Eur. Phys. J. D **35**, 405–410 (2005)
DOI: 10.1140/epjd/e2005-00239-9

The European Physical Journal D

Structures in dissociative electron attachment cross-sections in thymine, uracil and halouracils

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Received 22 April 2005

Abstract. The low energy parts (0–3 eV) of the dissociative electron attachment (DEA) cross-sections in uracil, thymine, and the halouracils 5-BrU, 5-ClU, 6-ClU, 5-FU, have been revisited with an improved energy resolution, focussing onto the puzzling structures observed on most cross-sections of the various anions fragments versus electron energy. The elastic electron scattering cross-sections near zero energy have also been recorded. In most cases they present a few features (cusps) related to the low energy peaks found in DEA cross-sections. Substantial differences are found in the detailed spectra of the fragments produced in 5-ClU and 6-ClU. Several interpretations already proposed to explain the previous observations, in terms of different thresholds and/or contributions of vibrational Feshbach resonances, and their limits, are discussed in the light of our new results. We expect that our more detailed results will stimulate theoretical work for a better understanding of the features observed.

PACS. 34.80.Ht Dissociation and dissociative attachment by electron impact

1 Introduction

The collision process involving a low energy electron (below the thresholds for positive ionisation and electronic excitations) and a molecule, is dominated by the formation of "resonances", i.e. temporary very short lived anion states produced by the capture of the incident electron by the target, occurring at selected energies. The decay of these resonances occurs via two competing processes: (i) the rejection of the extra electron leading to the initial molecule (resonant elastic scattering), or to the molecule vibrationally excited (resonant vibrational excitation), (ii) dissociative electron attachment (DEA) i.e. dissociation of the transitory anion giving a stable negative ion and one or several fragments. This last process may have in some cases very large cross-sections ($>10^{-16}$ cm^2) and is well-known to efficiently break molecular bonds well below the thermodynamical value of the involved bond energy, even at zero energy, if the electron affinity of the fragment is large enough.

After the demonstration that low energy electrons can efficiently damage DNA material [1] several papers have appeared in the last few years dealing with the production of negative ions in DNA bases, uracil and halouracils ([2–9] and references therein). In the halouracils enormous cross-sections ($>10^{-15}$ cm^2) were found for some fragments, generally below 3 eV. Detailed studies for uracil [5], 5-ClU and 6-ClU [6,7] thymine [8] and 5-BrU [3,8] have shown surprising sharp structures in the cross-sections versus electron energy for most fragments. Even if several interpretations of these structures have been proposed, a lot of questions concerning their origin are still open. In the present paper we have revisited with an improved energy resolution the DEA cross-sections of the major fragments produced below 3 eV in uracil, and several halouracils (5-BrU, 5-ClU, 6-ClU, 5-FU). The elastic electron scattering cross-sections near zero energy has also been recorded. For the halouracils they present a few features related to the low energy peaks found in DEA cross-sections. Cross-sections for $(\text{T–H})^-$ fragments in both deuterated thymine (thymine methyl d3 d6, i.e. deuterium on the methyl group and on the position 6, see Sect. 3) and regular thymine are also presented. Our data confirm, in a more convincing way, the recent results of Abdoul-Carime et al. [10] and their conclusions.

Several interpretations already proposed to explain the previous observations, in terms of different thresholds and/or contributions of vibrational Feshbach resonances, and their limits, are discussed in the light of our new results.

2 Experimental set-up

The device used for the present experiment is an electrostatic electron spectrometer using two hemispherical energy analysers in tandem both in the gun and the analyser sections. The electron optics and magnetic shielding have

