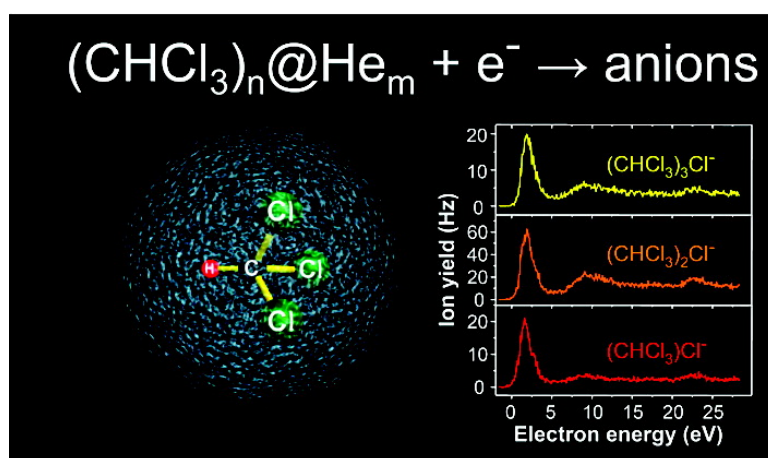Article

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# Inelastic Electron Interaction with Chloroform Clusters embedded in Helium Droplets

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***Abstract:*** The inelastic electron interaction (ionization/attachment) with chloroform embedded in helium droplets has been studied utilizing a two-sector field mass spectrometer. Positive mass spectra have been recorded at the electron energy of 70 eV and are compared with previous results in the gas phase and with other systems embedded in helium droplets. Moreover, the negative ion mass spectrum has been recorded at the electron energy of 1.5 eV. Both negative and positive mass spectra show that chloroform clusters are easily formed by embedding single molecules in the helium droplets. Moreover, for anions appearing in the mass spectrum, the ion yield has been determined as function of the electron energy. While no parent anion of chloroform can be observed in the gas phase, the present cluster environment allows the stabilization of the transient negative ion. The influence of the helium droplet upon the ionization or attachment process of the embedded chloroform is discussed.

## 1. Introduction

Chloroform ($CHCl_3$), belongs to the class of halogenated hydrocarbons which are of relevance in atmospheric chemistry and also in biochemistry.[1,2] These molecules found also practical applications in plasma etching[3] and gas phase dielectrics.[4] Especially the behavior upon electron attachment is of great interest as halogenated hydrocarbons possess high cross sections for low energy electrons.[5] Thus, electron attachment to halogenated methanes in the gas phase has been investigated many times in experimental and theoretical studies.[6–15] Most studies focused on the determination of the vertical attachment energies,[6–8] the total dissociative attachment cross section[9–12]

and the ion yield of mass selected fragment anions as a function of the electron energy.[13–15] In the latter studies it turned out that chloroform always dissociates upon electron attachment (most efficiently below 1 eV) with the captured electron becoming part of the chlorine anion.[13–15] This is attributed to the high electron affinity of the halogen radicals (EA(X) = 3.40, 3.61, and 3.36 eV for X = F, Cl, and Br, respectively[16]). For many chlorinated molecules the dissociative electron attachment (DEA) process then becomes energetically exothermic, i.e. the dissociation limit of the chlorine anion and the neutral fragment is below the ground state of the neutral molecule.[17,18] Recently we studied DEA to isolated chloroform in the gas phase,[19] utilizing two different experimental setups, (i) a two-sector field mass spectrometer with very high sensitivity and (ii) a hemispherical electron monochromator providing high electron energy resolution. In this study we were able to observe 10 anions formed via DEA to chloroform.[19] In contrast, formation of positive ions of chloroform by means of electron impact has been less intensively studied than that of negative ions. In the NIST database[16] the mass spectra recorded at 70 eV and appearance energy values of various fragment ions are given. Moreover, determinations of the ionization energy of chloroform by means of photoionization and photoelectron spectroscopy can also be found in ref 16, and a photoionization mass spectrum of chloroform with the use of a helium lamp (photon energy: 21.21 eV) is reported in ref 20.

(1) Kley, D.; Crutzen, P. J.; Smit, H; G, J.; Vömel, H.; Oltmans, S. J.; Grassl, H.; Ramanathan, V. *Science* **1996**, *274*, 230–233, and references cited therein.
(2) Bass, A. D.; Gamache, J.; Ayotte, P.; Sanche, L. *J. Chem. Phys.* **1996**, *104*, 4258–4266, and references cited therein.
(3) Field, D.; Jones, N. C.; Lunt, S. L.; Ziesel, J.-P.; Gulley, R. J. *J. Chem. Phys.* **2001**, *115*, 3045–3052.
(4) VanBrunt, R. J. *J. Appl. Phys.* **1987**, *61*, 1773–1787.
(5) Christodoulides, A. A.; Schumacher, R.; Schindler, R. N. *J. Phys. Chem.* **1975**, *79*, 1904–1911.
(6) Burrow, P. D.; Modelli, A.; Chiu, N. S. *J. Chem. Phys.* **1982**, *77*, 2699–2701.
(7) Falcetta, M. F.; Jordan, K. D. *J. Phys. Chem.* **1990**, *94*, 5666–5669.
(8) Guerra, M.; Jones, D.; Distefano, G.; Scagnolari, F.; Modelli, A. *J. Chem. Phys.* **1991**, *94*, 484–490.
(9) Spence, D.; Schulz, G. J. *J. Chem. Phys.* **1973**, *58*, 1800–1803.
(10) Chu, S. C.; Burrow, P. D. *Chem. Phys. Lett.* **1990**, *172*, 17–22.
(11) Aflatooni, K.; Burrow, P. D. *J. Chem. Phys.* **2000**, *113*, 1455–1464.
(12) Wan, H.-X.; Moore, J. H.; Tossell, J. A. *J. Chem. Phys.* **1991**, *94*, 1868–1874.
(13) Dorman, F. H. *J. Chem. Phys.* **1966**, *44*, 3856.
(14) Johnson, J. P.; Christophorou, L. G.; Carter, J. G. *J. Chem. Phys.* **1977**, *67*, 2196–2215.
(15) Scheunemann, H.-U.; Illenberger, E.; Baumgärtel, H. *Ber. Bunsenges. Phys. Chem.* **1980**, *84*, 580–585.

