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Dissociative electron attachment to the volatile anaesthetics enflurane and isoflurane and the chlorinated ethanes pentachloroethane and hexachloroethane

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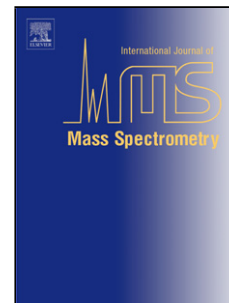
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Highlights

1. Investigation of dissociative electron attachment processes for four chlorinated chemicals (two isomers enflurane and isoflurane ($C_3H_2ClF_5O$) and two chloroethanes (C_2HCl_5 and C_2Cl_6).
2. An interesting observation is that there is no zero electron attachment for the two isomers.
3. Quantum chemical calculations providing thermochemical thresholds of anion formation.

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Dissociative electron attachment to the volatile anaesthetics enflurane and isoflurane and the chlorinated ethanes pentachloroethane and hexachloroethane

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Abstract

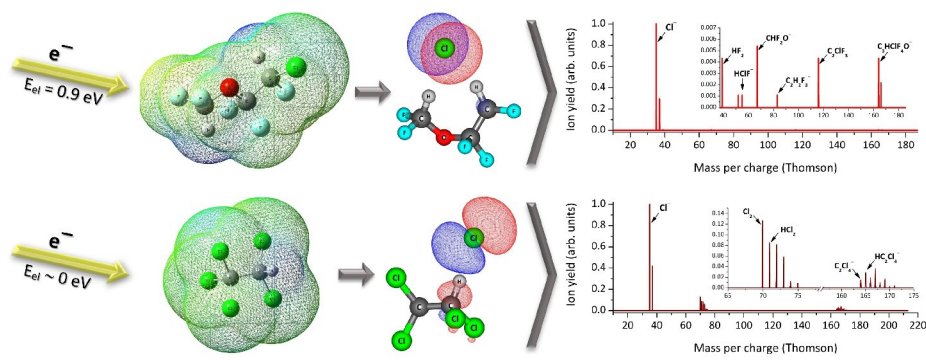
Negative ion formation through dissociative electron attachment to the gas-phase volatile anaesthetics enflurane and isoflurane ($C_3H_2ClF_5O$) and to two chlorinated ethanes, pentachloroethane (C_2HCl_5) and hexachloroethane (C_2Cl_6), have been studied in a crossed electron-molecular beam two sector field mass spectrometer experiment. Anion efficiency curves for the negatively charged fragments have been measured over an electron energy range of approximately 0 – 17 eV, with an energy resolution of ~ 1 eV. For the chlorinated ethanes, resonance features were generally found at ~ 0 eV and at 7.5 eV. For the volatile anaesthetics, no zero energy resonances were observed. Instead, product anions were detected mainly in the 2–3 eV and 9 eV energy regions, with the exception of Cl^- , whose dominant resonance occurs at approximately 0.6 eV and 0.9 eV for isoflurane and enflurane, respectively. To aid in the interpretation of the experimental results, quantum chemical calculations providing thermochemical thresholds of anion formation are also presented.

Keywords: Dissociative electron attachment, volatile anaesthetics, enflurane, isoflurane, chlorinated ethane, pentachloroethane, hexachloroethane

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Graphical Abstract



1. Introduction

Chlorinated molecules may be used in ion-mobility spectrometers as possible dopants to manipulate the ion-chemistry and hence to improve specificity of detection. A recent ion mobility spectrometric study by us investigating four chlorinated compounds showed that within the electron swarm environment of an ion mobility spectrometer (IMS) system, resulting in a mean electron energy of approximately 0.3 eV, electron attachment to pentachloroethane and hexachloroethane is very efficient, whereas that to the isoflurane and enflurane is not, despite their calculated electron affinities (DFT calculations using the B3LYP functional and the 6-31+G(d,p) basis set) being positive, 1.2 and 1.9 eV, respectively [1]. Chloride ion production following electron attachment was also calculated to be exothermic. We postulate that this unexpected behaviour may be due to the strongly positive Vertical Attachment Energies (VAE) calculated for isoflurane and enflurane to be 0.62 and 0.77 eV, respectively. To test this hypothesis we decided to investigate the electron attachment of the above molecules in more detail. The goal of this work is to determine the energy resonances and anion efficiencies of electron attachment, which to our knowledge have not previously been reported.

The present study represents a new experimental contribution for the measurement of negative ion yields for enflurane ($\text{CHFCl-CF}_2\text{-O-CHF}_2$), isoflurane ($\text{CF}_3\text{-CHCl-O-CHF}_2$), pentachloroethane (C_2HCl_5) and hexachloroethane (C_2Cl_6) molecules upon low-energy electron attachment. Although for an explanation of the IMS results energy resonances at less than 1 eV are of key importance, with the apparatus available we have taken the opportunity to investigate electron attachment to the above molecules over an electron energy range of 0 – 17 eV, which is of fundamental interest. To complement the experimental results, we have also carried out quantum chemical calculations on the electronic properties of all molecules studied in the present work. In the following sections we provide details on the experimental apparatus and the measurement technique that have been used. This will be followed by a brief discussion on the computational methods adopted and a presentation and discussion of the experimental results.

2. Experimental details

Dissociative electron attachment (DEA) to the volatile anaesthetics and chlorinated ethanes was investigated by means of a crossed electron-molecular beam set-up utilizing a double focusing two-sector field mass spectrometer equipped with a standard Nier-type ion source [2]. The electron energy resolution close to 0 eV is about 1 eV full width at half maximum

(FWHM). This low electron energy resolution is compensated by the high sensitivity that is available owing to the large electron current. The electron current is regulated to 10 μA , which is achieved for electron energies higher than 2 eV. Below 2 eV the electron current decreases linearly down to a value of approximately 2 μA at 0 eV. This reduction in current must be considered when comparing peak intensities below 2 eV to those above 2 eV for any particular energy scan for a given product anion. An effusive molecular beam emerges from an orifice of 3 mm diameter which is crossed with an electron beam to generate anions. A voltage drop of 6 kV accelerates product anions from the ion source towards the sector fields. Negative ion yields are obtained as a function of the electron beam energy. The electron energy scale and the electron energy resolution are calibrated to within ± 0.2 eV using the well-known $\text{SF}_6^-/\text{SF}_6$ signal near 0 eV and the resonances of the F^-/SF_6 and F_2^-/SF_6 anions at higher electron energies.