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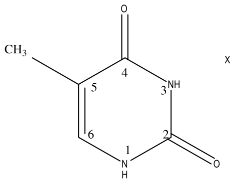
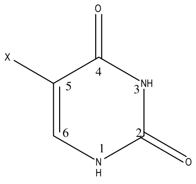
been carefully designed to allow both the electron gun and the electron analyser to go down to zero energy, preserving close to zero energy, an electron energy resolution of about 0.040 eV FWHM. Above 1 eV, the best resolution is about 0.025 eV FWHM. In the present experiments electron currents used were in the range 0.5–5 nA with a resolution of about 0.025–0.06 eV. Calibration of the energy scale is achieved by using the SF_6^- signal at zero energy, SF_6 being removed during the measurements, after energy scale calibration. Mass analysis of both positive (to check the neutral beam composition) and negative ions is achieved with a time of flight system based on a McLaren-Wiley geometry, the ions being collected onto microchannel plates. An effusive beam of molecules is produced by vaporizing commercial products (Merck) in a double stage tantalum oven, using a needle on top to allow a better definition of the collision center. After one day of outgassing, the beam is obtained around 150–180 °C. The whole electron spectrometer and the time of flight system are heated at about the same temperature to reduce insulating deposits which forbid any experiment after one or two hours. In these conditions runs of a few days could be performed before a full cleaning of the device.

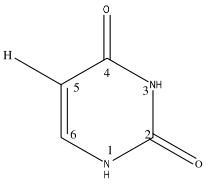
3 Results and discussion



Thymine



5-halouracil



Uracil

3.1 Uracil

In the case of uracil, several peaks have been found between 0.7 and 3 eV in the cross-section of the (U–H)$^-$ ion obtained after an H loss [5, 11a]. The first interpretation by these authors on the basis of quantum chemical calculations was to attribute these peaks to different (U–H)$^-$ isomers as the H ablation can occur from 4 sites (positions 1,3,5,6). Taking into account the excellent precision expected for the calculations (0.1 eV), the agreement for the first 2 peaks was acceptable but rather poor for the other processes. Other experiments carried out on a partially deuterated thymine, (deuterium on the methyl group and on the position 6) by Abdoul-Carime et al. [10] showed a spectrum of (T–H)$^-$ quite resembling the (T–H)$^-$ spectrum of the non deuterated molecule. They concluded that the H loss can only occur from the N1 and N3 sites. In fact if the 2 spectra presented great similarity, they were not identical. We have revisited this problem and our results (Fig. 1) exhibit 2 really identical spectra, presenting even the same small structures. The similarity between the 2 spectra can lead one to question if we were really dealing with deuterated thymine. This was obviously checked by the m/e of the observed fragment. We have not observed any peak corresponding to the loss of a D atom. Our observation totally confirms, in a more convincing way, the conclusions of these authors: the H ablation occurs exclusively from the N sites. The assignment of the peaks was then reduced to 2 sites (around 0.7 eV and 1 eV). Our results show that another small peak is clearly observed in between at 0.8 eV (this peak was also suspected in uracil, although not clearly observed). The 3 separated bumps at about 1.2 eV, 1.4 eV and 1.7 eV are however not clearly explained, even if the contribution of a π^* resonance has been evocated.

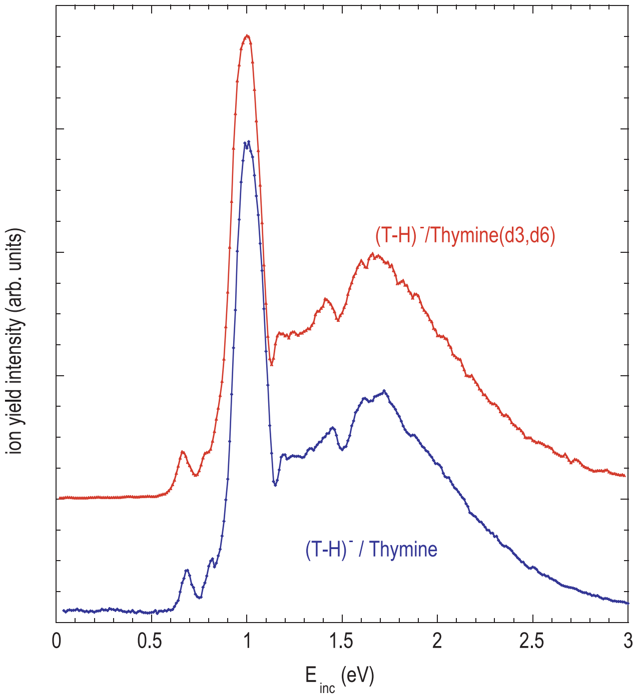


Fig. 1. Ion yield versus incident electron energy of (T–H)$^-$ fragments originating from either regular thymine ($m/e = 125$) and partially deuterated thymine (methyl d3, d6, $m/e = 129$), i.e. 3 D atoms on the methyl group and one D atom on position 6, see Sect. 3). The 2 curves are really identical demonstrating that H ablation occurs only from the N sites of the molecules.