(16) NIST Chemistry Web Book. http://webbook.nist.gov.
(17) *Electron-Molecule Interactions and their Applications*; Christophorou, L. G., Ed.; Academic Press: Orlando, FL, 1984; Vols. *I, II*.
(18) Matejcik, S.; Foltin, V.; Stano, M.; Skalny, J. D. *Int. J. Mass Spectrom.* **2003**, *223*, 9–19.
(19) Denifl, S.; Mauracher, A.; Sulzer, P.; Bacher, A.; Märk, T. D.; Scheier, P. *Int. J. Mass Spectrom.* **2008**, *265*, 139–145.

Recently we started another series of experiments carried out in our laboratories where we study the inelastic electron interaction with pure and doped helium droplets.[21–23] The interest in the studies of helium clusters doped with atoms or molecules[24,25] can be explained by the remarkable ability of helium droplets in picking up atoms and molecules and the subsequent possibility to create new molecular complexes inside the droplet. Helium droplets provide thereby an extremely low temperature environment at $T = 0.37$ K. Embedded neutral atoms or molecules are cooled efficiently by the transfer of their internal energy to the surrounding helium matrix. Subsequently, this excess energy is then released by thermal evaporation of the loosely bound helium atoms from the droplet. This can cause a substantial shrinking of the droplet as the binding energy of a helium atom in the droplet is only 0.6 meV.[24]

So far experiments with pure and mixed doped clusters of atmospherical and biological relevance have been mainly carried out by means of optical spectroscopy (see reviews in refs 24 and 25). Also recently several electron impact ionization studies of molecules embedded in helium droplets have been reported.[26–31] In contrast, electron attachment processes to (doped) helium droplets have been less often studied (see review in ref 32). Northby et al. proposed that electron capture to pure helium clusters is only possible in large droplets ($N > 0.75 \times 10^5$) and that electron attachment produces bubbles in the interior of the cluster.[33] Indeed the smallest pure helium cluster anion with a size of $9.3 \times 10^4$ was observed by Toennies and co-workers.[34] Moreover, electron attachment to $SF_6$, $O_2$, and $H_2O$ embedded in He clusters was observed indirectly by the decrease of the neutral cluster yield.[35] Very recently we have published the first mass spectrometric investigation of negative ions formed via electron attachment to molecules embedded in helium clusters.[23] The molecules chosen for this first study have been the nucleobases adenine, thymine and partially methylated or deuterated thymine, respectively. Previously these biomolecules were studied intensively in the gas phase where a remarkable site selectivity of the DEA was observed[36] which also remained when studying the helium droplet (see ref 23).

Here we present a detailed study of electron attachment to chloroform embedded in helium droplets which we have chosen as the first dopant in our systematic investigations with doped helium droplets which has a very high cross section in dissociative electron capture close to zero eV. We present the negative mass spectrum of chloroform recorded at the electron energy of 1.5 eV, and for anions identified in the spectra we show the corresponding ion efficiency curves in the electron energy range from about 0 eV up to about 27 eV. Keeping in mind our previous results for the biomolecules, we are also elucidating the influence of the helium matrix on the process of electron attachment to the embedded molecules by comparing the present results with previous observations for gas-phase chloroform. In addition to our study of negative ions we have also recorded the positive mass spectrum at the electron energy of about 70 eV which is compared with the mass spectrum of chloroform in the gas phase.

## 2. Experimental Setup

The present measurements are performed with a He cluster source, a pick-up chamber containing the vapor of chloroform and a double focusing mass spectrometer. More details about the mass spectrometer and the helium cluster source can be found elsewhere.[23] The helium cluster beam is formed by supersonic expansion of highly purified helium (>99.9999%) through a nozzle with an orifice of 5 $\mu$m which is cooled by a closed-cycle helium cryostat. The cryostat provides stable nozzle temperatures of 9.4 $\pm$ 0.1 K controlled by a silicon diode sensor and a resistive heater. The present experiments are carried out at helium expansion pressures in the range of 10–15 bar. The mean size of the helium droplets is estimated to be $N \approx 10^4$ under these operating conditions.[23] The He droplets pass a skimmer 1 cm downstream with a diameter of 0.8 mm and enter a differentially pumped pick-up chamber where chloroform is introduced via a gas inlet. Chloroform has been purchased from Sigma-Aldrich with a stated purity of >99%. Then the doped He droplets pass a second skimmer (diameter of 2 mm) and enter the ion source chamber. All three chambers (cluster source, pick up, and ion source, respectively) are pumped differentially by turbomolecular pumps. The ion source is a conventional Nier type ion source providing maximum electron currents up to 1 mA. The positive or negative ions produced are accelerated by 3 kV and enter a double focusing mass spectrometer. The mass-selected ions are finally detected by a channeltron type secondary electron multiplier. Mass spectra are recorded at fixed electron energies while scanning the magnet over a predefined mass range. Anion yields of mass-selected molecules and clusters are recorded as a function of the electron energy. The energy scale is determined by measuring the ion yield of a calibration gas under identical conditions. The following electron attachment reaction is used for this calibration:[37]

$$SF_6 + e \rightarrow SF_6^- \tag{1}$$

The ion yield of $SF_6^-$ exhibits a sharp peak at about 0 eV originating from s-wave attachment to the neutral molecule. The electron energy resolution is determined as the full-width at half-maximum of this zero eV peak. The present experiments with negative ions are performed with an electron energy resolution of about 1 eV and electron currents of about 5–10 $\mu$A. We estimate the accuracy of the reported peak positions to be $\pm 0.25$ eV. The electron impact ionization mass spectrum is recorded at the electron current of about 100 $\mu$A.

