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Direct Observation and Characterization of Neutral Radicals from a Dissociative Electron Attachment Process

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Despite decades of gas-phase studies on dissociative electron attachment (DEA) to various molecules, as yet there has been no direct detection and characterization of the neutral radical species produced by this process. In this study, we performed stepwise electron spectroscopy (SWES) to directly measure and characterize the neutrals produced upon zero-electron-energy DEA to the model molecule, carbon tetrachloride (CCl₄). We observed the direct yield of the trichloromethyl radical (CCl₃•) formed by DEA to CCl₄ and measured the appearance energies of all the other neutral species. By combining these experimental findings with high-level quantum chemical calculations, we performed a complete analysis of both the DEA to CCl₄ and the subsequent electron-impact ionization of CCl₃•. This work paves the way toward a complete experimental characterization of DEA processes, which will lead to a better understanding of the low-energy electron-induced formation of radical species.

Low-energy electrons (< 15 eV) can resonantly attach to molecules to form a short-lived transient state that quickly decays through molecular dissociation into a negative ion and neutral (radical) fragment(s). This process, commonly known as dissociative electron attachment (DEA), appears to have great significance in nature and technology, and has attracted a huge amount of scientific attention in recent decades. DEA represents a doorway for sub-ionization and even sub-excitation energy electrons to induce the decomposition of complex molecular species. Consequently, DEA studies are shedding new light on important research topics, such as radiation damage [1], and on the development of industrial applications, such as high-resolution nanolithography [2,3]. In addition, DEA is also a doorway for low-energy electrons to produce highly reactive radical species, which, themselves, play a crucial role in a variety of important biological and industrial processes. Nevertheless, despite intensive gas-phase DEA research, there has been no report of the direct detection and characterization of neutral radicals produced in DEA performed under well-defined single-collision conditions.

DEA to carbon tetrachloride (CCl₄) represents one of the most studied of these processes. At incident electron energies close to 0 eV, DEA to CCl₄ leads to the formation of only Cl⁻ ions [4], while the other reaction product is surmised to be the trichloromethyl radical (CCl₃•):



The intermediate anion CCl₄^{-*} quickly dissociates within 5–10 ps [5]. The resonant Reaction (1) attains a maximum at

0 eV with a large DEA cross section (1.3x10⁻¹⁴cm² [6]), and thus represents a convenient process for our experimental investigation on the direct yield of neutral species. Moreover, CCl₃• radicals can be efficiently produced by Reaction (1) even from, *e.g.*, presolvated electrons [7], enzymes acting as electron donors in electron transfer reactions [8], thermal electrons in plasma [9], and photoelectrons produced on surfaces (both below and above vacuum level) [10]. Therefore, Reaction (1) is involved (or considered to be involved) in a number of important processes that span many distinct fields from Earth's atmospheric processes [11], to plasma applications [12,13], surface photochemistry [10,14], and toxicology [8,15,16].

To directly measure the yield of CCl₃• radicals as a function of the electron energy *E* upon DEA to CCl₄ (1), we performed stepwise electron spectroscopy (SWES) of gaseous CCl₄. The main rationale for using this technique was to detect neutral radical species formed through DEA by using electron impact ionization subsequent to the DEA process (see Fig. 1). In each step, we chose the desired combination of electron interaction time, ion acquisition time, and impact electron energy. Moreover, we also chose the step in which to acquire the selected ionic species.

Therefore, for each type of measurement we designed an acquisition algorithm, which we executed for the desired number of cycles, to provide data streaming from which we ultimately extracted the yield (counts per second) of the desired ionic species (*m/z*) acquired during a given step, and as a function of the electron energy in the first step (*E_I*).

