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## Negative ion chemistry of Deoxyribose and THF upon potassium atom collisions

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**Abstract.** Negative ion formation in collisions of potassium atoms with tetrahydrofuran (THF) and D-Ribose (DR) were performed in a crossed molecular beam setup equipped with a time-of-flight (TOF) mass spectrometer. Owing to the role of these molecules as possible representations of the sugar unit in the DNA/RNA, the fragmentation patterns obtained for different collision energies were compared and the role of K<sup>+</sup> post-collision interaction with the molecular is evaluated.

### 1. Introduction

Low energy electron (LEE) interaction with DNA has recently been established as one of the main mechanism that may lead to mutagenic disorders[1]. Even at sub-excitation energies, these LEEs are extremely efficient in damaging DNA owing to their ability to promote fragmentation through the decomposition of its building blocks[2]. Indeed, such mechanism is now very well established to be described at the molecular level. As such, the importance of negative ion chemistry of isolated biological relevant molecules can provide valuable insights on the underlying mechanisms, with the uttermost need to evaluate such processes within the physiological environment.

This negative ion chemistry can be studied not only in the context of free electron interactions, but also from the point of view of atomic/anionic collisions. In these collisions, an electron is transferred from a donor projectile to the target molecule inducing different fragmentation pathways than those obtained from free electron attachment studies (see e.g. ref. [3] for neutral projectiles and [4] for anionic projectiles). Here we are just interested in atom-molecule collisions, where a valence electron is transferred from the donor projectile (neutral potassium) to the target molecule. This mechanism occurs due to a non-adiabatic coupling of the ionic and covalent potential energy surfaces (PES) in the atom-molecule system. This leads after the collision path to the formation of a positive ion K<sup>+</sup> and a

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molecular anion, allowing access to parent molecular states which may not be accessible in free electron attachment experiments[3,5,6]. In effect, even if the free negative molecular ion is unstable towards autodetachment, in the collision complex it can be stabilized at distances shorter than the crossing between the two potential energy surfaces. This is due to the attractive interaction with the positive ion ( $K^+$ )[6]. The negative molecular ion lifetime will depend on the collision time and not only on the natural lifetime of the resonant anionic state. Indeed, when the parent negative ion has a lifetime longer than the fragmentation times, the excess energy may be distributed over the available internal degrees of freedom and so influence the type of fragmentation ions formed in the collision. Previous electron transfer experiments in potassium collisions with pyrimidine bases and halogenated/methylated derivatives have been performed[3,5]. In order to better understand some of the underlying molecular pathways, studies on site and bond selectivity mechanisms yielding  $H^-$  and  $CNO^-$  formation were also performed[7,8], as well as on N-site demethylation[9]. This set of studies highlighted the need to continue exploring the dynamics of these collisional systems. Indeed, from the point of view of understanding the potential damaging effects to DNA/RNA, studies towards more complex molecules, namely thymidine, the sugar unit and its surrogate, appear to be of considerable importance. This work is part of an on-going effort in using atomic collisions to better understand low-energy electron damage to DNA/RNA-constituent molecules. Some previous studies on pyrimidine bases and their derivatives have shown significant differences in the fragmentation patterns between Dissociative Electron Attachment (DEA) and electron transfer experiments[3,6], which for the latter have been attributed primarily to delayed autodetachment due to the presence of the potassium cation post-collision. As mentioned before, THF shares its cyclic ester ring geometry with deoxyribose, the sugar unit in DNA, which lends support to consider THF as a possible surrogate candidate for the DNA sugar unit. This fact is even more critical since it was recently shown that the dominant conformer of deoxyribose in the gas-phase is the pyranosic ring form, in contrast to the furanosic form which is present within the DNA frame[10]. As such, in the gas-phase the molecular geometry of THF is more similar to the DNA sugar unit than the D-Ribose itself.

Herein we report negative ion time-of-flight (TOF) mass spectra for potassium collisions with D-ribose and THF. In the next section, a brief introduction to the experimental setup will be given, followed by a discussion of the TOF mass spectra. Finally, some conclusions will be drawn.