Enflurane was purchased from Chempur. All other samples were purchased from Sigma-Aldrich with a minimum stated purity of 99%. Enflurane, isoflurane and pentachloroethane are liquid at room temperature and were degassed by a repeated freeze-pump-thaw cycle prior to experiments. Hexachloroethane is solid at room temperature but with a sufficient vapour pressure for it to be admitted into vacuum without the need for heating.

3. Computational details

To aid in the interpretation of the experimental results, we have used several high-level extrapolation schemes for the determination of diverse quantum chemical properties, such as binding energies, (adiabatic) electron affinities and reaction thresholds. In particular we compare results from G3(MP2) [3], G4(MP2) [4] and CBS-4M [5, 6] which yield similar accuracy. CBS-4M yields a mean absolute deviation (MAD) of 2.0 kcal/mol for the G2 test set [7], G3(MP2) yields a MAD of 1.3 kcal/mol for the G2/97 test set [8, 9], whereas G4(MP2) yields the lowest MAD of 1.04 kcal/mol for the G3/05 test set [10]. A comparison of different extrapolation schemes is often valuable as they might yield worse performance in individual cases than reflected by the average accuracy evaluated for selected systems in the respective test sets. For instance, it is well-known that G3(MP2) is (on average) more suitable for the hydrogen bonded complexes in the G3/05 test set. In general, it is found that G3(MP2) and G4(MP2) energies are very similar, whereas CBS-4M exhibits convergence problems for a few fragments under consideration. Therefore we shall restrict ourselves to reporting energies from G4(MP2) level of theory. In the case of isomers we take the one providing the

lowest energy. Note, for comparison of the theoretically derived values with the experimental data, the former corresponds to the threshold of a resonance rather than the position of its maxima.

In addition to the above we employed the MP2/6-311++G(3df,2p) level of theory and its density to visualize the natural orbitals of the parent transient negative ions (TNIs). All calculations were performed using the Gaussian 09 suite of programs [11].

4. Results and discussion

Electron capture by a polyatomic molecule generates a TNI, which is seen as a quasi-bound state embedded in the auto-detachment continuum and unstable towards the loss of the extra electron. Therefore, the TNI may either be subject to auto-detachment or fragmentation (DEA). In the latter case, the TNI can decompose via single bond cleavages or undergo structural rearrangement. Symbolically these two processes can be written as:



where $(ABC)^{* -}$ represents the TNI. In the case of isoflurane, enflurane and pentachloroethane, the computational work shows that optimization of the anionic state results in significant geometrical changes compared to the neutral molecule promoting the formation of a chloride ion and a neutral fragment rather than a single covalently bound anionic compound as can be seen in Figure 1A-C. In contrast, for the optimized anionic hexachloroethane the excess charge is distributed over two distant chlorine atoms in para position. The highest occupied natural orbitals (HONOs) plotted in Figures 1A-C correspond nicely to the HONO of an isolated chloride ion. However, for hexachloroethane we observe a much delocalized HONO, see Figure 1D. The two previously mentioned distant chlorine atoms (left- and right-chlorine atoms in Figure 1D) show σ^* like bonding character, whereas the other chlorine atoms yield π^* bonding character overall weakening all C-Cl bonds. These calculations suggest that no parent anions will be observed in the experiment, because within the detection time of a few microseconds the parent anion would have dissociated. Table 1 and Table 2 provide the computational calculations of the threshold energies for formation of the experimentally observed product anions via single bond cleavages for the anaesthetics and chloroethanes, respectively. Results were obtained at G4(MP2) and CBS-4M level of theory.

In agreement with the theoretical predictions and despite the high sensitivity of the instrument, we were not able to detect any parent anion, instead DEA dominates. This indicates that auto-detachment or fragmentation occurs in a time window shorter than the detection time, resulting in the absence of an observable parent negative ion. The m/z values of the most significant anion products resulting from DEA are listed in Table 3 and 4 for the anaesthetics and chlorinated ethanes, respectively, together with their possible assignments and the peak position of the corresponding resonances. The error in the peak positions is considered to be ± 0.2 eV, based on shifts of calibration peaks during the run of an experiment. For all compounds the dominant product anion is Cl^- . However, a surprising result is that although the elimination of Cl^- resulting from electron attachment to the anaesthetics is exothermic (Table 1), the resonance for Cl^- production peaks at relatively high electron energy (0.9 eV and 0.6 eV for enflurane and isoflurane, respectively). This experimental result therefore indicates that there must be an energetic barrier for zero energy electron attachment, explaining the results from the IMS study.

4.1. Anion Mass Spectra

Negative ion mass spectra are presented to provide an overview of the product anions at the electron energy corresponding to the peak resonance with the largest intensity. These spectra give an indication of the relative intensities of the product anions. For ease of comparison, intensities have been normalised relative to the dominant anion Cl^- which has been given an intensity of 1. Figure 2 shows the negative ion mass spectra of isoflurane and enflurane measured at 0.9 eV electron energy (corresponding to the lowest energy resonance peak observed for enflurane and close to that for isoflurane). In contrast to the anaesthetics, the chloroethanes have their dominant resonance closer to 0 eV. Therefore, Figure 3 shows the mass spectra for the anions formed by DEA to pentachloroethane and hexachloroethane at an electron energy of approximately 0 eV. Again for ease of comparison the intensities of all the anions have been normalised to that of Cl^- which has been set at a value of 1. As mentioned above, Cl^- is by far the most dominant anion product. However, for both the chloroethanes Cl_2^- and for pentachloroethane HCl_2^- are non-negligible product anions. The production of the anions is discussed in more detail in the following section.

4.2 Electron Attachment Energy Resonances

Figures 4-6 and figures 7-8 provide electron energy scans for all the observed product anions for the anaesthetics and the chloroethanes, respectively. Again to aid comparison, for these

figures we have set the maximum peak intensity to one if an identical product anion was observed for the two molecules. Energy resolution plays a crucial role on the shape of the low energy resonances which are typically at electron energies of less than 4 eV, but it is not so relevant for the high-energy region owing to the broad nature of the observed features. The negative ion states at energies above 4 eV, can be considered to be formed via core excited resonances, which means, transient anions with the extra electron bound to an electronically excited state of the neutral. Moreover, the energy features in the range 9–11 eV can also be associated to Rydberg excitations [12].

