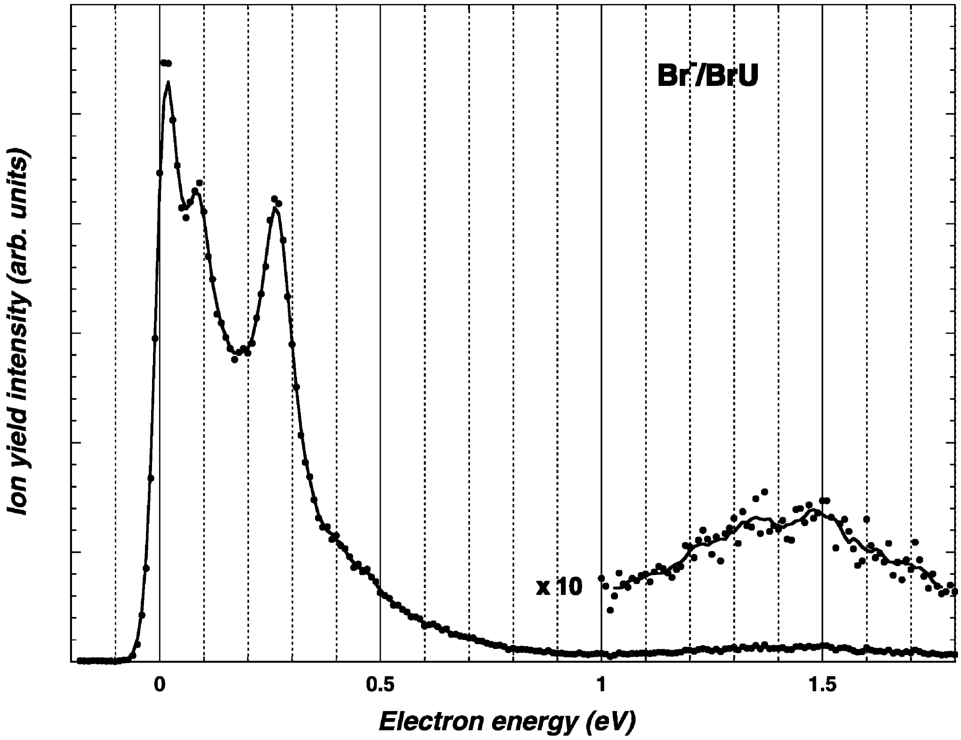

Fig. 2. Ion yield vs. incident electron energy for Br^-/BrU. The peaks are located at 0.02, 0.09 and 0.28 eV (all values ± 0.02 eV) followed by a weak bump around 1.45 eV. The energy scale is calibrated as in Fig. 1.

to vibrational motions of the neutral ground state, or to vibrations of a common negative ion state.

Structures in negative ion cross sections originating from the ground neutral state have already been observed at low energy in dissociative attachment (DA) in hydrogen halides [12–14]. They reveal the competition between resonant vibrational excitation and DA after the formation of the transitory negative ion. If we consider, for example, the case of Cl^-/HCl [13], at threshold around 0.75 eV, the resonant state $(HCl^-)^*$ can decay either by DA giving Cl^- ions or by rejection of the electron, leaving the HCl molecule vibrationally excited. At 0.75 eV the only vibrational exit channels opened in competition with DA are $v = 0$, 1 or 2. When the incident energy increases, new vibrational exit channels open up, reducing the DA cross section. Opening of these vibrational levels of the neutral HCl appear therefore as a series of decreasing steps in the Cl^- cross section. Obviously, we are not dealing in the present case with decreasing steps but rather with peaks in the cross section. This suggest that the structure observed is related to the vibration of a common negative ion state. This state should have a lifetime long enough to allow some vibration. Several observations are in favour of a long lived transitory anion state close to zero: (i) the presence of the BrU^- parent ion in our measurements indicates a lifetime at zero longer than 1 μs; (ii) the appearance of a structure in the derivated transmission spectrum in uracil is interpreted as the evidence of a rather long lived resonance [4]; and (iii) the existence of a dipole bound anion state demonstrated in closely related molecules, thymine and uracil [5,6]. In uracil, Desfrançois et al. [7] have proved experimentally, that a valence state anion is also present close to the dipole bound state. Using DFT calculations, they found it having a positive