A totally different interpretation has been proposed in a recent paper by Scheer et al. [12], partly based on the contribution of vibrational Feshbach resonances. Assuming an H loss originating mainly from the N1 site, and considering the dissociation process as a diatomic like process along the N1-H coordinate, they developed convincing arguments involving vibrational levels of a dipole bound state quite "mimic" of the neutral state and previously observed to lie about 90 meV [13, 14] below the ground neutral state. The DEA peaks at around 0.6 eV and 1 eV are attributed to the vibrational Feshbach resonances $v = 2$ and $v = 3$ respectively. However the non appearance of

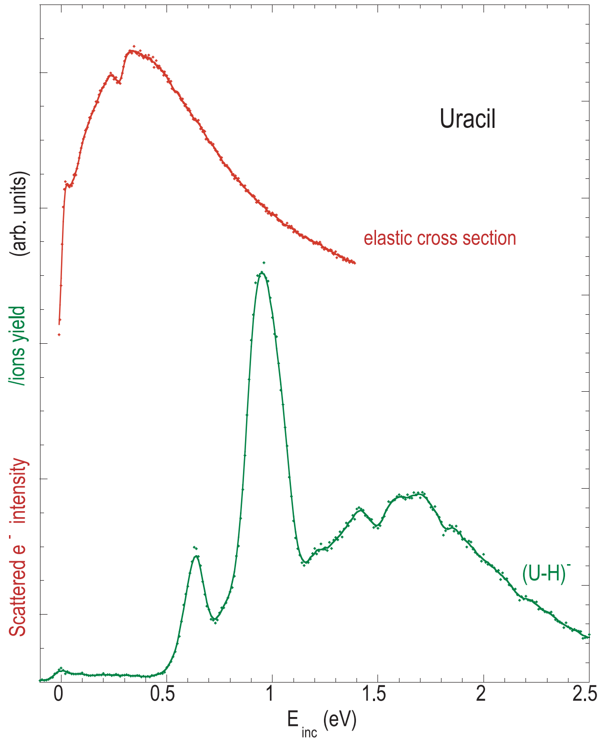


Fig. 2. Ion yield of (U–H)$^-$ fragments from uracil, and elastic scattering cross-section at 90° versus incident electron energy. A cusp appears at 0.26 eV also observed in ETS [12]. No structure is observed in the elastic cross-section corresponding to the onset of the major peaks at 0.64 eV and 0.95 eV.

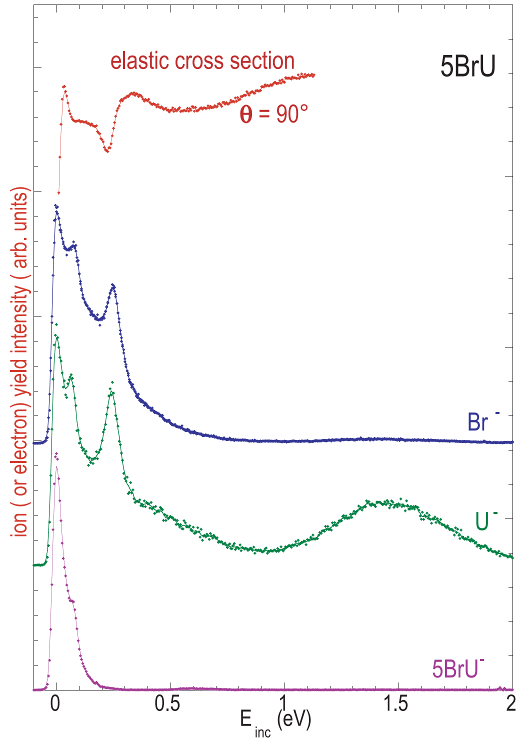


Fig. 3. Ion yield of fragments and parent anion from 5-BrU, and elastic scattering cross-section at 90° versus incident electron energy. U$^-$ holds for (Uyl)$^-$ obtained after the Br loss in 5-BrU. Note the similar energy position of the structures observed on the different curves.

