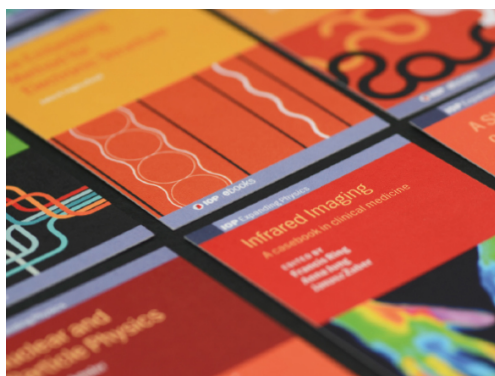


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Electron transfer to phenyl boronic acid upon potassium collisions

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Abstract. We present negative ion formation from collisions of neutral potassium atoms with neutral phenylboronic acid $C_6H_5B(OH)_2$ molecules in the lab frame energy range from 10 to 1000 eV. From the assignment of the negative ion time-of-flight (ToF) mass spectra, BO^- is the main fragment detected at energies below 100 eV, however above 100 eV BO_2^- is the predominant fragment accounting on average for 30% of the total anion yield for collision energies above 250 eV. The rich fragmentation pattern results in the formation of more than thirty fragment anions, with twenty boron containing ions.

1. Introduction

Low-energy electron (LEE) interactions studies with biomolecules have attracted the attention of the international scientific community for almost two decades. Sanche and co-workers have described the interaction of such electrons with plasmid DNA, in an energy range up to 20 eV [1,2], showing that LEE interactions can be very efficient in inducing single and double strand breaks (SSB and DSB) as well as loss of supercoiled DNA. The underlying molecular mechanisms of such reactions [2] have been attributed to dissociative electron attachment (DEA) interactions, showing that DNA damage in condensed films upon LEE irradiation occurs at the same energy as resonance capture from isolated constituents, such as water, cytosine and thymine and sugar unit [1,3,4]. Gas phase electron capture has been studied in a wide range of target molecules leading to dissociation through resonant processes. In the case of thymine and cytosine, the anions formed with the highest yield have been assigned to the dehydrogenated parent anions; however, due to ring opening above 4 eV other fragments, such as CNO^- , are formed with considerable intensities [5]. Additionally, we note that comprehensive characterisation of the fragmentation pathways induced by free electrons was reported for uracil RNA base [3], valine [6,7] in bare and hydrated environments, and the simplest amino acid glycine [8]. Moreover, H^- formation from thymine and uracil upon DEA has been shown to be not only bond selective i.e. (C-H) versus (N-H), but site selective (N1 versus N3 site) [9]. Site selective fragmentation at hydrogen sites has been also shown for different functional groups, in the particular case of carboxylic acids, alcohols and amines [10]. The effect of hydration on pyrimidine [11] by surrounding water molecules has been shown to be an efficient quenching mechanism regarding fragmentation of such a relevant biomolecule. Furthermore, different environments, such as helium nanodroplets matrix, have been extensively investigated in order to give insight on the role of the surrounding matrix dictating the dissociation channels in electron capture processes. Simple organic molecules such as formamide [12],



acetic acid [13] and some amino acids [14,15] have been studied in such cold environments and differences compared with DEA in bare target molecules. Moreover, LEE studies on molecular targets that may act as potential drug cancer agents have been performed, namely cis-platinum [16] and bromo pyruvic acid [17]. Moreover we note electron transfer studies yielding negative ion formation in potassium collisions with several biological molecules, in particular for DNA/RNA bases showing that the underlying molecular decomposition mechanism leading to H^- formation is site and bond selective [18]. Furthermore, and within the scope of electron transfer studies, the anionic fragmentation pattern of aliphatic amino acids [19–21] and halogenated uracil derivatives used as potential radiosensitizers have been comprehensively investigated [22]. Upon electron transfer in neutral potassium-neutral molecule collisions, the presence of a potassium cation in the vicinity of a temporary negative ion leads to a relevant coulombic complex which induces new fragmentation pathways that are not allowed in free electron capture [23].