4.2.1 Anion Yield Curves for Isoflurane and Enflurane ($C_3H_2ClF_5O$)

For ease of discussion, the anion yields of isoflurane and enflurane obtained in the DEA experiments have been placed into one of four groups (i) – (iv) according to their intensities. In order of relative intensities we have (i) Cl^- (35 u) and HF_2^- (39 u); (ii) F^- (19 u), CFO^- (47 u) and the species at m/z 67 and 116 where the former can be assigned to CHF_2O^- and the latter to $C_2ClF_3^-$; (iii) anions at m/z 55, 59, 79, 113 and 133, which are assigned as $HClF^-$, C_2FO^- , $C_2HF_2O^-$, $C_2ClF_2O^-$ and $C_2HCIF_3O^-$, respectively; (iv) anions at m/z 83, 85 and 164 are only observed to come from DEA of enflurane and are assigned to $C_2H_2F_3^-$, $CClF_2^-$, $C_3H_2ClF_5^-$, respectively, whereas m/z 183 is only observed to result from DEA of isoflurane and is identified to be $(M-H)^-$.

4.2.1.1 Ion yields of Cl^- (35 u) and HF_2^- (39 u)

Cl^- is formed via rearrangement of the molecule upon electron attachment (see Figure 1) and subsequent expulsion of the chloride ion, whereas HF_2^- formation requires breaking at least two of the five C–F bonds and one of the C–H bonds.

The maximum ion yield of Cl^- is observed at electron energies of 0.9 and 0.6 eV for enflurane and isoflurane, respectively. The energy balance at G4(MP2) level of theory predicts in both cases an exothermic reaction. Optimized geometries are used in these calculations, and therefore given that the neutral fragment $(M-Cl)$ undergoes substantial geometrical changes in comparison to the structure shown Figure 1, there is a lowering the total energy of the products.

The formation of HF_2^- is endothermic with a reaction threshold of 1.73 eV for enflurane. It is of note that the complementary exothermic DEA reactions, i.e. formation of the heavy anions $(C_3H_2ClF_5O-Cl)^-$ and $(C_3H_2ClF_5O-HF_2)^-$ are absent meaning that the charge remains on the small fragments as the TNI dissociates.

The ionic yields of Cl^- and HF_2^- upon DEA to isoflurane and enflurane are shown in Figure 4B and 4C, respectively. It is to be noted that the anion efficiency curves measured show a full width at half maximum (FWHM) greater than the electron energy resolution (~ 1 eV). This can be related to high initial kinetic energy of these low-mass fragments. The strong extraction fields of the sector field instrument enhance substantially higher ion collection efficiency. The chloride ion provides a considerable contribution to the total anion formation, particularly via its low-energy resonance at ~ 0.9 eV for enflurane and ~ 0.6 eV for isoflurane.

4.2.1.2 Ion yields of F^- (19 u), CFO^- (47 u), CHF_2O^- (67 u) and C_2ClF_3^- (116 u)

Figures 4 and 5 present the yields of the fragment anions for F^- , CFO^- , CHF_2O^- and C_2ClF_3^- . DEA leading to CFO^- , CHF_2O^- and C_2ClF_3^- formation, require considerable rearrangement. Comparisons between isoflurane and enflurane anion efficiency curves show clear distinctions in regard to the lowest resonance peak position maxima (see Table 3) whilst for the higher energy resonances (> 8 eV) such differences are not present. Such behaviour can be due to the identical nature of the possible Rydberg states contributing to these resonances, i.e. in the two-particle one-hole mechanism, the delocalized electron may experience the same interaction of the cationic core in both isomeric volatile anaesthetics.

4.2.1.3 Ion yields of HCIF^- (55 u), C_2FO^- (59 u), $\text{C}_2\text{HF}_2\text{O}^-$ (79 u), $\text{C}_2\text{ClF}_2\text{O}^-$ (113 u) and $\text{C}_2\text{HCIF}_3\text{O}^-$ (133 u)

These set of anions have the lowest intensities detected and constitute relative to Cl^- formation just 0.03–0.6% for isoflurane and 0.04–1.0% for enflurane of the total anion signal. The resonance peak positions are shown in figures 4-5 and are listed in Table 3. The fragment ion $\text{C}_2\text{HF}_2\text{O}^-$ shows a weak resonance structure at 3.2 eV for enflurane which is absent for isoflurane.

4.2.1.4 Ion yields of $\text{C}_2\text{H}_2\text{F}_3^-$ (83 u), CClF_2^- (85 u), $\text{C}_3\text{HCIF}_4\text{O}^-$ (164 u) and $\text{C}_3\text{HCIF}_5\text{O}^-$ (183 u)

Figure 6 shows the yields of the fragment ions resulting only from enflurane at 83, 85, and 164 u and from isoflurane at 183 u. The 83 u anion is assigned to be $\text{CHF}_2\text{-CHF}^-$. 85 u is attributed to CClF_2^- . 164 u is assigned to be $\text{C}_3\text{HCIF}_4\text{O}^-$.

The dehydrogenated parent anion at 183 u is only observed for isoflurane. Our calculated values for the threshold energies are in a range of 1.69 – 2.38 eV depending on the site of hydrogen loss. A major difference between the two isomeric volatile anaesthetics

becomes apparent. The lowest threshold energies for the dehydrogenated enflurane and isoflurane anions are at 2.11 and 1.69 eV, respectively. A possible explanation for the absence of the dehydrogenated enflurane anion is competing channels. In the case of enflurane, threshold energies for the formation of F^- and $(M-Cl)^-$ via single bond cleavages (see Table 3), are below the dehydrogenated enflurane anion threshold value, whereas in the case of isoflurane only the F^- channel is competitive according to our calculations within the estimated accuracy of 0.2 eV. Thus it is not possible to determine the most favourable channel solely from theory. However, from the experimental resonance energies we can determine that F^- is formed at higher electron energies than the calculation suggests (see Table 1). Also we can rule out $(M-Cl)^-$ since it is not experimentally observed. We note, that there are some fragments formed well below the range of the $(M-H)^-$ thresholds, i.e. Cl^- and $C_2HClF_3O^-$ (see Table 1 and 3). Owing to the resonant nature of DEA, these two channels do not compete in the formation of the dehydrogenated parent anion for both volatile anaesthetics under consideration.