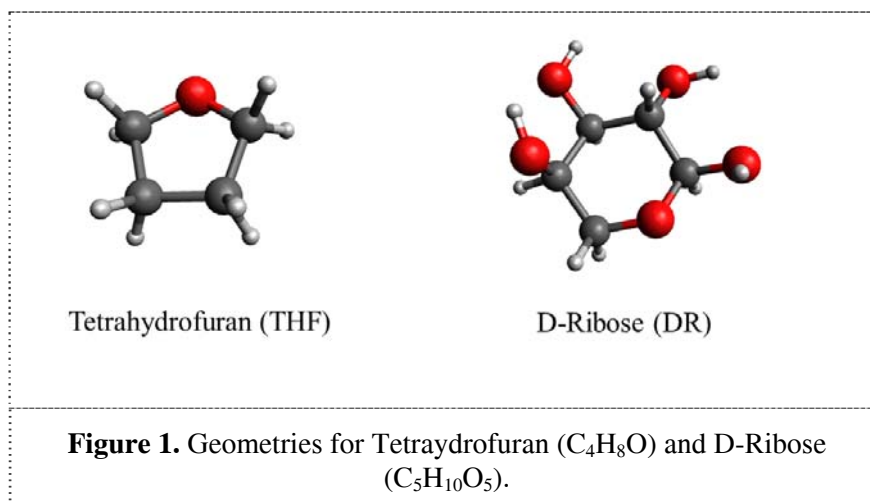
## 2. Experimental setup

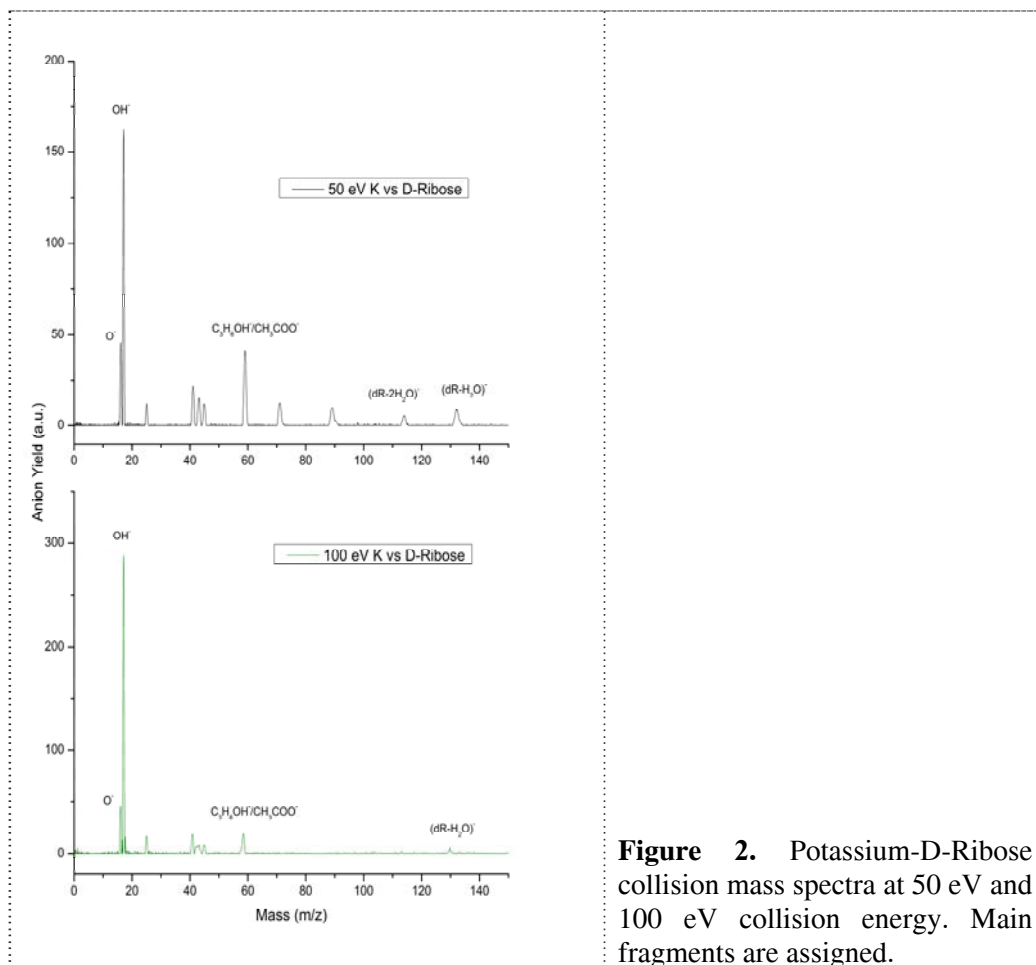
The experimental setup has been already discussed in previous work (see e.g. [3]). Briefly, a beam of  $K^+$ , created through a filament-heated ion source, is forced to pass through a small chamber containing neutral potassium atoms at thermal energies. Through resonant charge exchange, the accelerated  $K^+$  ions are donated an electron from the thermal K neutrals, thereby creating a hyperthermal neutral potassium beam with the desired kinetic energy. A set of deflecting plates outside the chamber is used to deflect the accelerated  $K^+$  ions that did not undergo charge exchange. The resulting hyperthermal neutral potassium beam is monitored using a Langmuir-Taylor surface detector. Ionic currents can range from hundreds of pA to 1 pA, depending on the energy of the beam.