(20) Lago, A. F.; Santos, A. C. F.; de Souza, G. G. B. *J. Chem. Phys.* **2004**, *120*, 9547–9555.
(21) Denifl, S.; Stano, M.; Stamatovic, A.; Scheier, P.; Märk, T. D. *J. Chem. Phys.* **2006**, *124*, 054320–054328.
(22) Feil, S.; Gluch, K.; Denifl, S.; Zappa, F.; Echt, O.; Scheier, P.; Märk, T. D. *Int. J. Mass Spectrom.* **2006**, *252*, 166–172.
(23) Denifl, S.; Zappa, F.; Mähr, I.; Lecointre, J.; Probst, M.; Märk, T. D.; Scheier, P. *Phys. Rev. Lett.* **2006**, *97*, 043201–043204.
(24) Toennies, J. P.; Vilesov, A. F. *Angew. Chem., Int. Ed.* **2004**, *43*, 2622–2648, and references cited therein.
(25) Stienkemeier, F.; Lehmann, K. K. *J. Phys. B: At. Mol. Opt. Phys.* **2006**, *39*, R127–R166.
(26) Lewerenz, M.; Schilling, B.; Toennies, J. P. *J. Chem. Phys.* **1995**, *102*, 8191–8207.
(27) Ruchti, T.; Forde, K.; Callicoatt, B. E.; Ludwigs, H.; Janda, K. C. *J. Chem. Phys.* **1998**, *109*, 10679–10687.
(28) Zappa, F.; Denifl, S.; Mähr, I.; Lecointre, L.; Rondino, F.; Echt, O.; Märk, T. D.; Scheier, P. *Eur. Phys. J. D* **2007**, *43*, 117–120.
(29) Yang, S.; Brereton, S. M.; Wheeler, M. D.; Ellis, A. M. *J. Phys. Chem. A* **2006**, *110*, 1791–1797.
(30) Yang, S.; Brereton, S. M.; Wheeler, M. D.; Ellis, A. M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 4082–4088.
(31) Yang, S.; Brereton, S. M.; Wheeler, M. D.; Ellis, A. M. *Int. J. Mass Spectrom.* **2006**, *253*, 79–86.
(32) Northby, J. A. *J. Chem. Phys.* **2001**, *115*, 10065–10077.
(33) Northby, J. A.; Kim, C.; Jiang, T. *Physica B* **1994**, *197*, 426–434.
(34) Henne, U.; Toennies, J. P. *J. Chem. Phys.* **1998**, *108*, 9327–9338.
(35) Farnik, M.; Toennies, J. P. *J. Chem. Phys.* **2003**, *118*, 4176–4182.
(36) Ptasinska, S.; Denifl, S.; Scheier, P.; Illenberger, E.; Märk, T. D. *Angew. Chem., Int. Ed.* **2005**, *44*, 6941–6943.

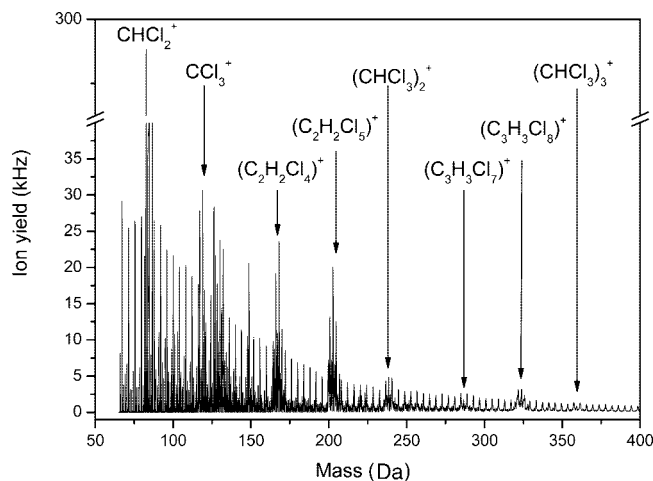(37) Christophorou, L. G.; Olthoff, J. K. *Int. J. Mass Spectrom.* **2001**, *205*, 27–41.

**Figure 1.** Positive ion mass spectrum of chloroform embedded in helium droplets in the mass range between 85 and 400 Da recorded at the electron energy of 70 eV. The most abundant peaks are designated tentatively with the corresponding molecular sum formula. Other visible peaks can be assigned to helium clusters (appearing every 4 Da) or background signal (e.g., the peak at mass 149 Da).

**Table 1.** Relative Intensities of Cations Formed upon Electron Impact Ionization of Chloroform[a] Embedded in Helium Droplets at the Electron Energy of 70 eV

| ion | mass (Da)[b] | relative intensity (arb. units) |
|---|---|---|
| $CHCl_2^+$ | 83 | 100 |
| $CCl_3^+$ | 117 | 18.2 |
| $(C_2HCl_4)^+$ | 165 | 8.7 |
| $(C_2H_2Cl_4)^+$ | 166 | 18 |
| $(C_2HCl_5)^+$ | 200 | 5.8 |
| $(C_2H_2Cl_5)^+$ | 201 | 16.5 |
| $(C_2HCl_6)^+$ | 235 | 2.0 |
| $(CHCl_3)_2^+$ | 236 | 3.7 |
| $(C_3H_3Cl_7)^+$ | 284 | 2.0 |
| $(C_3H_3Cl_8)^+$ | 319 | 3.9 |
| $(CHCl_3)_3^+$ | 354 | 0.8 |

[a] The partial pressure of chloroform in the pick up chamber is $1.2 \times 10^{-5}$ mbar. [b] Represents the lowest mass for each isotopic combination.

## 3. Results and Discussion

**3.1. Positive Ions.** Figure 1 shows the electron impact ionization mass spectrum of chloroform embedded in helium droplets recorded at the electron energy of 70 eV. The mass scan is recorded in the mass range between 65 and 400 Da. The partial pressure of chloroform in the pick-up chamber is $1.2 \times 10^{-5}$ mbar which is high enough that helium droplets can pick up a few chloroform molecules, leading to the production of chloroform clusters inside the helium droplets. Table 1 presents an overview of the chloroform cations observed within the detection limit of our apparatus. The relative intensities listed in Table 1 are derived from the sum of all isotopomers for each ion. Of course we have to note that the observation of higher-order clusters depends strongly on the experimental conditions. By far the dominant ion is $(CHCl_2)^+$ which is also the most abundant cation formed in the gas phase. For the mass spectrum of gas-phase chloroform we refer to the mass spectrum shown in the NIST database. Embedding chloroform in helium droplets has a strong effect on the abundance of the parent cation; in contrast to the NIST data we observe no appreciable amount of the parent cation, and moreover, the abundance of the dehydrogenated parent cation $(CCl_3)^+$ is increased by more than a factor of 10 in comparison