The results provided in Table 3 reveal a multitude of resonance energies close to the lowest calculated threshold energies for the formation of the dehydrogenated parent anions. HF_2^- , CFO^- , $HCIF^-$, C_2FO^- , $C_2H_2F_3^-$, CF_2Cl^- and $C_2ClF_3^-$ are formed via multiple bond cleavages, and are thus less likely to occur than the simple $(M-H)^-$ channel. Although CHF_2O^- can be formed via a single bond cleavage, it will not be in competition with the formation of formation of the dehydrogenated parent anion. Owing to enhanced Coulomb and Pauli repulsion in the vicinity of the lone pair electrons of the oxygen atom, the attachment of a free electron in this region of the molecule is less likely. Hence, it appears that for enflurane the lack of an $(M-H)^-$ anion for enflurane is considered to the result of having a more favourable channel F^- . In contrast, in the case of isoflurane there are no other channels able to compete with $(M-H)^-$ formation at the resonance energy.

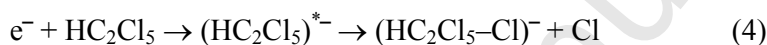
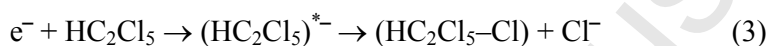
4.2.2 Anion Yield Curves for the chlorinated ethanes, $C_2HCl_5^-$ and $C_2Cl_6^-$

The anion efficiency curves of the most intense fragment anions observed in the negative ion mass spectra of pentachloroethane and hexachloroethane are shown in Figures 7 and 8, where the most intense DEA signals can be found close to 0 eV. Several fragment anions are also formed in an extended electron energy range showing resonance features at around 3 and 8 eV. However, the intensities of these high-energy resonances is for most of the fragment anions at least one order of magnitude lower than the feature close to 0 eV.

The fragment anions assigned in DEA experiments to pentachloroethane (HC_2Cl_5) and hexachloroethane (C_2Cl_6) are given in Table 4 and these will be discussed below. Given the larger number of product anions observed for pentachloroethane, for ease of discussion the anion yields has been separated into three different groups depending on intensities. The first group is Cl^- and HC_2Cl_4^- , the second contains Cl_2^- , HCl_2^- and C_2Cl_4^- , and the third CCl_2^- and CCl_3^- .

4.2.2.1 Ion yields of Cl^- (35 u) and HC_2Cl_4^- (165 u) from pentachloroethane

The anions Cl^- and HC_2Cl_4^- are formed via complementary DEA processes:



Figures 7 and 8 show the ion yield curve for Cl^- and $(\text{HC}_2\text{Cl}_5-\text{Cl})^-$, respectively. G4(MP2) calculations show that for zero energy electrons reactions (3) and (4) are exothermic (see Table 2).

In contrast to its complementary fragment anion, HC_2Cl_4^- , which is restricted to the ~ 0 eV resonance, the Cl^- signal extends to higher energies (see Figure 7). If we assume that the excess energy of the transient negative ion $(\text{HC}_2\text{Cl}_5)^{-*}$ is statistically distributed over the vibrational degrees of freedom, the large fragment should take about 93% of the energy obtained from the electron attachment. In the case of Cl^- the neutral counterpart will become increasingly unstable towards dissociation which does not influence the anion efficiency curve of Cl^- . However, if the charge stays on the heavy fragment, the excess energy will drive further decomposition into lower mass fragments and thus the anion yield for 165 u at higher electron energies will be suppressed. Of relevance, is the fact that the heavier fragment anions (82 and 117 u) show a resonance at medium energies (~ 3 eV) with suppression of the high energy feature ($\sim 7-8$ eV) while the lighter fragment anion (70 u) also exhibits the high energy resonance (see Figures 7 and 8). This indicates that the subsequent decomposition of $(\text{HC}_2\text{Cl}_5-\text{Cl})^{-*}$ may contribute to the formation of these anions.

4.2.2.3 Ion yields of Cl_2^- (70 u), HCl_2^- (71 u) and C_2Cl_4^- (164 u) from pentachloroethane

These product anions are mainly formed at virtually no electron kinetic energy (~ 0 eV), arising from surprisingly complex reactions associated with multiple bond cleavages and structural and electronic rearrangement. This is in line with our G4(MP2) calculations

yielding -0.89, -0.35 and -0.2 eV for the threshold energies for the formation of Cl_2^- , HCl_2^- and C_2Cl_4^- from pentachloroethane, respectively. Fragment anions 71 u and 164 u assigned to HCl_2^- and C_2Cl_4^- , respectively, are formed at 0 eV resonance only, whereas Cl_2^- shows an extra resonance feature at ~ 7 eV (see Table 4). Above an electron energy of 10 eV, the anionic signal intensity is observed to slightly increase which could be a result of ion-pair formation.

4.2.2.4 Ion yields of CCl_2^- (82 u) and CCl_3^- (117 u) from pentachloroethane

The shape and position of the only resonance feature at ~ 3 eV for the fragment anion CCl_2^- (82 u) and CCl_3^- (117 u) are very similar, which may indicate that these anions have common precursor transient anion states. CCl_2^- and CCl_3^- formation are endothermic with a threshold of 1.36 and 1.16 eV, respectively. From Figures 7 and 8 we note that the experimental appearance energy is around 1.5 eV, a value which, within the current electron energy resolution of ~ 1 eV, is in good agreement with the calculated threshold.

4.2.2.5 Ion yields of Cl^- (35 u), Cl_2^- (70 u), CCl_3^- (117 u) and C_2Cl_5^- (199 u) from hexachloroethane

DEA to C_2Cl_6 is found to result in four fragment anions; Cl^- , Cl_2^- , CCl_3^- and C_2Cl_5^- , of which three (Cl^- , Cl_2^- and C_2Cl_5^-) have resonance features at 0 eV (see Table 4). This is in line with our computational calculations which yield -0.67, -1.02, 0.93 and -0.13 eV for the formation of Cl^- , Cl_2^- , CCl_3^- and C_2Cl_5^- , respectively. These anions are all formed via the cleavage of one of the six C-Cl bonds and the C-C bond, whereas Cl_2^- formation requires additional internal rearrangement. It is interesting to note that CCl_3^- formation from hexachloroethane, can proceed through two resonances at 2.8 and 7.2 eV, whereas in the case of pentachloroethane it proceeds via the lowest resonance only.

5. Conclusions

In this study of the dissociative electron attachment of two volatile anaesthetics (enflurane, isoflurane) and two chlorinated ethanes (pentachloroethane, hexachloroethane), we have obtained the anionic yields measured in the electron energy range of 0 – 17 eV with an energy resolution of ~ 1 eV and a peak position accuracy of ± 0.2 eV. Such experiments have been performed in a crossed electron-molecular beam setup equipped with a double focusing two-sector field mass spectrometer with a standard Nier-type ion source.