In recent years, boronic acid-containing molecules have been considered to be very promising compounds with potential biomedical applications. Boron is the fifth element of the periodic table and has an electronic structure similar to carbon, conferring to it a high potential for use in pharmaceutical drug design as well as in medicinal chemistry [24]. Amongst the different applications of boronic acids, we stress its relevance as fluorescent cellular dyes [25], saccharide sensors (particularly important for the controlled release of drugs in vivo) [26], dopamine sensors and several enzymatic inhibitors [27]. Furthermore, they have been proven helpful in the treatment of HIV, cancer, diabetes and obesity. The characteristics that allow such a wide range of applications are mostly chemical, namely their reactivity and stability [28]. These acids continue to prove their importance in medical practices, although some fundamental chemical properties and action mechanisms still remain unknown. In the present communication we describe recent electron transfer experiments in potassium collisions with phenylboronic acid (figure 1).

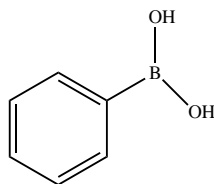


Figure 1. Phenyl boronic acid chemical structure

2. Experimental set-up

The phenyl boronic acid, $C_6H_5B(OH)_2$, sample was purchased from Sigma-Aldrich with a minimum stated purity of 99% and was used as delivered. The sample was heated up to 423 K and temperature controlled by a PID unit. In order to test for thermal decomposition products in the target beam, mass spectra were recorded at different temperatures. No differences were observed in the relative peak intensities as a function of temperature. The negative ion time-of-flight mass spectra were obtained from neutral potassium atoms collisions at different energies. The present crossed beam set-up configuration was described by Antunes *et al.* [29] and further modified as described in Mendes *et al.* [30]. In brief, K^+ ions produced in a commercial source from Heatwave lab, US, were accelerated from 10 to 1000 eV. The accelerated K^+ ions pass through an oven where they resonantly charge-exchanges with neutral potassium to produce a beam of fast (hyperthermal) atoms. Before and after collecting time-of-flight (ToF) mass spectra, the hyperthermal K beam is monitored by a Langmuir-Taylor detector. The phenyl boronic acid effusive beam was introduced into the collision chamber by a 1 mm diameter aperture, where it crossed with the neutral hyperthermal K beam in between two parallel electrostatic plates. The produced anions were extracted into a reflectron ToF (KORE R-500-6) by a pulsed electrostatic field ($\sim 290 \text{ V cm}^{-1}$) and detected by a MCP device. The base pressure in the collision chamber was typically $6 \times 10^{-5} \text{ Pa}$ and the working pressure was $4 \times 10^{-4} \text{ Pa}$. From the obtained mass spectra (resolution $m/\Delta m$

≈ 700) background signal was subtracted (without the heated sample) and the mass calibration was performed based on well-known nitromethane negative ions formed in potassium collisions [29].

3. Results and discussion

Figure 2 presents a ToF mass spectra of phenyl boronic acid. In the upper panel (A), the mass spectrum was obtained from K collisions at 43 eV available energy (70 eV collision energy in the lab frame) whereas in the lower panel (B) the mass spectrum was obtained at 200 eV available energy (300 eV in the lab frame), with more than thirty fragment anions assigned. The present measurements were carried out at the lowest centre-of-mass collision energy of 2.5 eV (6.8 eV collision energy); however, only when the available energy rises above 12.8 eV negative ion formation from phenylboronic acid was observed. In table 1 the assigned negative anions formed after potassium collisions are listed.

Figure 2. ToF mass spectra obtained for phenyl boronic acid after collisions with potassium atoms at 43 eV (A) and 200 eV (B) available energy (70 and 300 eV collision energy, respectively). The most intense fragment anions are assigned; all fragments are listed in table 1.