to that of the gas phase. This is quite surprising as Yang et al.,[29] who recently studied electron impact ionization of haloalkanes in helium droplets, reported the weak formation of $(CHCl_3)^+$ ($<1\%$ of $(CHCl_2)^+$) but none of $(CCl_3)^+$. Yang et al.[29] used similar helium expansion conditions as in the present experiments. However, in their experiment they purposely used low partial pressures of chloroform in order avoid any formation of chloroform clusters in the helium droplet. Thus, from the comparison of the present results with the data in ref 29 the environmental influence upon the (dissociative) ionization of a chloroform molecule can be deduced when it either is singly embedded in a pure helium droplet as in ref 29 or is a constituent of a chloroform cluster in the droplet as in the present study.

The present mass spectrum shows parent cluster ion formation up to the trimer. Nevertheless, fragment cluster ions are formed much more efficiently by loss of $Cl_n$ ($n = 1,2$) from the cluster, and very weakly we can also observe the cluster ion formed by loss of $HCl_n$ ($n = 1,2$) (see Table 1). So we can conclude that the molecular chloroform clusters embedded in helium droplets undergo strong fragmentation upon electron impact ionization. An analogous result was also observed in our previous experiments of helium droplets doped with nucleobases.[28] However, for the biomolecules studied, the fragmentation pattern differs completely because in that case protonated cluster ions have been observed which arise by fragmentation of higher-order molecular clusters.

In general, the electron impact ionization process of a species embedded in a helium droplet is assumed to occur indirectly: first a helium atom close to the surface is ionized by the incoming electron, followed by migration of the positive hole via other helium atoms into the droplet before finally the charge localizes on the molecular cluster.[24] This leads then to the almost complete evaporation of the remaining helium layer covering the cation, or the ionized dopant is ejected from the droplet.[27] However, a careful inspection of the mass spectra shows that we also observe a weak presence of helium-solvated chloroform cations. The ionization energy of helium (24.59 eV) is much higher compared to that of chloroform (values reported in NIST range between 11.3 and 11.5 eV).[16] Considering these differences in the ionization energies it can be expected that a large amount of excess energy is transferred to chloroform which leads to enhanced fragmentation when it is ionized via charge exchange with He$^+$. Competitively, the excess energy could be removed by evaporative cooling of the ionized molecular complex, leading to reduced fragmentation, i.e. so-called soft ionization of the dopant in the helium as reported previously for NO dimers[38] and triphenylmethanol.[39] The present mass spectrum of chloroform (cluster) cations shows that fragmentation is the dominant process and the cooling rate is too low to suppress dissociation. In the case of chloroform no quenching of the fragmentation of the monomer occurs, and instead we even observe stronger formation of $(CCl_3)^+$. Such enhancement of the dehydrogenated parent cation was also observed previously for aliphatic alcohol clusters in helium droplets which was ascribed to a cage effect by the surrounding helium.[30,31] The latter effect favors the ejection of small (fast) fragments. In contrast, for higher-order chloroform clusters the situation changes significantly, and the larger the cluster the weaker the

(38) Callicoatt, B. E.; Mar, D. D.; Apkarian, V. A.; Janda, K. C. *J. Chem. Phys.* **1996**, *105*, 7872–7875.
(39) Lewis, W. K.; Applegate, B. E.; Sztaray, J.; Sztaray, B.; Baer, T.; Bemish, R. J.; Miller, R. E. *J. Am. Chem. Soc.* **2004**, *126*, 11283–11292.
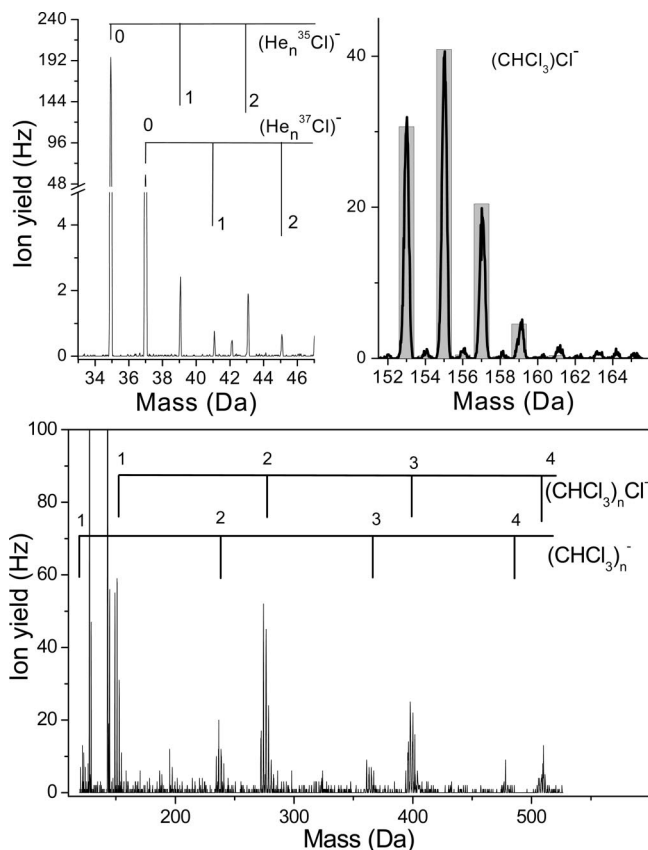
**Figure 2.** Negative ion mass spectrum of chloroform embedded in helium droplets in the mass range from 115 Da up to 520 Da (bottom). The mass spectrum is recorded at the electron energy of 1.5 eV. The high intense peaks at 127 and 146 Da can be ascribed to $SF_5^-/SF_6$ and $SF_6^-/SF_6$, respectively. (Panel top left) Mass region close to $Cl^-$ (not background corrected, see text). (Panel top right) Measured spectrum (line) for the chlorinated monomer anion compared with the calculated isotope pattern (gray columns).

dissociation. Assuming a fragment cation is always formed upon dissociation of at least the next higher-order cluster, the present results show that, for chloroform clusters embedded in the helium droplet, the excess energy can be distributed more efficiently than in the case of the monomer; i.e. fragmentation can be more effectively quenched by the chloroform cluster than by the helium droplet.