The results show that the cross-section for the capture of an electron with virtually no kinetic energy by the volatile anaesthetics is very small. In fact the peak for electron attachment leading to the elimination of Cl^- occurs at just below 1 eV for both molecules. The opposite is true for pentachloroethane and hexachloroethane, for which there are zero electron attachment energy resonances with large cross-sections. These results explain our observations of the low and high electron attachment efficiencies of the anaesthetics and chlorinated ethanes, respectively, observed in the swarm (low mean electron energy) environment of an IMS system. We have proposed that the absence of zero energy electron attachment resonances for the anaesthetics results from an energy barrier. The onset of the low energy resonances for isoflurane and enflurane are in good agreement with the VAE values that we have calculated.

Although isoflurane and enflurane are isomers, interestingly they exhibit different DEA patterns. Only in the case of isoflurane it is possible to detect a dehydrogenated parent anion, whereas in the case of enflurane this fragmentation channel turns out to be entirely suppressed due to other dominant channels being available at the electron energy region for its formation, i.e. for $(\text{M-Cl})^-$ and F^- . In the case of enflurane additional anions at mass 83 and 85 u have been detected. We propose that the high-energy attachment resonances in these isomers must originate from core-excited resonances, consisting of two electrons in normally unoccupied molecular orbitals moving in the field of the positive core.

The most dominant signal from DEA reactions to the chlorinated ethanes is the formation of Cl^- at electron energies ~ 0 eV and ~ 7 eV, the latter with a yield an order of magnitude lower than the former. The second most intense ion signal assigned to Cl_2^- shows also the same energy positions for these two resonances. Other reactions like the loss of several other neutral units with an onset of the resonant ionic yields at zero energy are observed as well.

Acknowledgments

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Figure captions

Figure 1. Highest occupied natural orbitals for the anionic states of (A) Enflurane, (B) Isoflurane, (C) Pentachloroethane, and (D) Hexachloroethane. Visualisation of the natural orbitals obtained using MP2/6-311++G(3df,2p) density.

Figure 2. Negative ion mass spectrum of isoflurane (upper panel) and enflurane (lower panel) measured at 0.9 eV electron energy. For ease of comparison both graphs were normalised to the highest signal intensity (Cl^-), which is set at a value of 1.

Figure 3. Negative ion mass spectrum of hexachloroethane (upper panel) and pentachloroethane (lower panel) measured at ~ 0 eV electron energy. For ease of comparison both graphs were normalised to the highest signal intensity (Cl^-), which is set at a value of 1.

Figure 4. Anion efficiency curves of the isoflurane (black solid line) and enflurane (light-grey solid line) for the fragment ions (A) F^- , (B) Cl^- , (C) HF_2^- , (D) CHF_2O^- , and (E) C_2ClF_3^- . The width of the electron energy distribution is about 1 eV. For ease of comparison, the highest peak for each anion efficiency curve for both molecules have been normalised to a signal intensity of one.

Figure 5. Anion efficiency curves of the isoflurane (black solid line) and enflurane (light-grey solid line) for the fragment ions (A) CFO^- , (B) HCIF^- , (C) C_2FO^- , (D) $\text{C}_2\text{HF}_2\text{O}^-$, (E) $\text{C}_2\text{ClF}_2\text{O}^-$, and (F) $\text{C}_2\text{HClF}_3\text{O}^-$. The width of the electron energy distribution is about 1 eV. For ease of comparison, the highest peak for each anion efficiency curve for both molecules have been normalised to a signal intensity of one.

Figure 6. Anion efficiency curves of the isoflurane (black solid line) and enflurane (light-grey solid line) fragment ions (A) $\text{C}_2\text{H}_2\text{F}_3^-$, (B) CClF_2^- , (C) $\text{C}_3\text{H}_2\text{ClF}_5^-$, and (D) $(\text{M-H})^-$. The width of the electron energy distribution is about 1 eV.

Figure 7. Anion efficiency curves of the pentachloroethane (light-grey solid line) and hexachloroethane (black solid line) of the fragment ions: Cl^- (upper panel), Cl_2^- (middle panel), and CCl_3^- (lower panel). The width of the electron energy distribution is about 1 eV. For ease of comparison, the highest peak for each anion efficiency curve for both molecules have been normalised to a signal intensity of one.

Figure 8. Anion efficiency curves of the pentachloroethane (light-grey solid line) and hexachloroethane (black solid line) fragment ions (A) HCl_2^- , (B) CCl_2^- , (C) C_2Cl_4^- , (D) HC_2Cl_4^- , and (E) C_2Cl_5^- . The width of the electron energy distribution is about 1 eV.

Table captions

Table 1. Calculated threshold energies for formation of anions via single bond cleavages for the anaesthetics. Results are obtained at G4(MP2) level of theory. Several numbers are given if more than one abstraction sites are possible. All energies are given in eV.

Table 2. Calculated threshold energies for formation of anions via single bond cleavages for the chloroethanes. Results are obtained at G4(MP2) level of theory. All energies are given in eV.

Table 3. Peak positions (eV) for the observed resonances corresponding to fragment anions of enflurane and isoflurane obtained in the DEA experiment.
(m/z of the dominant isotopes are only given.)

Table 4. Peak positions (eV) for the observed resonances corresponding to fragment anions of pentachloroethane and hexachloroethane obtained in the DEA experiment.
(m/z of the dominant isotopes are only given.)