3.1 BO^- and BO_2^-

The most intense fragment anions detected in the wide range of collision energies investigated in these experiments were assigned to BO^- and BO_2^- , with the sum of their yields accounting for more than 40% of the total anion intensities. In both cases, the isotopic ratio between the lighter (^{10}B) and the heavier (^{11}B) anions is $\sim 1/4$. Boron monoxide (BO^-) m/z 26 (and m/z 27) is observed at the lowest available energy, 12.8 eV, whereas for 6.2 eV no traces of such anion have been detected. Boron dioxide (BO_2^-) m/z 42 (and m/z 43) was only observed above 16.3 eV available energy. Boron monoxide and boron dioxide have high electron affinities, 2.51 and 4.46 eV [31], which is not surprising considering they are formed with high intensity in the ToF mass spectra. Figure 3 shows the branching ratio of these anions as function of the collision energy. For available energies below 100 eV, boron monoxide is the most predominant anion, whereas with increasing available energy (above 100 eV), its yield is less than 20% of the total anion yield. Of relevance, boron dioxide (BO_2^-) follows a opposite trending. For available energy above 250 eV, BO_2^- formation is predominant reaching a plateau. In conclusion, the formation of these negative ions is strongly dependent on the collision energy. It is clear that for low collision energies, excision of the B-O bond against the O-H bond is the predominant pathway, while at available energies above 100 eV, O-H bond rupture becomes dominant (see figure 4).

Figure 3. Branching Ratios for BO^- (m/z 26 and m/z 27) and BO_2^- (m/z 42 and m/z 43) ions as a function of the collision energy. Green line with triangles is for boron dioxide. Purple line with full circles is for boron monoxide with the contribution of the isobaric fragment C_2H_2^- . The dashed line represents the branching ratio of boron monoxide without the C_2H_2^- contribution and was obtained out of the isotopic ratio of ^{11}B and ^{10}B .

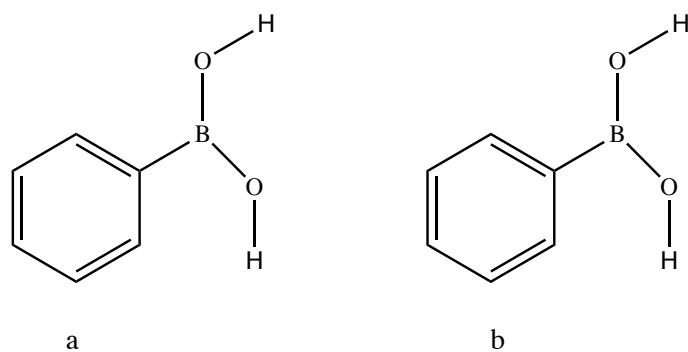


Figure 4. a) Schematic bond rupture leading to BO^- formation; b) schematic bond rupture leading to BO_2^- formation.

Table 1. Assignment of the negative ions formed in potassium collisions with phenyl boronic acid

Anion	Mass (a. m. u.)
$\text{C}_6\text{H}_4\text{BO}^-$	103
$\text{C}_5\text{H}_4^{11}\text{BO}^-$	91
$\text{C}_5\text{H}_4^{10}\text{BO}^-$	90
$\text{C}_5\text{H}_2^{11}\text{BO}^- / \text{C}_6\text{H}_6^{11}\text{B}^-$	89
C_6H_5^-	77
C_6H_3^-	75
$\text{C}_3\text{H}_3^{11}\text{BO}^-$	66
C_5H_5^-	65
$\text{C}_5\text{H}_4^- / \text{C}_3\text{H}^{11}\text{BO}^- / \text{C}_4\text{H}_5^{11}\text{B}^-$	64
$\text{C}_5\text{H}_3^- / \text{C}_3\text{H}^{10}\text{BO}^- / \text{C}_4\text{H}_5^{10}\text{B}^-$	63
$\text{C}_2^{11}\text{BO}^- / \text{C}_3\text{H}_3^{11}\text{B}^-$	51
$\text{C}_2^{10}\text{BO}^- / \text{C}_3\text{H}_3^{10}\text{B}^-$	50
$\text{C}_3\text{H}_2^{11}\text{B}^-$	49
$^{11}\text{BO}_2\text{H}_3^-$	46
$^{11}\text{BO}_2^-$	43
$^{10}\text{BO}_2^-$	42
$\text{C}^{11}\text{BOH}^- / \text{C}_3\text{H}_4^-$	40
$\text{C}^{11}\text{BO}^- / \text{C}_3\text{H}_3^-$	39
$\text{C}_2\text{H}_3^{11}\text{B}^- / \text{C}_3\text{H}_2^-$	38
$\text{C}_2\text{H}_2^{11}\text{B}^- / \text{C}_3\text{H}^-$	37
O_2^-	32
CH_2O^-	30
$^{11}\text{BO}^-$	27
$^{10}\text{BO}^-$ and C_2H_2^-	26
C_2H^-	25
$\text{CH}^{11}\text{B}^- / \text{C}_2^-$	24
OH^-	17
O^-	16
CH_2^-	14
CH^-	13
C^-	12