The molecular target beam is obtained through the use of a regular lamp-heated oven. Owing to THF's relatively high vapour pressure, the effusive molecular beam is obtained through a sample admission system at room temperature. In contrast, previous experiments on deoxyribose required heating the sample to 383 K or even higher temperatures[10], which may affect the isomeric ratios in the effusive target beam. The TOF mass spectrometer is a home-made Wiley-McClaren type with a  $\sim 1\mu s$  width pulsed extraction voltage of  $\sim 242 V.cm^{-1}$ . The mass resolution is 125. Systematic background spectra were obtained in order to enable for residual gas contributions to be subtracted from the sample spectra. Owing to the high extraction voltage in comparison to the expected kinetic energy release of the fragments, the transmission of the TOF spectrometer is expected to be independent of the mass.

## 3. D-Ribose measurements

A set of negative ion mass spectra of potassium-D-ribose collisions at different energies are presented in Fig. 2, with complete peak assignments presented in Table 1. A glancing analysis of the spectra clearly shows OH<sup>-</sup> as the dominant fragment for all collision energies. There is no evidence of formation of either the parent or its dehydrogenated anion formation. It is also clear that, for increasing collision energies, the higher mass fragments tend to have lower relative yields. A more detailed analysis on each of the main fragments will be discussed below, with particular attention to (DR-H<sub>2</sub>O)<sup>-</sup> and (DR-2H<sub>2</sub>O)<sup>-</sup> formation.





**Figure 2.** Potassium-D-Ribose collision mass spectra at 50 eV and 100 eV collision energy. Main fragments are assigned.

**Table 1.** Fragmentation table of D-Ribose for different collision energies.

Mass (m/z)	Assignment	50 eV	100 eV
16	O <sup>-</sup>	√	√
17	OH <sup>-</sup>	√	√
25	C <sub>2</sub> H <sup>-</sup>	√	√
41	C <sub>2</sub> HO <sup>-</sup>	√	√
43	C <sub>2</sub> H <sub>3</sub> O <sup>-</sup>	√	√
45	HCOO <sup>-</sup>	√	√
59	C <sub>3</sub> H <sub>6</sub> OH <sup>-</sup> /CH <sub>3</sub> COO <sup>-</sup>	√	
72	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> <sup>-</sup>	√	
89	C <sub>3</sub> H <sub>5</sub> O <sub>3</sub> <sup>-</sup>	√	
114	(dR-2H <sub>2</sub> O) <sup>-</sup>	√	
132	(dR-H <sub>2</sub> O) <sup>-</sup>	√	√

### 3.1. $\text{OH}^-$

$\text{OH}^-$  is the dominant fragment for all collision energies. Its formation is assigned to the abstraction of an hydroxyl group from one of the C-sites, which implies that the ring will most likely not break. The dominance of this fragment anion is in sharp contrast with DEA experiments, in which, while present, has a much lower yield than the dominant water-abstraction channels[11]. A plausible explanation lies on a recent DEA study which shows a resonance profile for  $\text{OH}^-$  formation consisting of one dominant peak at near-zero energy and a weak, wider structure at around 7 eV, the latter assigned to a shape resonance[11]. Additionally, the DEA study presents quantum chemical calculations that provide an assignment of a  $\pi^*$  anionic state to the shape resonance with a lifetime of the order of 3.1 fs[11]. This therefore can lead one to propose a  $\text{OH}^-$  formation mechanism similar to that responsible for  $\text{CNO}^-$  as in uracil and thymine[3], i.e. in the case of D-Ribose the potassium cation will, in effect, increase the lifetime of the anionic state formed at 7 eV, therefore allowing for fragmentation to successfully compete with autodetachment, which naturally leads to an enhancement of the  $\text{OH}^-$  yield. Considering that in electron transfer, autodetachment suppression is much more efficient in the case of ionic scattering, the collision dynamics for  $\text{OH}^-$  formation may be reasonably described by the major contribution of this type of scattering.