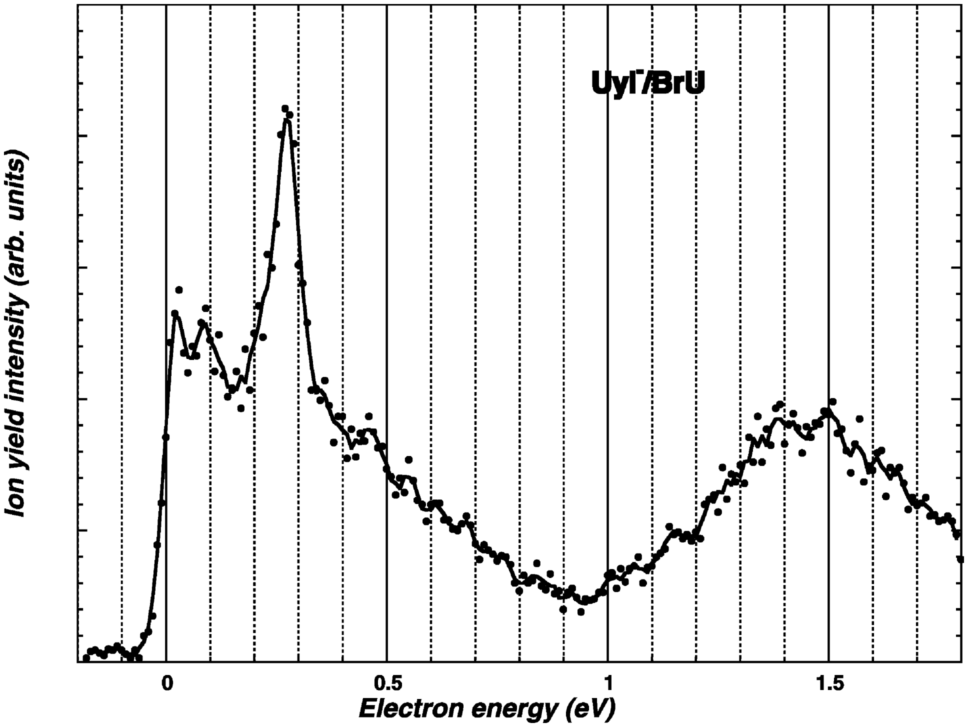

Fig. 3. Ion yield vs. incident electron energy for Uyl$^-$/BrU. Peaks close to zero are at the same positions as for Br$^-$ (see Fig. 2), a wider process is observed at 1.45 eV. The energy scale is calibrated as in Fig. 1.

electron affinity (0.07 eV), and located at an equilibrium distance slightly larger than the dipole bound state. Assuming a similar situation in BrU, we therefore propose that the dipole bound state is predissociated close to zero by a Π^* resonance (a valence anion state), leading both to Br$^-$ or to Uyl$^-$ ions. As the incident energy is increased above zero, vibrational levels are observable, but with increasing energy the lifetime of the anion is strongly reduced and only a few levels can be observed.

Note that similar predissociation processes of rather long lived anion states (Feshbach resonances in that cases), have already been reported in F$^-$/HF around 12 eV [15] and in H$^-$/H$_2$ [16].