3.2 Other boron containing fragments

Apart from boron monoxide and boron dioxide, twenty-one other boron-containing negative ions have been assigned. The heavier fragment formed is assigned to $\text{C}_6\text{H}_4\text{BO}^-$ m/z 103; this is the only fragment that does not result from the opening of the ring. In the unimolecular decomposition, the reaction leading to $\text{C}_6\text{H}_4\text{BO}^-$ formation may yield $\text{H}_2\text{O} + \text{H}^\bullet$, or $\text{OH}^\bullet + \text{H}_2$ (or even $\text{OH}^\bullet + \text{H} + \text{H}$). Given that such anion yield is particularly low (see figure 2), its isotopic anion at mass 102 m/z is not discernible above the background noise. The fragments m/z 91 and m/z 90 were assigned to $\text{C}_5\text{H}_4^{11}\text{BO}^-$ and $\text{C}_5\text{H}_4^{10}\text{BO}^-$.

Formation of such fragment anions requires the opening of the ring with loss of $\text{CH} + \text{H}_2\text{O}$. The fragments m/z 89 and m/z 66 were assigned to $\text{C}_5\text{H}_2^{11}\text{BO}^-$ and $\text{C}_3\text{H}_3^{11}\text{BO}^-$ and no traces of the isotopic contributions were detected. However, for the latter, such formation requires ring opening leading to the loss of three carbon atoms and four hydrogen atoms, as well as the loss of one oxygen atom. Fragment anion m/z 64 was assigned to $\text{C}_3\text{H}^{11}\text{BO}^- / \text{C}_4\text{H}_5^{11}\text{B}^-$ while m/z 63 to the respective isotopic forms ($\text{C}_3\text{H}^{10}\text{BO}^- / \text{C}_4\text{H}_5^{10}\text{B}^-$). Although the ToF mass intensity of the latter anion is discernible from the background noise it also shows the isotopic contribution of $\text{C}_3\text{H}^{11}\text{BO}^- / \text{C}_4\text{H}_5^{11}\text{B}^-$, the current mass resolution it is not sufficient to unambiguously assign such isobaric contributions. The same rationale applies to anions m/z 51 and m/z 50, $\text{C}_2^{11}\text{BO}^-$ and $\text{C}_3\text{H}_3^{11}\text{B}^-$ and the corresponding isotopic contributions $\text{C}_2^{10}\text{BO}^-$ and $\text{C}_3\text{H}_3^{10}\text{B}^-$. Fragment anion m/z 49 was assigned to $\text{C}_3\text{H}_2^{11}\text{B}^-$; the mechanism leading to the formation of such anion implies the rupture of both B-O bonds. The negative ion m/z 46 was assigned to $^{11}\text{BO}_2\text{H}_3^-$; the reaction producing this anion involves the break of the B-C bond and an H transfer from the phenyl ring to the BO_2H_2 end. The anionic species m/z 40 and m/z 39 were assigned to $\text{C}^{11}\text{BOH}^-$ and C^{11}BO^- ; it is interesting to note that, although these fragments are formed with low intensities, the C-B bond is preserved. Finally, fragments m/z 38 and m/z 37 were assigned to $\text{C}_2\text{H}_3^{11}\text{B}^-$ and $\text{C}_2\text{H}_2^{11}\text{B}^-$, where the C-B bond is preserved against the B-O bond. The lightest boron-containing fragment anion has been assigned to CH^{11}B^- , m/z 24.