### 3.2. $(\text{DR-H}_2\text{O})^-$ & $(\text{DR-2H}_2\text{O})^-$

The peaks of mass 132 m/z can safely be assigned to the loss of a hydroxyl and hydrogen, whereas 114 m/z corresponds to abstraction of two hydroxyl groups, as well as two hydrogen atoms. This assignment raises the question as to whether for each of these  $\text{OH}^- + \text{H}^-$  abstractions, a water molecule will be formed.

In the context of the present measurements, it is clear that for higher energies, the relative yield for both of these fragmentation channels decreases, i.e. while for 50 eV both of the peaks are present, for 100 eV the 114 m/z channel is no longer present and the 132 m/z is barely visible. At this point, one main consideration has to be taken into account that is unique to these collisional systems; the formation of a  $(\text{K}^+ + \text{DR}^-)$  coulombic complex will occur when the neutral hyperthermal potassium atom donates its electron at the first crossing radius  $R_c$ . We therefore suggest that this coulombic complex will enhance water formation during its lifetime (which will be related to the collision time, and therefore to the velocity of the potassium atom). As such, it is plausible to say that for lower potassium velocities, an enhancement in the formation of a water molecule from the abstraction of  $\text{OH}^-$  and  $\text{H}^-$  radicals occurs, while for higher potassium velocities, the coulombic complex will no longer be efficient enough for this chemical reaction process to occur. This lends support to present the data where most of the higher mass peaks tend to decrease their relative yield for increasing collision energies.

Alternatively, another rationale lies in the fact that for higher potassium velocities the ionic scattering collisional process becomes less relevant, thereby opening more possibilities for the existence of covalent scattering. In covalent scattering, since the potassium cation is farther away from the molecular anion, the coulombic complex will not be formed. As such, we can also assign the decrease of the  $(\text{DR-H}_2\text{O})^-$  and  $(\text{DR-2H}_2\text{O})^-$  relative yield to the fact that they are more prevalent in ionic scattering than in covalent scattering conditions.

### 3.3. $\text{C}_3\text{H}_4\text{O}_2^-$ & $\text{C}_3\text{H}_5\text{O}_3^-$

Mass peaks 89 m/z and 72 m/z were assigned to  $\text{C}_3\text{H}_5\text{O}_3^-$  and  $\text{C}_3\text{H}_4\text{O}_2^-$ , respectively. These peaks, as is the case of the previously discussed water abstraction peaks, also only appear for lower potassium

energies and both are not reported in the higher energy spectrum. This leads to a similar rationale as the one made in the previous section, i.e., given the increase of covalent scattering in the potassium-D-Ribose collision system for higher potassium velocities, the formation of these fragments appears to require the creation of this complex for a significant period of time in order for these fragments to be formed.

### 3.4. $C_3H_6OH^-/CH_3COO^-$

Mass peak 59 m/z is the third most intense fragment in the 50 eV collision spectrum, whilst its yield greatly decreases for 100 eV collision energy. Such peak assignment can be attributed to isobaric fragments,  $C_3H_6OH^-/CH_3COO^-$ . As far as authors are aware, no data on thermochemical  $C_3H_6OH^-$  formation is available and so we tentatively assign 59 m/z to the acetyloxyl radical due to its significant electron affinity of 3.25 eV[12].