these structures (although very faint for $v = 2$) in their spectrum of Electron Transmission Spectroscopy, generally extremely sensitive technique for these features, was questionable. The $v = 3$ level, which gives rise to the most important peak in the DEA spectrum, with an appreciable cross-section of 3×10^{-16} cm^2 [11a] should be observed in the derivative of the total transmitted current. The authors suggested a possible existence of a "…window-like structure in the elastic cross-section cancelling the DEA contribution…". Our measurements of the elastic cross-section vs. electron energy reported in Figure 2 does not show any structure around 1 eV. The only cusp appearing is at 0.26 eV, as also observed in the ETS spectrum of Scheer et al. It should be mentioned that the figure given for the (U–H)$^-$ cross-section is only indicative and can possibly be strongly overestimated by as much as one order of magnitude [11b]. However, the ETS is usually sensitive to features of cross-sections of a several 10^{-17} cm^2, and Scheer et al. were able to detect in their spectrum a feature corresponding to a structure in the (U–H)$^-$ cross-section at 0.69 eV weaker than the major peak at 1 eV.

For thymine (Fig. 1), the situation of the (T–H)$^-$ anion is very similar to (U–H)$^-$. Another small peak appearing at 0.8 eV (which was possibly suspected in (U–H)$^-$), is also not explained by the proposed mechanism.

Another point, also interesting to mention, concerns the DEA observations recently published [15] in thymidine (thymine linked to a desoxyribose cycle by the N1 site). The most abundant ion observed is again the (T–H)$^-$ anion, with a variation vs. energy strongly resembling the spectrum of the (T–H)$^-$ ion in pure thymine. A peak around 1 eV is also observed, even if in this case there is no H atom present in the N1 site. Despite the various analysis proposed, it seems that a totally convincing explanation of the observed structures in uracil and thymine is still to be found.

3.2 Halouracils

The results for the major anions fragments observed below 3 eV in 5-BrU, 5-ClU, 5-FU, and 6-ClU are displayed in Figures 3 to 6. The elastic cross-sections recorded in the same energy region are also presented in the same figures. Figure 7 shows a comparison between the anions (ClU–H)$^-$ produced in 5-ClU and 6-ClU. We have already published earlier the results for 5-BrU [8]; slightly better resolved spectra are presented here for comparison with the other halouracils.

Our results for the XU, although in general agreement with the results of Abdoul-Carime [9], cannot be really compared as the rather low energy resolution used by these authors does not allow a detailed comparison. For 5-ClU and 6-ClU better resolved results have been published by Denifl et al. [6,7]. Our results for 5-ClU present

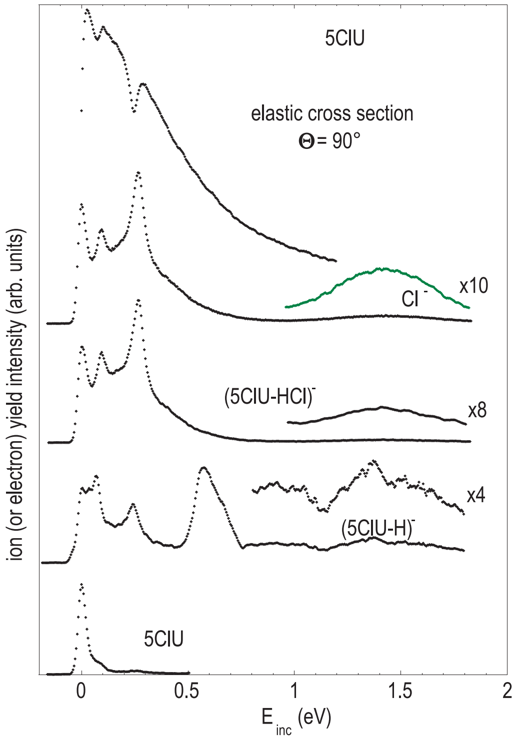


Fig. 4. Ion yield of anion fragments and parent from 5-ClU, and elastic scattering cross-section at 90° versus incident electron energy. Note the similar energy position of the structures observed on the different curves below 0.5 eV.