3.3 Other relevant fragments

Molecular oxygen anion, m/z 32, is formed for collision energies above 23 eV (available energy), despite its low electron affinity (0.4480 ± 0.0060 eV) [32]. The branching ratio of this anion amounts to 10% of all fragments formed. Fragment C_2H^- (m/z 25) is observed for the available energy above 23 eV with a branching ratio consistently between 8% and 11% of the total fragmentation pattern. Fragment C_2H_2^- (m/z 26) is isobaric with BO^- ; the contribution of these anions to the m/z 26 yield is observed for available energy above 100 eV, when the ratio between isotopic fragments increases, indicating that m/z 26 results also from the collision induced dissociation mechanism that opens a new channel leading to C_2H_2^- formation. Boron-free fragments C_5H_5^- (m/z 65) and C_5H_4^- (m/z 64) are formed through ring opening, the former via rupture of just two C-C bonds, the latter through an additional C-H bond excision. Finally, we note that C_5H_3^- (m/z 63) may also be related to two isobaric contributions, viz. C_3HBO^- and/or $\text{C}_4\text{H}_5\text{B}^-$ but due to the limited mass resolution it is not possible to unambiguously assign such anions, as well as the fact that there is no information about the thresholds of formation of such isobaric contributions.

3.4 Other fragments

The C_6H_5^- and C_6H_3^- ions are the ring counterpart anions to $\text{B}(\text{OH})_2$ and $\text{B}(\text{OH})_2 + \text{H}_2$ or $\text{B}(\text{OH})_2 + \text{H} + \text{H}$. Although the intensities of these two fragments are not particularly relevant in comparison with other anions, they are formed through the excision of the B-C bond, and in the case of C_6H_3^- via releasing of two extra hydrogen atoms. The electron affinities of C_6H_5 , BO and BO_2 are (1.0960 ± 0.0060 eV) [33], (2.510 ± 0.015 eV) [31] and (4.460 ± 0.030 eV) [31], respectively. Several low intensity fragment anions have been assigned to: C_3H_4^- , C_3H_3^- , C_3H_2^- , C_3H^- (m/z 40, m/z 39, m/z 38, m/z 37, respectively). These anions are isobaric with boron containing $\text{C}^{11}\text{BOH}^-$ and C^{11}BO^- , in the case of m/z 40 and m/z 39, and isobaric with $\text{C}_2\text{H}_3^{11}\text{B}^-$ and $\text{C}_2\text{H}_2^{11}\text{B}^-$ in the case of m/z 38 and m/z 37; however, due to their low yields in the ToF mass spectra it is difficult to precisely assign the corresponding anion. Fragment m/z 30 was assigned to CH_2O^- and m/z 25 to CH_2^- . The anion m/z 24 was assigned to C_2^- , although it can also be isobaric with CH^{11}B^- . Other lighter fragments have been assigned to OH^- , O^- , CH_2^- , CH^- and C^- with m/z 17, m/z 16, m/z 14, m/z 13 and m/z 12, respectively.

4. Conclusions

The present study describes negative ion formation in collisions of potassium atoms with phenylboronic acid. The ToF mass spectra show a very rich fragmentation pattern leading to the formation of several different boron-containing anions, mainly boron oxides (BO^- and BO_2^-). In the present work, it is

shown that the energetic threshold of formation of these anions lies at a few eV and the trending of the branching ratios with the collision energy was analysed. The main dissociation pathways for available energies below 100 eV lead to the formation of BO^- , but for energies above 100 eV these dissociation pathways are suppressed, resulting in the predominant formation of BO_2^- .