### 3.5. $C_3H_5^-/C_2HO^-$ , $C_2H_3O^-$ & $C_3H_5O_3^-$

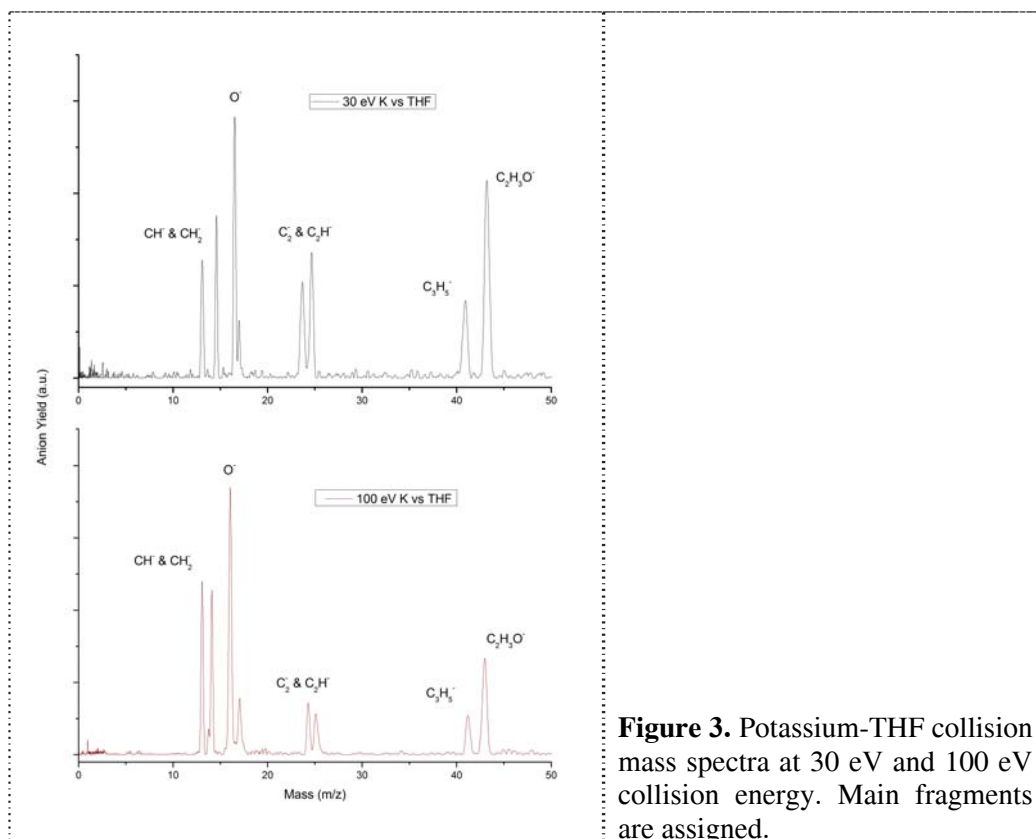
The mass peaks 41, 43 and 45 m/z are attributed to  $C_3H_5^-/C_2HO^-$ ,  $C_2H_3O^-$  and  $C_3H_5O_3^-$ , respectively. Unlike in the previous discussion where the relative yields greatly decrease for higher collision energies, these do not appear to be very sensitive to the role of the coulombic complex. Of interest their relative yields appear to remain relatively similar indicating that the fragments' formation is not dependent on the potassium collision energy. Another issue pertains to the assignment of the 41 m/z. While it is tempting to assign it to  $C_2HO^-$ , recent unpublished DEA measurements on deuterated THF have shown that this anion is actually assigned to  $C_3H_5^-$  [13]. As such, owing to the ring structures being somewhat similar, although in THF it is a furanose ring and in D-Ribose a pyranose ring, we tentatively assign mass 41 m/z to  $C_3H_5^-$ .

### 3.6. $O^-$

Mass 16 m/z can be unambiguously assigned to the formation of anionic oxygen, and presents itself as the second most intense fragment anion. Furthermore, unlike most other fragments, its relative yield does not seem to decrease with the increasing collision energy. As far as  $O^-$  formation is concerned, it can be obtained through two main fragmentation pathways: 1) decay product of hydroxyl abstraction; 2) result from multiple bond breaks of the pyranosic ring. It is worth mentioning that, as will be discussed below, the main fragment in THF is  $O^-$  and this has to stem from ring breaking. As such, we tentatively attribute this fragment to C-O bond breaking, which requires access to higher-energy  $\pi^*$  or  $\sigma^*$  anionic states.

## 4. THF measurements

Similarly to D-Ribose, a set of negative ion mass spectra at two different collision energies are presented in Figure 3, with mass assignments in Table 2. A quick look at THF negative ions spectra shows that, while they are qualitatively similar, the 100 eV spectrum shows a lower relative yield for the higher mass fragments. No presence of the parent anion, or any of the dehydrogenated versions was detected. Unlike the case for D-Ribose, all of the fragments appear for both collision energies, albeit with some significant differences in their relative yield. Finally, it is worth noting that a small, yet existing signal of  $H^-$  is also present at both collision energies. A more thorough discussion of each fragment is presented in the next section.