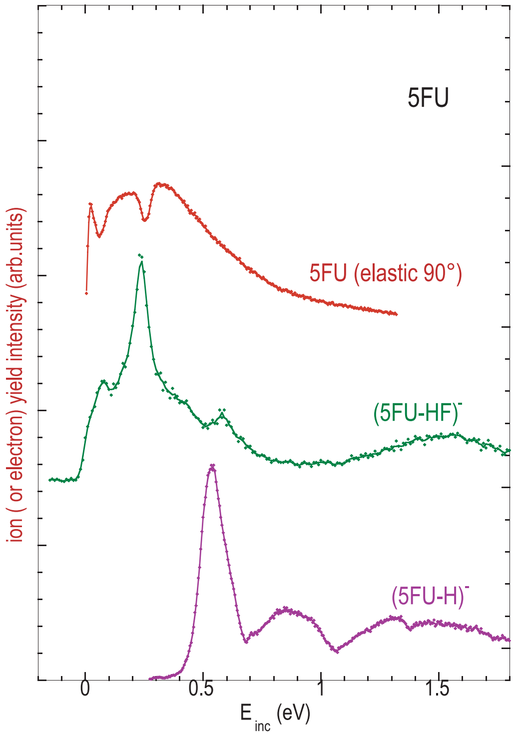


Fig. 5. Ion yield of anion fragments and parent from 5-FU, and elastic scattering cross-section at 90° versus incident electron energy. The cusps observed in the elastic cross-section correspond only to structures in (5FU–HF)$^-$. Contrary to 5 and 6ClU no structures below 0.5 eV appear in (5FU–H)$^-$.

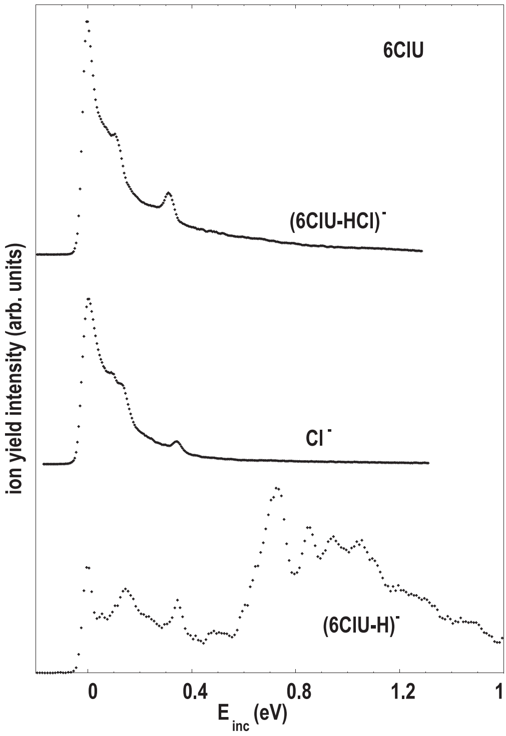


Fig. 6. Ion yield of anion fragments and parent from 6-ClU, versus incident electron energy. Note the similar energy position of the structures observed on the different curves below 0.5 eV. A developed vibrational structure (spacing about 0.110 eV) appears above 0.7 eV in (6ClU–H)$^-$, not observed in (5ClU–H)$^-$.

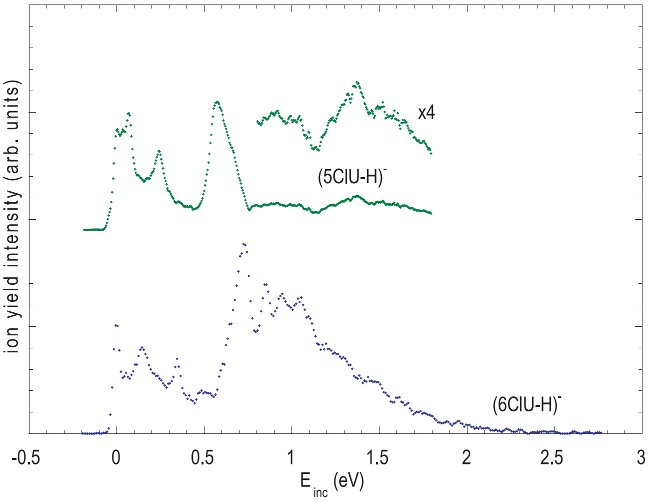


Fig. 7. Comparison of the (ClU–H)$^-$ anion yield versus incident electron energy for 5ClU and 6ClU.

strong similarity with those of Denifl et al. The reader is referred to their papers for a complete discussion. However, we have observed a few more peaks (Fig. 4), the presence of which may be important for a complete interpretation. For 6-ClU, our results for the (6ClU–H)$^-$ are definitely more detailed.