Figure 1 – width: 1 column

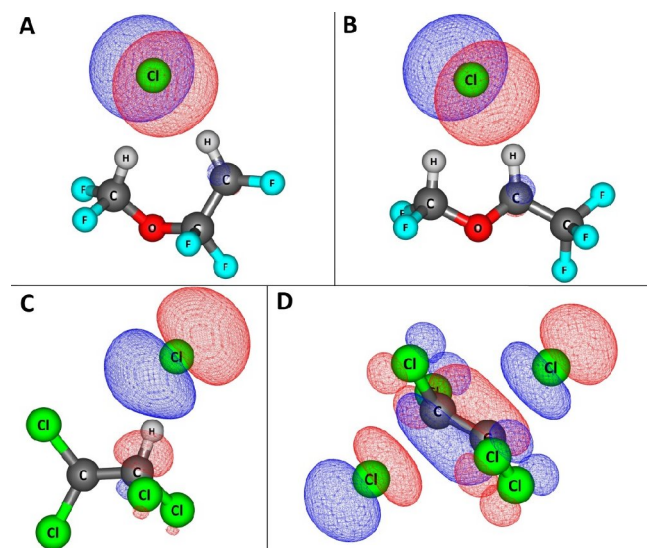


Figure 2 – width: 1 column

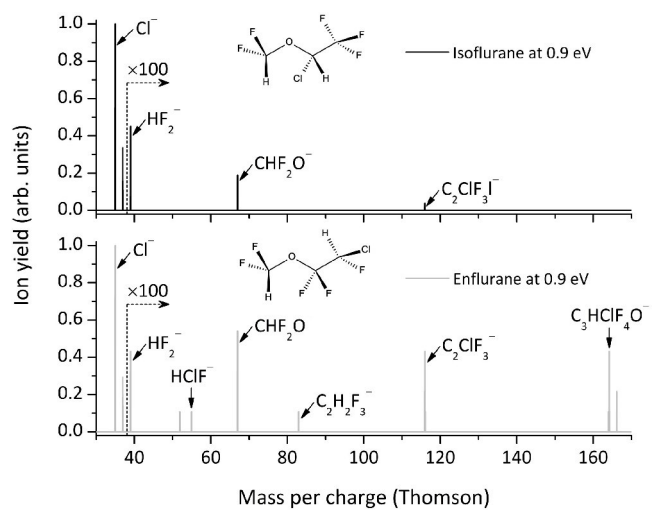


Figure 3 – width: 1 column

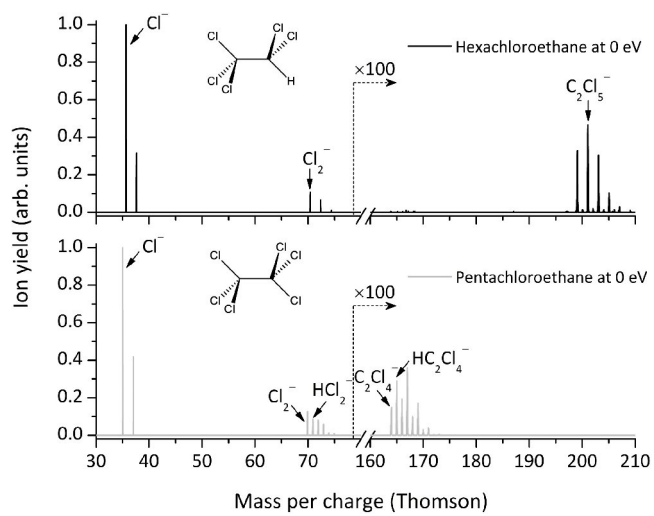


Figure 4 – width 1 column

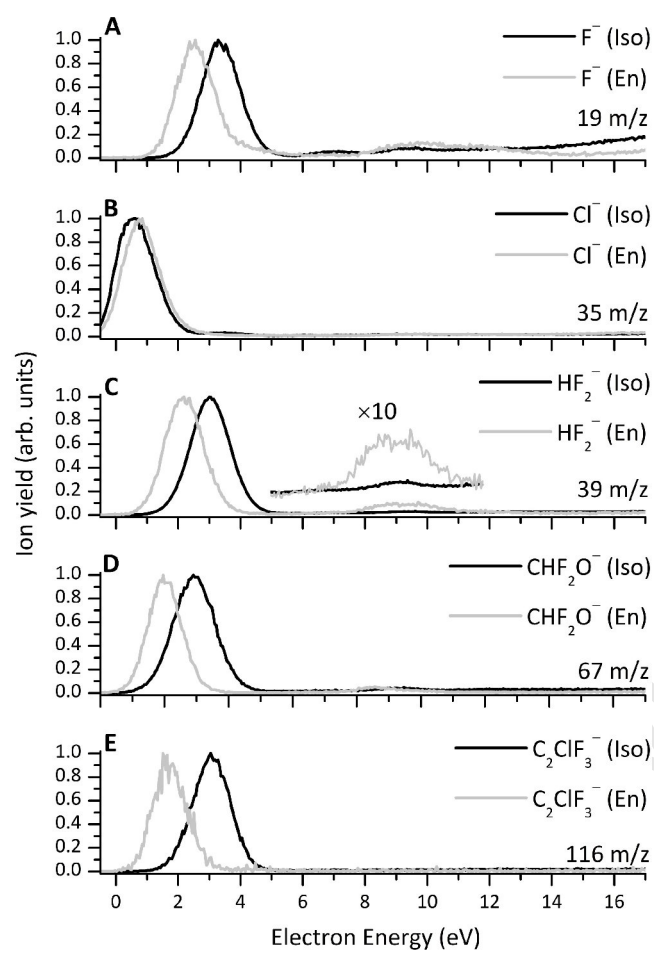