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References

- [1] Martin F, Burrow P D, Cai Z, Cloutier P, Hunting D and Sanche L 2004 DNA strand breaks induced by 0-4 eV electrons: The role of shape resonances *Phys. Rev. Lett.* **93** 068101
- [2] Boudaïffa B, Cloutier P, D Hunting D, Huels M A and L S 2000 Resonant Formation of DNA Strand Breaks by Low-Energy (3 to 20 eV) Electrons *Science* **287** 1658
- [3] Denifl S, Ptasińska S, Hanel G, Gstir B, Probst M, Scheier P and Märk T D 2004 Electron attachment to gas-phase uracil. *J. Chem. Phys.* **120** 6557
- [4] Simons J 2006 Electrons Cause DNA-Strand Breaks ? *Acc. Chem. Res.* **39** 772
- [5] Denifl S, Ptasińska S, Probst M and Hrus J 2004 Electron Attachment to the Gas-Phase DNA Bases Cytosine and Thymine *J. Phys. Chem. A* **108** 6562
- [6] Denifl S, Flosadóttir H D, Edtbauer A., Ingólfsson O, Märk T D and Scheier P 2010 A detailed study on the decomposition pathways of the amino acid valine upon dissociative electron attachment *Eur. Phys. J. D* **60** 37
- [7] Denifl S, Mähr I, Ferreira da Silva F, Zappa F, Märk T D and Scheier P 2008 Electron impact ionization studies with the amino acid valine in the gas phase and (hydrated) in helium droplets *Eur. Phys. J. D* **51** 73
- [8] dos Santos J S, da Costa R F and Varella M T D N 2012 Low-energy electron collisions with glycine. *J. Chem. Phys.* **136** 084307
- [9] Ptasińska S, Denifl S, Grill V, Märk T, Illenberger E and Scheier P 2005 Bond- and Site-Selective Loss of H- from Pyrimidine Bases *Phys. Rev. Lett.* **95** 093201
- [10] Prabhudesai V S, Kelkar A H, Nandi D and Krishnakumar E 2005 Functional group dependent site specific fragmentation of molecules by low energy electrons *Phys. Rev. Lett.* **95** 143202
- [11] Neustetter M, Aysina J, Ferreira da Silva F and Denifl S 2015 The Effect of Solvation on Electron Attachment to Pure and Hydrated Pyrimidine Clusters *Angew. Chemie Int. Ed.* **54** 9124
- [12] Ferreira da Silva F, Denifl S, Maerk T D, Doltsinis N L, Ellis A M and Scheier P 2010 Electron Attachment to Formamide Clusters in Helium Nanodroplets *J. Phys. Chem. A* **114** 1633
- [13] Ferreira da Silva F, Jaksch S, Martins G, Dang H M, Dampc M, Denifl S, Maerk T D, Limao-Vieira P, Liu J, Yang S, Ellis A M and Scheier P 2009 Electron attachment and electron ionization of acetic acid clusters embedded in helium nanodroplets *Phys. Chem. Chem. Phys.* **11** 11631
- [14] Ferreira da Silva F, Denifl S, Maerk T D, Ellis A M and Scheier P 2010 Electron attachment to amino acid clusters in helium nanodroplets: Glycine, alanine, and serine *J. Chem. Phys.* **132** 214306
- [15] Ferreira da Silva F, Bartl P, Denifl S, Maerk T D, Ellis A M and Scheier P 2010 Formation of the Magic L-Serine Octamer in Helium Nanodroplets *Chem. Phys. Chem.* **11** 90