Table 1. Energy position (eV) of the structures observed in the various cross-sections versus electron energy of the most abundant negative ions in thymine, uracil and halouracils and in the elastic cross-sections recorded at 90°.

		Energy (eV)							
Thymine and deuterated thymine (d3, d6)									
	$(T–H)^-$	0.67	0.82	1.00	1.19	1.45	∼1.7		
Uracil									
	e-elastic (dips)	0.040	0.270						
	$(U–H)^-$	0.00		0.64	0.95	1.22	1.41	∼1.6	∼1.9
5-BrU									
	elastic (dips)		0.070	0.225					
	Br^-	0.00	0.090	0.245					
	U^-	0.00	0.095	0.240					
	$5BrU^-$	0.00	0.095						
5-ClU									
	e-elastic (dips)		0.080	0.245					
	Cl^-	0.00	0.090	0.270					
	$(5ClU–HCl)^-$	0.00	0.095	0.265					
	$(5ClU–H)^-$	0.00	0.070	0.245	0.575	0.960	∼1.4		
	$5ClU^-$	0.00							
6-ClU									
	$(6ClU–HCl)^-$	0.00	0.110	0.315					
	$(6ClU–H)^-$	0.00	0.140	0.355	0.495	0.735	0.855	0.935	1.065
	Cl^-	0.00	0.085	0.125	0.345				
5-FU									
	e-elastic (dips)		0.060	0.250					
	$(5FU–HF)^-$	0.070	0.240	0.410	0.580				∼1.5
	$(5FU–H)^-$					0.560	0.85	1.28	∼1.5

Besides the appearance of both the parent anion and the fragments ions at zero energy, the striking features of these spectra is the existence of rather sharp structures at very low energy. These structures occur at the same energy in various fragmentation channels, namely around 0.09 eV and 0.26 eV for Cl^-, $(5ClU–HCl)^-$, $(5ClU–H)^-$. They are also observable in the elastic scattering cross-section (Fig. 4). This is a strong indication of vibrations of a common state. The feature at 0.26 eV is also observed in ETS by Scheer et al. [12], attributed to a vibrational Feshbach resonance. The situation is quite similar for the fragment Br^- and U_{yl}^- found in 5-BrU (Fig. 3), with structures at almost the same energies, also present in the elastic cross-section. Indeed, the ETS spectra of Scheer et al. look very similar for 5-BrU and 5-ClU presenting the same structure around 0.26 eV, also attributed to a vibrational Feshbach resonance. Li et al. [16] have computed potential energy surfaces for the dehalogenation of the halouracils using a DFT approach. They show along the C–X coordinate, close to the neutral equilibrium geometry, that the lowest anion states have a mixed π^* and σ^* character. These states could therefore be predissociated by the σ^* resonance leading to X^-+U fragments, the situation being very similar for 5-ClU and 5-BrU. One major point however remains: the processes leading to X^-+U_{yl} are calculated to be endothermic by 0.9 eV for 5-BrU and 0.78 eV for 5-ClU (a value of 0.83 eV is calculated for 5-ClU by Denifl et al. [7]). This model cannot therefore explain our observations of Cl^- and Br^- ions at 0.09 eV and 0.26 eV. The same problem occurs for the low energy peaks in the fragment $(5ClU–H)^-$ where a threshold is computed at 0.56 eV [7]. Note that the peak at 0.58 eV seems in excellent agreement with this value (Fig. 4). If there is a great similarity for the fragments Cl^- in 5-ClU and Br^- in 5-BrU, strong differences also appear as neither $(5BrU–H)^-$ nor $(5BrU–HBr)^-$ are observed.