Figure 5 – width: 1 column

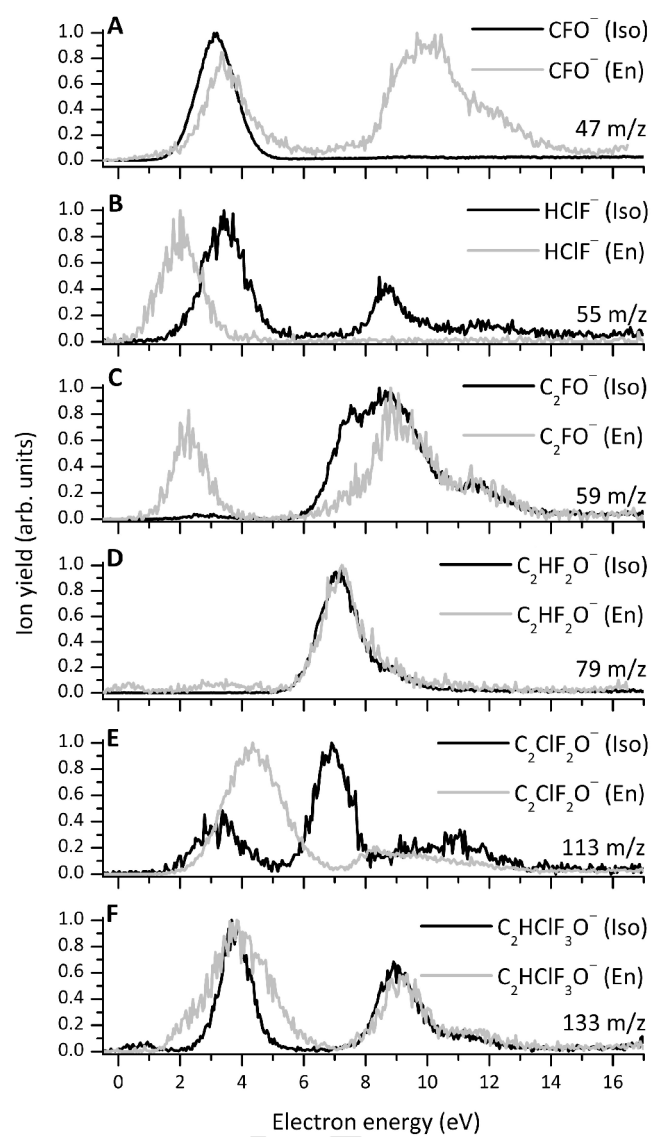


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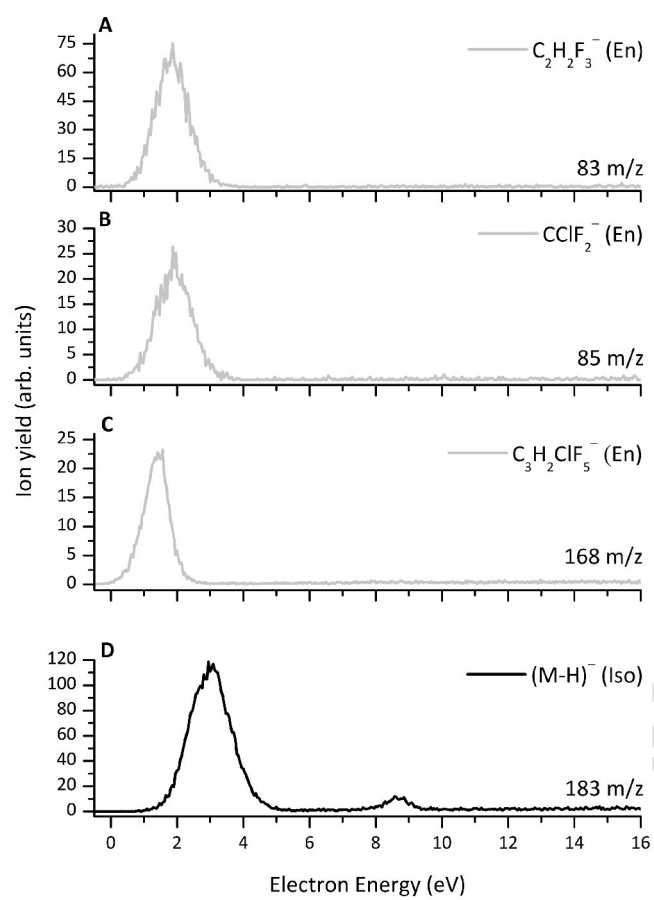


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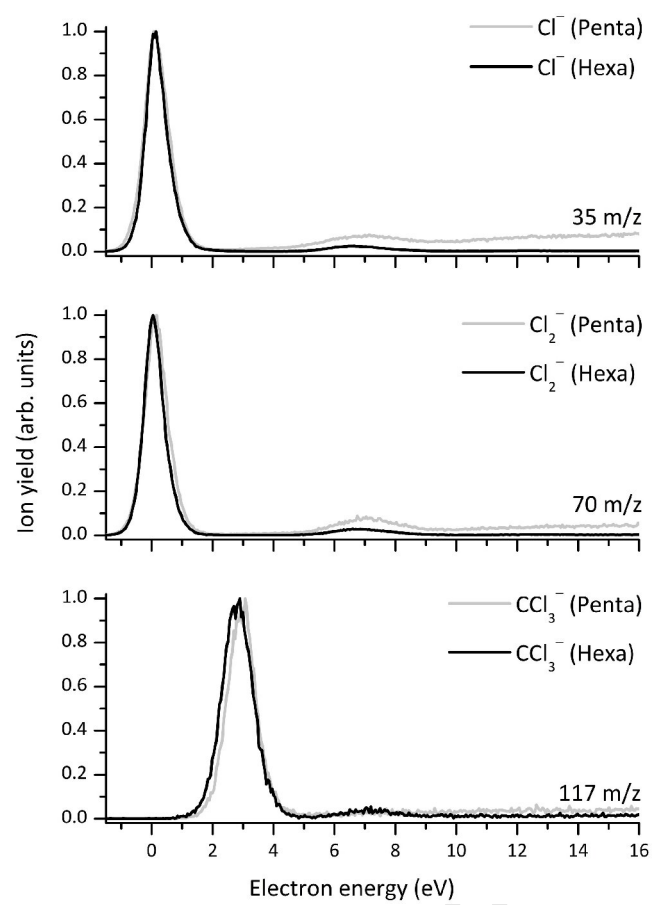