**Figure 3.** Potassium-THF collision mass spectra at 30 eV and 100 eV collision energy. Main fragments are assigned.

**Table 2.** Fragmentation table of THF for different collision energies.

Mass (m/z)	Assignment	30 eV	100 eV
1	H <sup>-</sup>	√	√
13	CH <sup>-</sup>	√	√
14	CH <sub>2</sub> <sup>-</sup>	√	√
16	O <sup>-</sup>	√	√
17	OH <sup>-</sup>	√	√
24	C <sub>2</sub> <sup>-</sup>	√	√
25	C <sub>2</sub> H <sup>-</sup>	√	√
41 <sup>a</sup>	C <sub>3</sub> H <sub>5</sub> <sup>-</sup>	√	√
43	C <sub>2</sub> H <sub>3</sub> O <sup>-</sup>	√	√

<sup>a</sup> Latest DEA measurements with deuterated THF confirmed the present assignment.

#### 4.1. O<sup>-</sup>

Mass 16 m/z can be definitely attributed to O<sup>-</sup> formation and appears as the highest fragment for both 30 and 100 eV collision energies spectra. Its formation will necessarily require ring breaking of both

C-O bonds, implying access to higher energy  $\pi^*$  or  $\sigma^*$  resonances. A recent DEA study points towards the formation of an initial linear chain ester anion upon electron capture, by cleavage of the C-O bond[14]. This linear chain ester anion will be vibrationally excited and therefore easily breaking through several possible pathways, of which O seems to be the high intensity anion in electron transfer measurements.

#### 4.2. $C_3H_5^-$ & $C_2H_3O^-$

Mass 41 and 43 m/z can be assigned to  $C_3H_5^-$  and  $C_2H_3O^-$ , respectively. Comparing their relative yields for the two different collision energies shows that these, much like the discussion presented in the previous section for D-Ribose, are enhanced due to the coulombic collision complex, which means the dominance of ionic scattering. This is supported by the fact that (multiple) ring breaking fragmentation requires a much longer time scale than simple abstraction, as is the case of the C-H bond breaking. Also, while the initial assignment of 41 m/z could be due to  $C_2HO^-$ , recent unpublished DEA measurements on deuterated THF report 46 m/z as  $C_3D_5^-$ , implying that for THF 41 m/z is due to  $C_3H_5^-$ .

#### 4.3. $CH^-$ , $CH_2^-$ , $C_2^-$ & $C_2H^-$

This set of four mass peaks 13, 14, 24 and 25 m/z, can be safely assigned to  $CH^-$ ,  $CH_2^-$ ,  $C_2^-$  and  $C_2H^-$ , respectively. Moreover, much like the discussion in the previous sub-section, due to the transient metastable anion being in a vibrationally excited state, bond breaks in the alkyl side of the linear ester anion will decay into these different fragments. However, it is worth noting that, in the case of  $CH^-$  and  $CH_2^-$ , their relative yield does not decrease as much as in the case of the higher mass  $C_2^-$  and  $C_2H^-$ . This difference of relative yields may be due to the increasing energy transfer by the potassium projectile during the collision.

#### 4.4. $OH^-$

Mass 17 m/z is assigned to the hydroxyl anion. Given that the only oxygen available in THF is not bonded to a hydrogen atom, we therefore propose a concerted mechanism for such anion formation. As such, the oxygen will capture a hydrogen from either the C1 or C4 positions where this process may be enhanced due to the creation of the coulombic complex allowing for enough time to lead to such  $OH^-$  formation.

### 5. Conclusions

The present work provides the first study on negative ion formation in collisions of potassium atoms with D-Ribose, the DNA/RNA sugar unit and THF, one of its most common surrogates. For the case of D-Ribose, the two main features are the dominance of the hydroxyl anion and the decrease in the relative yield of the higher mass fragments as the collision energy is increased. By comparing with a recent unpublished DEA study, the dominant presence of  $OH^-$  was attributed to suppression of auto-detachment in a high-lying resonant state that, in the context of DEA, would not result in fragmentation, but rather in electron rejection. The other main issue pertains to the decrease in the relative yield of the higher mass fragments. This highlights the importance of the dynamics surrounding the collision complex. This coulombic complex seems to greatly influence the resulting

fragmentation pathways in sharp contrast to DEA experiments. As far as THF is concerned, although being referred as a sugar unit surrogate, the fragmentation pattern shows differences from D-Ribose. Indeed, it was shown that most of the fragmentation of THF lies in the access of high-lying  $\pi^*$  and  $\sigma^*$  states, which have been shown to be core-excited resonances. This seems to be also the case of the present measurements. However, it is important to note the role of the coulombic complex dictating the fragmentation patterns in atom-molecule collision experiments.

## 6. Acknowledgments

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