3.2. Thymine

In thymine numerous negative ions have been reported in the 0–20 eV energy range by Huels et al. [3]. The most intense ion is attributed to the parent ion T$^-$. The cross section is reported to peak at 0.18 eV and extends above 15 eV. The authors interpret this results as an evidence of the direct capture by T of an electron, leading to a very long lived anion (>10 μs). If long lived anions are very common in polyatomic molecules, it is really unusual to produce them over such a broad energy range. The only observation of such a behaviour has been reported in fullerenes, which are definitely larger molecules and very peculiar systems (see for example [17–19] and references therein). In our observations, the most intense peak in T does not appear to be due to T$^-$ ions but to thymine ions having lost one hydrogen atom (T–H)$^-$, the process giving rise to these ions being the common DA process.

The shape of the cross section vs. incident energy for (T–H)$^-$ recorded in the present study is displayed in Fig. 4. It looks quite different from the results

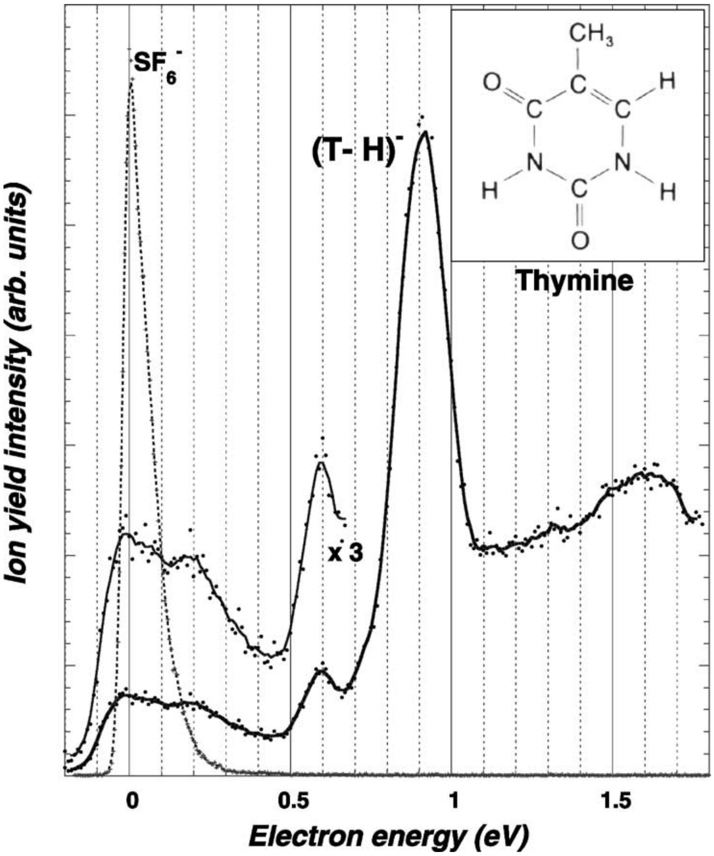

Fig. 4. Ion yield vs. incident electron energy for $(T–H)^-/T$. Peaks are located at 0.00, 0.20, 0.60, 0.75 and 0.90 eV (all values ± 0.02 eV) followed by a wider process around 1.6 eV. The energy scale is calibrated as in Fig. 1.

of Huels et al. [3]. Instead of a wide single peak at 0.18 eV, in the energy range 0–3 eV, the cross section in our observations appears to peak at 0.90 eV and other peaks are observed at 0.00, 0.20, 0.60 and 0.75 eV (shoulder) (all values ± 0.02 eV), followed by a large bump around 1.6 eV. The shape of this cross section appears quite unusual but was repeatably observed. Even if the relative intensities of the peaks are quite different, this cross section, below 1 eV has some similarities with the Br^- and Uyl^- ions in BrU. Like in this case, the interpretation could involve a predissociation process in the region 0–0.90 eV. However, it may appear surprising that the long lived T^- ion allowing vibrational motion up to 0.90 eV be not observed like the BrU^- parent anion. It can simply means that the lifetime of this T^- ion is definitely shorter than 1 μs, but long enough to allow vibrational modes ($t > 10^{-13}$ s). The wider peak around 1.6 eV is similar to the 1.45 eV process observed for the fragments in BrU. It is due to DA via the second Π^* resonance observed in the transmission experiment at 1.71 eV [4].