In 6-ClU (Fig. 6) the same fragments are observed as in 5-ClU. Variation of the cross-section of $6ClU^-$ was exactly identical to previous results; it is not presented here. The elastic cross-section (not presented) does not show any structure. We note the existence of structures in $(6ClU–HCl)^-$ at 0.11 eV and 0.31 eV. In Cl^-they are observed at 0.13 eV and 0.34 eV, but clearly less developed than in similar fragments of 5-ClU; this may explain why we did not see any structure on the elastic cross-section. If the general shape of the $(6ClU–H)^-$ fragment is in agreement with the results of Denifl et al. [7], it presents rather new features, exhibiting, besides the peak at zero energy, 2 low energy peaks, like for $(5ClU–H)^-$, at 0.14 eV and 0.35 eV. Above 0.7 eV a well developed vibrational structure with spacing around 0.1 eV appears clearly, not observed before. Figure 7 presents the comparison of the $(5ClU–H)^-$ and $(6ClU–H)^-$ fragments. If there is some analogy for the low energy part, the shape is quite different above 0.5 eV. In 5ClU (see above), we have already mention the good fit between the computed threshold at 0.56 eV and the observation. For 6ClU these authors have calculated a threshold at 0.42 eV for $(6ClU–H)^-$, in poor agreement with our observations at 0.72 eV.

For 5-FU (Fig. 5), even if 2 clear structures are observed in the elastic cross-section at 0.06 eV and 0.25 eV, the 2 low energy peaks appearing in BrU and ClU below

0.4 eV, do not appear at all in the fragment $(5FU–H)^-$. Above 0.5 eV the spectrum look similar to the case of $(5ClU–H)^-$ showing 4 peaks around 0.56 eV; 0.85 eV; 1.28 eV and 1.5 eV. Again, the loss of an HX from the parent ion is observed and the $(5FU–HF)^-$ ion shows structures strongly related to the cusps observed in the elastic cross-section. An additional feature not observed in the elastic cross-section is present at 0.58 eV followed by a wide bump around 1.5 eV.

The energy position of the features observed in the various cross-sections are presented in Table 1.

4 Conclusion

The shape of the DEA fragments cross-sections vs. electron energy presents a great complexity for uracil, thymine and the halouracils. Denifl et al. [11a] in their analysis in terms of thresholds of the processes assigned the first 2 peaks in $(U–H)^-$ being associated with the H ablation from the N sites. The observed threshold for the removal of an H atom from N1 site at 0.69 eV (0.64 eV in the present work), agrees fairly well with their calculations (0.8 eV). The situation is not as good for the N3 site at 1.01 eV (0.95 eV in the present work), where the calculated value of 1.4 eV compares poorly with the experiment. The wider bumps around 1.4 eV and 1.7 eV would be due to fragmentation via the second π^* resonance lying in this energy region. For the structures observed in $(U–H)^-$, even if several objections are still to be overcome, one should stress that only Scheer et al. [12] are really proposing a mechanism for the dissociation process, via the coupling of the dipole bound state and the low lying σ^* resonances.

The interpretation of $(T–H)^-$ in thymine is certainly very similar to uracil, even if another small peak appearing at 0.8 eV has to be explained. It is then clear that the various analysis proposed are not totally convincing.

The situation for the halouracils is even less comfortable particularly for the lowest energy part of the spectra of some fragments where, besides the unexpected zero energy peak, several peaks are observed below the thermodynamical threshold as Li et al. [16] indicate that the separation at infinity in Uyl radical and Br^- or Cl^- is unfavourable respectively by 0.9 eV and 0.78 eV. As it has been showed [5,11] that charge transfer reactions between uracil and anions coming from the calibrating gas (peaking at zero energy), can efficiently create artificial zero energy peaks, all our measurements have been carried out in absence of the calibrating gas. Understanding the mechanism generating the peaks observed at the energy position of resonances around 0.1 eV and 0.25 eV is of importance as some fragment ions have huge cross-sections which cannot be considered as negligible phenomena.

We have tried in the present work to obtain experimental results as detailed as possible in order to stimulate further theoretical work to fully understand the DEA processes in these molecules.

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