- [16] Kopyra J, Koenig-Lehmann C, Bald I and Illenberger E 2009 A single slow electron triggers the loss of both chlorine atoms from the anticancer drug cisplatin: Implications for chemoradiation therapy *Angew. Chemie - Int. Ed.* **48** 7904
- [17] Ferreira da Silva F, Márcio M T, Jones N C, Vørnning Hoffmann S, Denifl S, Bald I and Kopyra J 2019 Electron-Induced Reactions in 3-Bromopyruvic Acid *Chem. - A Eur. J.* **25** 5498
- [18] Almeida D, Ferreira da Silva F, García G and Limão-Vieira P 2013 Selective bond cleavage in potassium collisions with pyrimidine bases of DNA *Phys. Rev. Lett.* **110** 023201
- [19] Ferreira da Silva F, Lança M, Almeida D, García G and Limão-Vieira P 2012 Anionic fragmentation of glycine upon potassium-molecule collisions *Eur. Phys. J. D* **66** 78
- [20] Ferreira da Silva F, Rafael J, Cunha T, Almeida D and Limão-Vieira P 2014 Electron transfer to aliphatic amino acids in neutral potassium collisions *Int. J. Mass Spectrom.* **365–366** 238
- [21] Ferreira da Silva F, Meneses G, Ingólfsson O and Limão-Vieira P 2016 Side chain effects in reactions of the potassium-tyrosine charge transfer complex *Chem. Phys. Lett.* **662** 19
- [22] Ferreira da Silva F, Almeida D, Antunes R, Martins G, Nunes Y, Eden S, Garcia G, Limao-Vieira P, Ferreira da Silva F and Limão-Vieira P 2011 Electron transfer processes in potassium collisions with 5-fluorouracil and 5-chlorouracil. *Phys. Chem. Chem. Phys.* **13** 21621
- [23] Ferreira da Silva F, Matias C, Almeida D, García G, Ingólfsson O, Flosadottir H D, Omarsson B, Ptasinska S, Puschnigg B, Scheier P, Limao-Vieira P and Denifl S 2013 NCO-, a Key Fragment Upon Dissociative Electron Attachment and Electron Transfer to Pyrimidine Bases: Site Selectivity for a Slow Decay Process *J. Am. Soc. Mass Spectrom.* **24** 1787
- [24] Ban H S and Nakamura H 2015 Boron-based drug design *Chem. Rev.* **15** 616
- [25] Santos F M F, Rosa J N, Candeias N R, Carvalho C P, Matos A I, Ventura A E, Florindo H F, Silva L C, Pischel U and Gois P M P 2016 A Three-Component Assembly Promoted by Boronic Acids Delivers a Modular Fluorophore Platform (BASHY Dyes) *Chem. - A Eur. J.* **2** 1631
- [26] Mader H S and Wolfbeis O S 2008 Review Boronic acid based probes for microdetermination of saccharides and glycosylated biomolecules *Microchim Acta* **162** 1
- [27] Fu H, Fang H, Sun J, Wang H, Liu A, Sun J and Wu Z 2014 Boronic Acid-based Enzyme Inhibitors: A Review of Recent Progress *Curr. Med. Chemistry* **21** 3271
- [28] Cambre J N and Sumerlin B S 2011 Biomedical applications of boronic acid polymers *Polymer (Guildf)*. **52** 4631
- [29] Antunes R, Almeida D, Martins G, Mason N J, Garcia G, Maneira M J P, Nunes Y and Limão-Vieira P 2010 Negative ion formation in potassium-nitromethane collisions. *Phys. Chem. Chem. Phys.* **12** 12513
- [30] Mendes M, Pamplona B, Kumar S, Ferreira da Silva F, Aguilar A, García G, Bacchus-Montabonel M-C and Limao-Vieira P 2019 Ion-Pair Formation in Neutral Potassium-Neutral Pyrimidine Collisions: Electron Transfer Experiments *Front. Chem.* **7** 1
- [31] Zhai H-J, Wang L-M, Li S-D and Wang L-S 2007 Vibrationally Resolved Photoelectron Spectroscopy of BO- and BO2-: A Joint Experimental and Theoretical Study *J. Phys. Chem. A* **111** 1030
- [32] Ervin K M, Anusiewicz I, Skurski P, Simons J and Lineberger W C 2003 The Only Stable State of O2- Is the X 2Πg Ground State and It (Still!) Has an Adiabatic Electron Detachment Energy of 0.45 eV *J. Phys. Chem. A* **107** 8521
- [33] Guniona F R, Gillesa K M, Polaka L M and Lineberger W C 1992 Ultraviolet photoelectron spectroscopy of the phenide, benzyl and phenoxide anions, with ab initio calculations *Int. J. Mass Spectrom. Ion Process.* **117** 601