**3.2. Negative Ions.** Figure 2 shows the negative mass spectrum of chloroform embedded in helium in the mass range from about 115 Da up to 530 Da. The mass spectrum is recorded at the electron energy of 1.5 eV; close to the energy where the strongest signal of anion formation can be observed. Analogous to the positive mass spectrum we can observe weakly nondissociated cluster anions of chloroform, but more intense are the ion yields of anions formed via fragmentation of chloroform clusters upon DEA. This result is in accordance with many previous experiments with homogeneous clusters (albeit not available for chloroform) showing that fragment cluster anions formed by intracluster fragmentation are more abundant than undissociated cluster anions.[40] However, the fragmentation pattern is clearly different from the positive ion case. As can be seen in Figure 2, the most abundant fragment anions are the chlorinated cluster anions, whereas for positive ions single or double dechlorination of the parent cluster ions is the main

**Table 2.** Solvation Energies of Cl and Cl⁻ with He Atoms Arranged on a Sphere with the Halogen Atom in the Center (Energies in eV)

| He atoms | aug-cc-pvtz | | aug-cc-pvqz | |
|---|---|---|---|---|
| | Cl | Cl⁻ | Cl | Cl⁻ |
| 10 | 0.01 | 0.04 | 0.01 | 0.04 |
| 28 | 0.02 | 0.12 | 0.02 | 0.11 |
| 35 | 0.03 | 0.17 | 0.03 | 0.16 |

fragmentation process. Also included in Figure 2 is a close up of the mass region of the $Cl^-$ anion. This mass spectrum shown is not corrected for the background ion signal of $^{35}Cl^-$ and $^{37}Cl^-$ resulting from electron attachment to isolated chloroform streaming along the droplets into the ion source. Therefore, most of the ion signal appearing at masses 35 and 37 Da arises from DEA to isolated chloroform carried into the ion source. The background-corrected energy scan shows that only very little of the signal originates at this electron energy from DEA to chloroform in the droplet (see below and Figure 7). However, emphasis should be placed on the series of peaks visible above $Cl^-$ which can be unambiguously ascribed to $Cl^-$ with attached helium atoms. The abundance of the latter species is about half of the bare anion, while for larger fragment anions this helium solvation effect is much weaker, and the abundance is reduced to a few percent of the bare anion, e.g. see top right panel in Figure 2, where the measured spectrum for the chlorinated monomer anion is compared with the calculated isotope pattern.

We have calculated the solvation energy of the anions with the use of a density functional for $CH_3Cl^-$ and $Cl^-$ while the solvent was modeled self-consistently as a classical polarizable continuum.[41,42] The B3LYP[43] functional and Dunning's correlation-consistent basis sets in triple (for $CH_3Cl^-$) and quadruple (for $Cl^-$) contraction,[44] augmented with diffuse functions, were used. This mixed approach is approximate, but it has the advantage of treating an extended solvent and both solute/solvent polarization and dispersion. The low polarizability of helium (0.2 $Å^3$) leads to small solvation energies of $-0.15$ eV (stabilizing) for $Cl^-$ and half of that for $CH_3Cl^-$. This agrees with the experimental findings that $Cl^-$ should be more strongly solvated than chloroform anion. The solvation energies of the corresponding neutral species were close to zero. In addition to these calculations we performed quantum chemical finite-size cluster calculations. One $Cl^-$ anion was surrounded by 10, 28, and 35 helium atoms; 35 atoms constitute one full shell, and the two smaller systems, partially filled shells. The He−Cl distance was taken as 4.284 Å from the energy minimum of the He−$Cl^-$ pair potential. The solvation energy was calculated with the "spin component scaling" MP2 - method[45] modified for the correct distance-dependence of the dispersion energy (MOS-MP2[46]). This method provides near coupled-cluster accuracy at bearable computational costs. Table 2 shows the results for the two basis sets mentioned above. One sees that for 35 He atoms a value quite similar to the energy from the continuum model is reached with both basis sets.

Moreover, molecular anions can boil off helium atoms due to their internal (vibrational) energy. In general it may be

(40) Illenberger, E. *Chem. Rev.* **1992**, *92*, 1589–1609.

(41) Cancès, M. T.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032–3041.
(42) Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *106*, 5151–5158.
(43) Becke, A. D. *J. Chem. Phys.* **1997**, *98*, 5648–5652.
(44) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358–1371.
(45) Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095–9102.
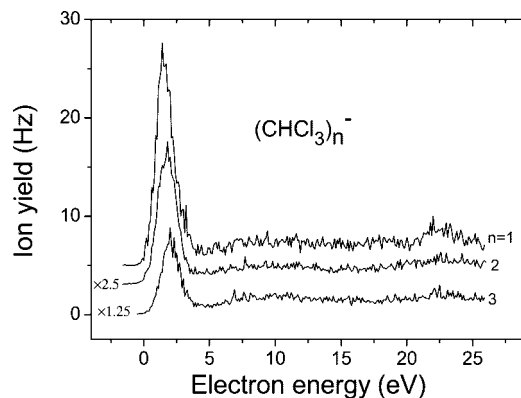(46) Lochan, R. C.; Jung, Y.; Head-Gordon, M. *J. Phys. Chem. A* **2005**, *109*, 7598–7605.

**Figure 3.** Ion yield of chloroform cluster anions ($n = 1-3$) formed via electron attachment to chloroform embedded in helium droplets.