4. Conclusion

Formation processes for negative ions in thymine and bromouracil in the energy region 0–2 eV appear more complex than was presented in earlier studies. A long lived parent anion is present in BrU but not in T where the most intense ion was found to be $(T–H)^-$

and not T^-. Several vibrational features are found in the cross section vs. energy of the fragment ions Br^-/BrU, Uyl^-/BrU and $(T–H)^-$/T. They are understood as due to a predissociation process of an anion state, possibly the dipole bound state, by a valence anion Π^* state. The predissociated state should have a lifetime long enough to allow some vibrational motion.

After the previous work by Abdoul-Carime et al. [5], we confirm the exceptionally large cross sections for negative ions production close to 0 eV in bromouracil, particularly for Br^- (in the 10^{-14} cm^2 range) but also for BrU^- and Uyl^- ions. For comparison $(T–H)^-$ ions cross section in thymine appears to be at least one order of magnitude smaller. The DA process giving Br^- ions gives also $(Uyl)^\bullet$ radicals with the same cross section. If the zero energy electron capture process in the aqueous biological medium is comparable, the existence of an intense process generating large amounts of radicals, causing damages to DNA, can be an element of understanding the radiosensitiser role of BrU.

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References

[1] B. Boudaïffa, P. Cloutier, D. Hunting, M.A. Huels, L. Sanche, Science 287 (2000) 1658.
[2] H. Abdoul-Carime, P.C. Dugal, L. Sanche, Radiat. Res. 153 (2000) 23.
[3] M.A. Huels, I. Hahndorf, E. Illenberger, L. Sanche, J. Chem. Phys. 108 (1998) 1309.
[4] K. Aflatooni, G.A. Gallup, P.D. Burrow, J. Phys. Chem. A 102 (1998) 6205.
[5] H. Abdoul-Carime, M.A. Huels, F. Bruning, E. Illenberger, L. Sanche, J. Chem. Phys. 113 (2000) 2517.
[6] C. Desfrançois, H. Abdoul-Carime, J.P. Schermann, J. Chem. Phys. 104 (1996) 7792.
[7] C. Desfrançois, V. Periquet, Y. Bouteiller, J.P. Schermann, J. Phys. Chem. A 102 (1998) 1274.
[8] S. Zamenhof, R. De Giovanni, S. Greer, Nature 181 (1958) 827.
[9] L.L. Ling, J.F. Ward, Radiat. Res. 121 (1990) 76.
[10] M. Katousian-Safadi, M. Charlier, J. Chim. Phys. 94 (1997) 326.
[11] C.L. Chen, P.J. Chantry, J. Chem. Phys. 71 (1979) 3897.
[12] J.P. Ziesel, I. Nenner, G.J. Schulz, J. Chem. Phys. 63 (1975) 1943.
[13] R. Abouaf, D. Teillet-Billy, J. Phys. B Atom. Mol. Phys. 10 (1977) 2261.
[14] R. Abouaf, D. Teillet-Billy, Chem. Phys. Lett. 73 (1980) 106.
[15] R. Abouaf, D. Teillet-Billy, J. Phys. B Atom. Mol. Phys. 13 (1980) L275.
[16] M. Tronc, F. Fiquet-Fayard, C. Schermann, R.I. Hall, J. Phys. B Atom. Mol. Phys. 10 (1977) 305.
[17] M. Lezius, P. Scheier, T.D. Märk, Chem. Phys. Lett. 203 (1993) 232.
[18] T. Jaffke, E. Illenberger, M. Lezius, S. Matejcik, D. Smith, T.D. Märk, Chem. Phys. Lett. 226 (1994) 213.
[19] O. Elhamidi, J. Pommier, R. Abouaf, J. Phys. B Atom. Mol. Phys. 30 (1997) 4633.