Figure 8 – width: 1 column

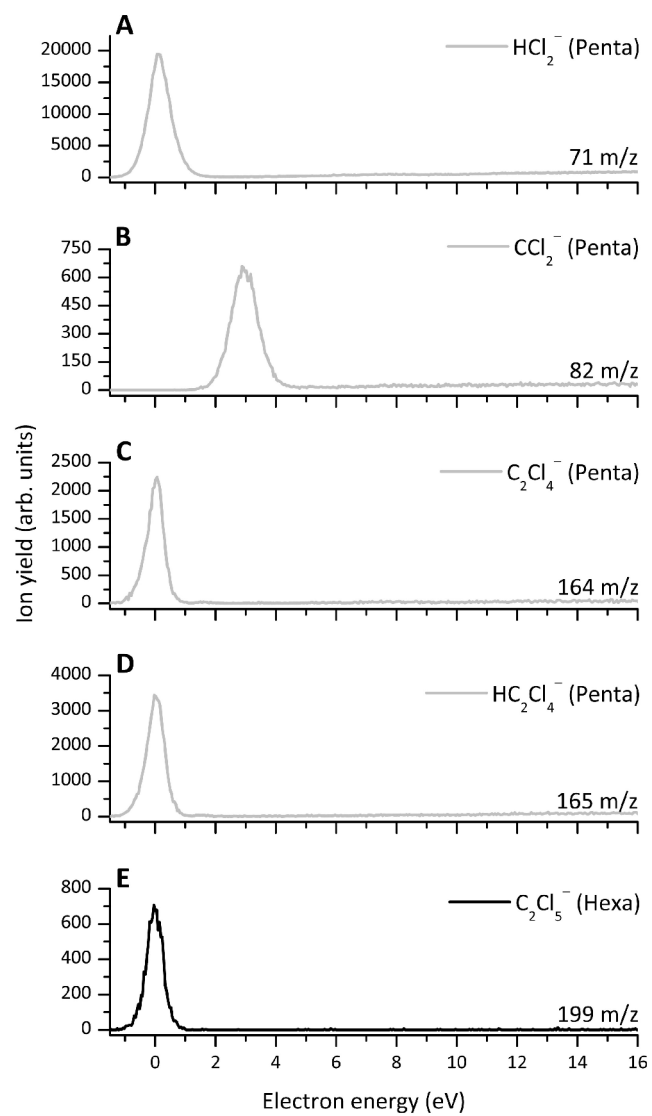


Table 1

| Anion Fragment | Enflurane | Isoflurane |
|-----------------------------|--------------------|--------------|
| | G4(MP2) (eV) | G4(MP2) (eV) |
| (M-H) ⁻ | 2.11 / 2.37 | 1.69 / 2.28 |
| (M-Cl) ⁻ | 1.92 | 2.02 |
| F ⁻ | 0.98 / 1.62 / 1.66 | 1.58 / 1.76 |
| Cl ⁻ | -0.23 | -0.38 |
| Adiabatic electron affinity | | |
| M | 1.25 | 1.52 |
| M-H | 2.00 / 1.96 | 2.29 / 1.96 |
| M-Cl | 1.49 | 1.84 |
| F | 3.50 | 3.50 |
| Cl | 3.64 | 3.64 |

Table 2

| Anion fragment | Pentachloroethane | Hexachloroethane |
|------------------------------|-------------------|------------------|
| | G4(MP2) (eV) | G4(MP2) (eV) |
| (M-Cl) ⁻ | -0.29 | -0.13 |
| Cl ₂ ⁻ | -0.89 | -1.02 |
| Cl ⁻ | -0.64 | -0.67 |
| Adiabatic electron affinity | | |
| M | 1.44 | 1.22 |
| M-Cl | 3.11 | 3.29 |
| Cl ₂ | 2.37 | 2.37 |

Table 3

| m/z (amu) | Anionic species | Peak positions in eV ^a | | | | | | | | | | | | | |
|-------------|---|-----------------------------------|-----|-----|-----|-----|-----|------|------------|-----|-----|-----|-----|------|------|
| | | Enflurane | | | | | | | Isoflurane | | | | | | |
| 19 | F ⁻ | – | 2.6 | – | – | – | 9.5 | 11.7 | – | – | 3.3 | 7.1 | 9.3 | – | – |
| 35 | Cl ⁻ | 0.9 | – | – | – | – | 9.4 | – | 12.2 | 0.6 | 3.3 | – | 9.2 | – | 12.6 |
| 39 | HF ₂ ⁻ | – | 2.2 | – | – | – | 9.3 | – | – | – | 3.0 | 6.9 | 9.5 | – | – |
| 47 | CFO ⁻ | – | – | 3.5 | – | – | 9.9 | – | 12.1 | – | 3.0 | – | 9.3 | – | 13.1 |
| 55 | HClF ⁻ | – | 2.0 | – | – | – | – | – | – | – | 3.4 | – | 8.7 | 11.9 | – |
| 59 | C ₂ FO ⁻ | – | 2.3 | – | – | 7.1 | 9.0 | 11.3 | – | – | 2.8 | 7.3 | 8.8 | 11.5 | – |
| 67 | CHF ₂ O ⁻ | – | 2.0 | – | – | 8.6 | 9.8 | – | – | – | 2.9 | – | 9.2 | – | – |
| 79 | C ₂ HF ₂ O ⁻ | – | – | 3.2 | 7.1 | 8.7 | – | – | – | – | – | 7.1 | 8.7 | – | – |
| 83 | C ₂ H ₂ F ₃ ⁻ | – | 1.8 | – | – | – | – | – | – | – | – | – | – | – | – |
| 85 | CClF ₂ ⁻ | – | 1.9 | – | – | – | – | – | – | – | – | – | – | – | – |
| 113 | C ₂ ClF ₂ O ⁻ | – | – | 4.4 | – | 8.3 | 9.6 | – | – | – | 3.3 | 6.9 | – | 10.9 | – |
| 116 | C ₂ ClF ₃ ⁻ | – | 1.7 | – | – | – | – | – | – | – | 3.1 | – | – | – | – |
| 133 | C ₂ HClF ₃ O ⁻ | – | – | 3.9 | – | – | 9.1 | 11.3 | – | 0.7 | 3.8 | – | 9.0 | 10.7 | – |
| 164 | C ₃ HClF ₄ O ⁻ | – | 1.4 | – | – | – | – | – | – | – | – | – | – | – | – |
| 183 | C ₃ HClF ₅ O ⁻ | – | – | – | – | – | – | – | – | – | 3.0 | – | 8.6 | – | – |

^aEstimated uncertainty in the peak value is ± 0.2 eV, based on shifts in calibration peaks during the run of an experiment.

Table 4

| Mass (amu) | Anionic species | Peak positions in eV ^a | | | | | | |
|------------|--|-----------------------------------|-----|-----|------------------|-----|-----|------|
| | | Pentachloroethane | | | Hexachloroethane | | | |
| 35 | Cl ⁻ | 0.1 | – | 7.2 | 0.1 | – | 6.8 | 12.5 |
| 70 | Cl ₂ ⁻ | 0.1 | – | 7.1 | 0.1 | – | 6.9 | 12.7 |
| 71 | HCl ₂ ⁻ | 0.1 | – | 7.9 | – | – | – | – |
| 82 | CCl ₂ ⁻ | – | 3.0 | – | – | – | – | – |
| 117 | CCl ₃ ⁻ | – | 3.0 | – | – | 2.8 | 7.2 | – |
| 164 | C ₂ Cl ₄ ⁻ | 0.0 | – | 8.0 | – | – | – | – |
| 165 | HC ₂ Cl ₄ ⁻ | 0.0 | – | – | – | – | – | – |
| 199 | C ₂ Cl ₅ ⁻ | – | – | – | 0 | – | – | – |

^aEstimated uncertainty in the peak value is ± 0.2 eV, based on shifts in calibration peaks during the run of an experiment.