**Table 3.** Peak Positions (in eV) for Cluster Anions and Fragment Anions Formed upon DEA to Chloroform Embedded in Helium Droplets

| anion | peak position (in eV) | | | | |
|---|---|---|---|---|---|
| $(CHCl_3)_n^-$ ($n = 1-3$) | 1.6 | | 10.3 | | 22.6 |
| | 1.8 | | 10.1 | | 22.6 |
| | 2.0 | | 9.9 | | 22.7 |
| $(CHCl_3)_nCl^-$ ($n = 1-3$) | 1.7 | | 9.5 | | 22.6 |
| | 1.9 | | 10.0 | | 22.9 |
| | 2.0 | | 9.7 | | 22.8 |
| $((CHCl_3)_nH)^-$ ($n = 1,2$) | 1.8 | 7.5 | 11.2 | 16.8 | 22.1 |
| | 1.7 | 7.8 | 10.5 | | 22.3 |
| $CHCl_2^-$ | 1.6 | 10.6 | 17.7 | | 21.7 |
| $CCl_2^-$ | 1.7 | 7.8 | 10.5 | | 22.3 |
| $HCl_2^-$ | 1.8 | 8.8 | 10.5 | 17.7 | 22.6 |
| $Cl_2^-$ | 2.0 | 9.2 | 10.7 | 17.5 | 22.1 |
| $Cl^-$ | 1.9 | 7.8 | 9.9 | 17.6 | 22.3 |

surprising that no stronger solvation of anions by helium atoms is present because the energy deposited in the electron attachment reaction to the dopand is surely not sufficient to boil off $10^4$ atoms (see below). Thus, more likely is the ejection of chloroform (fragment) anions out of the droplet once formed by electron capture. The calculations show that the solvation energies for the anionic species are higher than for the neutral atoms; that is, helium atoms may be grabbed during ejection out of the droplet. The stronger abundance of solvated $Cl^-$ than solvated $CHCl_3^-$ also implies that the fragmentation of the transient negative chloroform anion still occurs in the helium droplet and not after ejection out of the droplet because in the latter case no formation of solvated $Cl^-$ is possible.

Subsequently we have measured the ion yield as a function of the electron energy for the anions observed in the mass spectrum. The corresponding results are shown in Figures 3−7. The peak positions observed are summarized in Table 3.

In the present cluster experiment we can observe negatively charged cluster ions $(CHCl_3)_n^-$ which are formed via initial electron capture of a chloroform molecule within the chloroform cluster embedded in the helium droplet. Subsequent stabilization of the formed transient negative ion $(CHCl_3)^{*-}$ occurs via helium evaporation. These anions have their main resonance close to 2 eV (see Figure 3 and Table 3) and a second much weaker resonance at about 22.5 eV. Moreover, the trimer anion shows another very weak broad resonance at about 10 eV barely visible in the ion yield of the smaller parent cluster anions. It is interesting to note that, in contrast and as reported before, in electron attachment to bare chloroform, no stable parent anion can be observed, and the formation of $Cl^-$ (especially for electrons with energies close to zero eV[13-15,19]) is the major
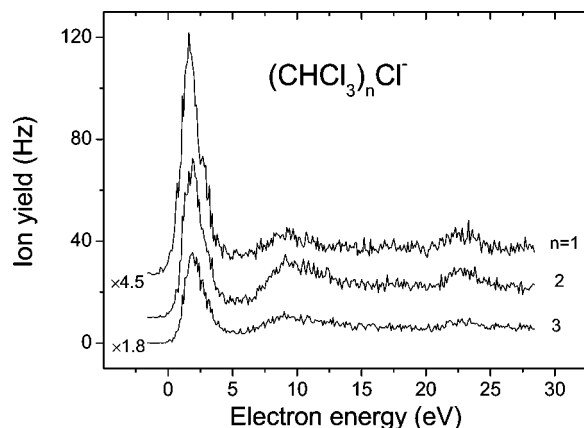


**Figure 4.** Ion yield of chlorinated chloroform cluster anions ($n = 1-3$) formed via electron attachment to chloroform embedded in helium droplets.

reaction channel via DEA. We have repeated our *ab initio* calculations for the adiabatic electron affinity reported in ref 19 with a higher level of theory. The present G3MP2 calculations show that chloroform has a positive adiabatic electron affinity of 0.29 eV where the optimized geometry of the anion is different than that of the neutral in respect to all C−Cl bond lengths. The difference in the bond length amounts to about 0.2 Å. Here in the cluster environment the intermediate negative ion formed can be stabilized into this relaxed configuration by the evaporation of other chloroform constituents in the cluster or by helium. Such a stabilization mechanism was also proposed in the studies of electron attachment to pure halomethane clusters such as $CF_3I$, $CF_3Cl$, and $CF_2Cl_2$,[47-49] respectively.

The ion yields of the highly abundant chlorinated cluster anions $(CHCl_3)_nCl^-$ are shown in Figure 4. From the thermodynamic point of view the formation of $(CHCl_3)_nCl^-$ is not surprising if one considers the high electron affinity of $Cl^-$ (3.61 eV). Thus, it is likely that a $Cl^-$ anion is solvated by other intact chloroform molecules. The ion yield curves (shapes) of the chlorinated cluster anions $(CHCl_3)_nCl^-$ are similar to those of the parent cluster anions; the main resonance is located at about 2 eV, and moreover, clear evidence is found for the resonance at 22.7 eV. However, the resonance for $(CHCl_3)_nCl^-$ at about 9 eV is more strongly pronounced than for the parent cluster ions.

Another anion not observed in the gas phase is the dehydrogenated chloroform anion. The sensitivity of the present experimental setup also allows us to observe the dehydrogenated anion for the dimer (see Figure 5). Below 15 eV both the dehydrogenated monomer and dimer anion show a nearly identical resonance structure; above 15 eV it differs strongly.

In addition, we can observe a few lower mass fragment anions; the corresponding ion yields are shown in Figure 6 ($CHCl_2^-$, $CCl_2^-$, $HCl_2^-$, and $Cl_2^-$) and Figure 7 ($Cl^-$). All of these are also formed upon dissociative electron attachment to isolated chloroform in the gas phase.[19] The corresponding anion efficiency curves for the isolated molecules are also included in the figures. All of these anions show a rich resonance spectrum with common resonances: a first resonance at about 2 eV, followed by broad resonance at about 10.5 eV. All lower

(47) Langer, J.; Matt, S.; Meinke, M.; Tegeder, P.; Stamatovic, A.; Illenberger, E. *J. Chem. Phys.* **2000**, *113*, 11063–11070.
(48) Oster, T.; Ingolfsson, O.; Meinke, M.; Jaffke, T.; Illenberger, E. *J. Chem. Phys.* **1993**, *99*, 5141–5150.
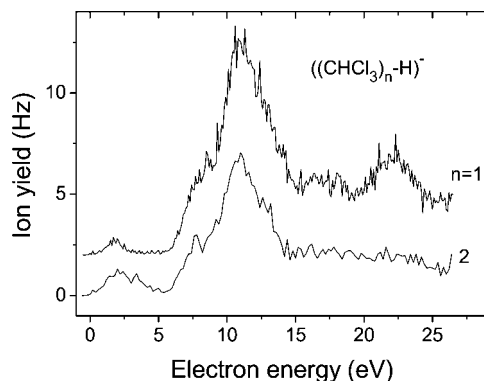(49) Kühn, A.; Illenberger, E. *J. Phys. Chem.* **1989**, *93*, 7060–7061.

**Figure 5.** Ion yield of dehydrogenated chloroform cluster anions ($n$ = 1,2) formed via electron attachment to chloroform embedded in helium droplets.
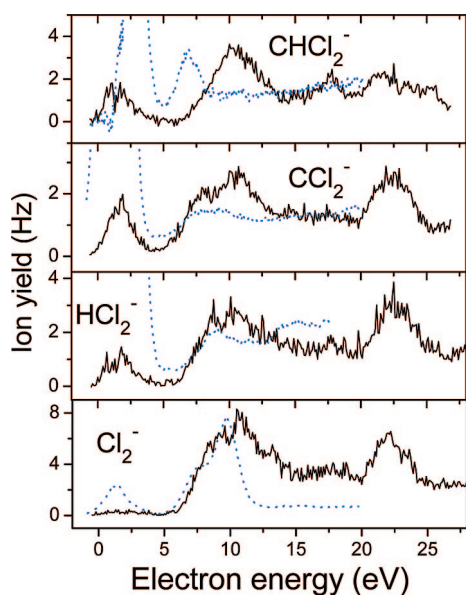


**Figure 6.** Ion yield of fragment anions of chloroform formed via electron attachment to chloroform embedded in helium droplets (full lines). Also included in the figures are the ion yields formed via free DEA to isolated chloroform in the gas phase[19] (in arbitrary intensities).

mass small fragment anions except $CHCl_2^-$ also show a shoulder on the low-energy side of the 10.5 eV peak. A barely visible resonance is located at about 17.5 eV. As already mentioned, besides pick-up by large droplets, smaller helium clusters or monomers push some gas-phase chloroform molecules to the ion source. Thus, the measured ion efficiency curves exhibit a contribution from the molecules embedded in helium and a contribution of these gas-phase molecules. Unfortunately, the cross section for DEA to gas-phase chloroform turns out to be much larger than the efficiency of anion formation in the droplets which complicates the situation by a superposition of resonances for molecules in the gas phase and embedded in the droplets. As all small fragment anions are also readily formed by electron attachment to residual chloroform in the ion source, we measured the background signal which can be determined at nozzle temperatures higher than 15 K, because at this temperature the helium droplets are too small to pick-up any chloroform molecules. For example, Figure 7 shows the intense background signal for $Cl^-$. The $Cl^-$ ion yield formed upon DEA to chloroform in the helium droplet is then obtained by subtraction of the background signal from the ion yield recorded at 9.5 K,
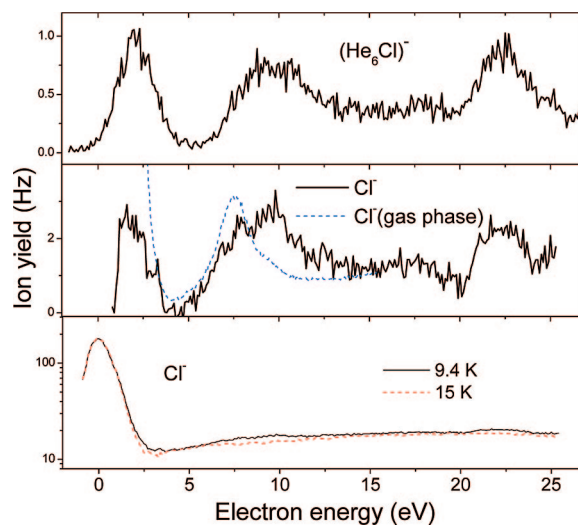


**Figure 7.** Ion yield of $Cl^-$ measured at the nozzle temperature of 9.4 K (solid line), and 15 K (dotted line) where no pick-up of chloroform by helium droplets occurs and $Cl^-$ is exclusively formed upon DEA to chloroform molecules carried by the fast helium jet to the ion source (bottom panel). $Cl^-$ resulting from DEA to chloroform in the helium droplet, which is shown in the middle panel as a solid line, is obtained by subtraction of the signal measured at 15 K from the signal at 9.4 K. Also included in this panel is the ion yield of $Cl^-$ in the gas phase[19] (in dotted line and arbitrary intensities). The top panel shows the ion yield of $He_6Cl^-$.

where the most efficient pick-up occurs (see Figure 7). Also included in Figure 7 is the electron energy scan of $He_6 \cdot Cl^-$ which is very similar to that of the bare $Cl^-$ anion.

Comparing the ion yields in Figures 3−7 and the resonance positions listed in Table 3, electron attachment to chloroform embedded in helium droplets occurs mainly in three electron energy regimes (close to ∼2 eV, ∼10 eV, and ∼22 eV) discussed in the following.

**3.2.1. Resonances at ∼2 eV.** In the previous attachment studies with pure halomethane clusters, the resulting anion yield of the parent anion showed a peak very close to zero eV as expected for an associative electron attachment event.[47−49] Here the first resonance of the parent anion is clearly off zero eV; however, this shift can be explained by the presence of the helium droplet. According to previous electron attachment experiments with pure helium clusters no peak at zero eV for the helium cluster anions can be observed,[34] as an incoming electron requires a minimum amount of energy to initially penetrate into the helium droplet entering the bottom of the conduction band prior to bubble formation. The conduction band of liquid helium lies about 1.1 eV above the vacuum level (bulk value),[34,50] while for smaller droplets the value decreases slightly (e.g., 0.86 eV for a cluster size of $6.5 \times 10^3$).[50] Once inside the helium droplet the electron repels surrounding helium and forms a bubble with a diameter of 34 Å. The energy of the electron is thereby reduced to the ground-state energy of 0.08 eV.[51] In pure helium droplets this ground-state energy reduces the lifetimes of electron bubbles which are determined to be 0.06 s for pure droplets.[35] However, in the presence of an embedded species in the droplet the electron finally localizes on the dopant before the metastable electron bubble decays spontaneously. Therefore, the position of the lowest-energy

(50) Rosenblit, M.; Jortner, J. *J. Chem. Phys.* **2006**, *124*, 194505-1–194505-8.

(51) Farnik, M.; Henne, U.; Samelin, B.; Toennies, J. P. *Phys. Rev. Lett.* **1998**, *81*, 3892–3895.

resonances observed for all anions in the present experiment with chloroform are very close to the position of the first resonance in the ion yields of pure helium cluster anions which showed their first resonance at about 1.8 eV (onset at about 1.1 eV).[34] Analogously we observed stable cluster anions with a main resonance at about 2 eV in our previous experiment with nucleobases embedded in helium droplets.[23]

**3.2.2. Resonances at ∼10 eV.** In our previous experiment with nucleobase (NB) clusters embedded in helium droplets[23] we observed the signature of the H⁻ anion in the ion yield of the complementary product anion (NB-H)⁻ which was interpreted in terms of an electron transfer from the initially formed H⁻ anion to the (NB-H) radical formed in the dissociative attachment process. Here no anion yield coincides with the resonance structures and positions observed for H⁻ in DEA to chloroform in the gas phase. Thus, we can exclude electron transfer reactions in the DEA processes for the system studied presently. However, in previous electron transmission spectroscopy experiments with chloroform a transient negative ion state was found at about 7.7 eV.[52] Keeping in mind the shift of resonances due to the penetration into the helium droplet, the present resonances are reminiscent of those temporary negative ion states of chloroform formed at higher electron energies. They are observed only weakly in the gas phase as at this energy range resonances are typically accompanied by electronic excitation of the molecule (core-excited resonances). However, here in the helium environment they are stabilized, which even leads to the weak presence of the undissociated (cluster) anions; however, the abundance relative to the low-energy resonances increases significantly for fragment anions.

**3.2.3. Resonances at ∼22 eV.** Another reminiscence of the interaction of the incoming electrons with the surrounding helium atoms can be observed by the resonance located at 22.5 eV. This peak most likely corresponds to an inelastic scattering event of the captured electron by helium prior to the attachment reaction. Since the lowest excitation energy of helium (2³S state) is 19.82 eV, this inelastic scattering process will remove most of the kinetic energy of the electron; however, as in the case of the 2 eV resonances, the electron enters the conduction band and forms a bubble and then attaches to chloroform in the droplet. Also this feature has been observed previously in experiments of negative ion formation in helium droplets[34] at about 22 eV. Thus, the formation of electron-excitation complex He*⁻ with its resonance energy at 19.37 eV cannot account for this peak. As in the present experiment the resonances observed are also clearly off this energy, the same argument can be used here, and anion formation via an ion–molecule reaction of He*⁻ and chloroform can be excluded. It is interesting to note that inelastic scattering events with electronic excitation of the target species as observed here have been extensively studied previously in electron attachment to van der Waals clusters which are formed in a seeded beam expansion with rare gases[53,54] and N₂,[40] respectively. The ion yields of cluster anions showed resonances at electron energies close to the excitation energies of the used expansion gas. Therefore, the authors in refs , 53, and 54 concluded that incoming electrons are scattered inelastically by the coexpanded species before they attach to the

cluster. All series of cluster anions observed in the present experiment show the tendency, that the relative intensity of the He scattering peak decreases with increasing cluster size of the chloroform, which can be related to the effect that, for each chloroform embedded in the helium droplet, the helium layer shrinks, which makes scattering events by helium less probable.

Further remarkable differences of the ion yields of fragment anions in the droplets compared to the gas phase can be observed: (i) fragment anions in the gas phase are formed far more abundantly in resonances below 2 eV, while presently observed resonances at higher electron energies dominate the ion yield curves; (ii) in the present study we observe these anions with an intensity within the same order of magnitude, while in the gas phase the relative intensity of the fragment anions spreads over 5 orders of magnitude. For the isolated molecule in the gas phase Cl⁻ is formed via s-wave electron attachment with a very high cross section[13–15,19] due to the reciprocal energy dependence of this reaction. The present results indicate that the large ion signal observed for the gas phase close to zero eV is quenched when the electron attachment process to the molecule occurs within the helium droplet. At an electron energy of 2 eV that is required for the electron to penetrate into the He droplet the electron capture cross section is orders of magnitude lower compared to zero eV. On the other hand a shift of 2 eV for the higher lying resonances has a much smaller effect on the capture cross section. This readily explains the dramatic decrease of the anion yield for resonances that are close to zero eV in the gas phase when the molecule is embedded in the He droplet. This is in agreement with the experimental observation that the anion formation in He droplets is within an order of magnitude the same for all resonances (see Figures 6 and 7).

## 4. Conclusion

In conclusion, we performed a detailed study of the electron interaction with chloroform embedded in helium droplets. The positive mass spectrum recorded at 70 eV shows that for the present molecule no quenching of fragmentation occurs and instead the relative abundance of the parent ion even decreases upon ionization inside the helium droplet. In addition, for higher cluster series of chloroform less fragmentation can be observed, i.e. a softening effect is rather induced by the presence of a chloroform cluster than by the helium droplet. In the case of negative ions a substantial difference to the processes in the gas phase can be observed: large cross sections at low energies which can be ascribed to s-wave attachment process (as for Cl⁻) are reduced to the same order of magnitude like core excited resonances at higher electron energies. The present results demonstrate that processes in the helium droplet environment can differ substantially from those of free electron attachment reactions in the gas phase.

(52) Burrow, P. D. Private communication.
(53) Rauth, T.; Foltin, M.; Märk, T. D. *J. Phys. Chem.* **1992**, *96*, 1528–1530.
(54) Klots, C. E.; Compton, R. N. *Chem. Phys. Lett.* **1980**, *73*, 589–591.