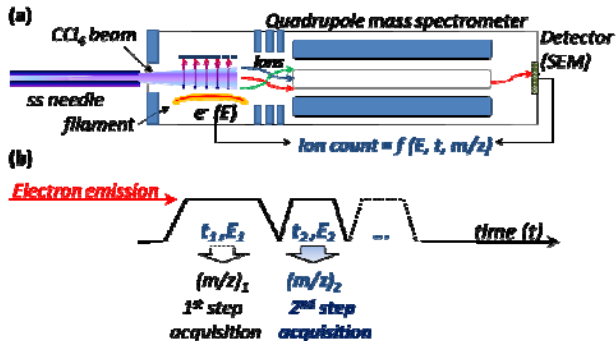


FIG. 1. Stepwise electron spectroscopy (SWES). (a) A schematic representation of the experimental setup. The CCl_4 beam ejected from a stainless steel needle of 1 mm diameter enters the QMS from the aperture on the front end. An ion source part situated at the front end of the QMS serves as the collision region, the core component of which is a metal grid cylindrical cage of diameter of 8 mm and the length of 13 mm. The metal cage is positively biased (~ 3 V) to trap the cations. The electron beam is emitted from an oxide-coated iridium filament which is placed 3 mm away from the cage. The emission current was controlled at 1 μA and energy resolution is 0.5 eV (Fig. 2a). The gas pressure is measured by a hot cathode ion gauge affixed to the wall of the vacuum chamber (around 0.4 m away from the reaction region). (b) A time flow of the experiment.

For example, in the 1st step of the acquisition scheme (see Fig. 1(b)), the electrons at energy E_1 interacted with molecules in the collision region during time t_1 , and Cl^- ions (formed by DEA to CCl_4) were acquired during the same time window t_1 . Therefore, by repeating this acquisition scheme at different energies E_1 , we measured the yield of Cl^- as a function of the incident electron energy E_1 , which represents a classical DEA experiment. The blue curve in Figure 2(a) presents the results, which shows the well-known resonance feature corresponding to the 0-eV DEA to CCl_4 [4,17], although it is somewhat broadened due to our lower energy resolution. It is worth noting that a secondary DEA process: $e^- + \text{CCl}_3 \rightarrow \text{Cl}^- + \text{CCl}_2$ is also possible [9] during interaction time t_1 and also is computed to be exothermic. Nevertheless, we consider that contribution of Cl^- from the secondary DEA to be negligible, based on the assumption of both a large difference in the target density between CCl_4 and CCl_3 and a very low probability of the occurrence of this two-step process under single-collision conditions.

Furthermore, we performed the 2-step acquisition scheme (Fig. 1(b)), where, in the first step, electrons at energy E_1 interacted with molecules in the collision region during the time $t_1 = 1$ s, followed by a second step, in which electrons at energy E_2 interacted with molecules in the collision region during a time interval $t_2 = 0.1$ s. The t_1 and t_2 were adjusted taken into account several technical considerations,

such as degradation of a filament, working at ~ 0 eV and at high electron emission, CCl_3 quenching time, time limitation needed to achieve a sufficient electron emission, and an optimal signal to noise ratio. We acquired the positive ions CCl_3^+ during this second step, t_2 . Note that CCl_3^+ can be produced by both the electron impact fragmentation (EIF) of CCl_4 molecules (in the target beam) and the electron impact ionization (EI) of the CCl_3 radical formed in Reaction (1) during time t_1 . However, if the 2nd-step electron energy E_2 is close to the ionization energy (IE) of CCl_3 and lower than the appearance energy (AE) of CCl_3^+ from EIF of CCl_4 , this acquisition scheme allows only for the detection of the CCl_3^+ species produced in Reaction (1). Therefore, by repeating this acquisition scheme at different energies E_1 , we measured the yield of CCl_3^+ from Reaction (1) as a function of the incident electron energy scanned over the DEA resonance. Since both Cl^- and CCl_3^+ are formed in the same reaction, the relative ion yields obtained from the 1st- and 2nd-step acquisition schemes should overlap. This is indeed shown in Fig. 2(a), in which the red circles represent the yield of CCl_3^+ for $E_2 = 11$ eV. Note that we normalized the significantly lower intensity CCl_3^+ curve to that of Cl^- and we calibrated the energy scale according to the decreasing slope of the Cl^- curve. To the best of our knowledge, this is the first direct measurement of the resonant yield of neutral species formed by gas-phase DEA.

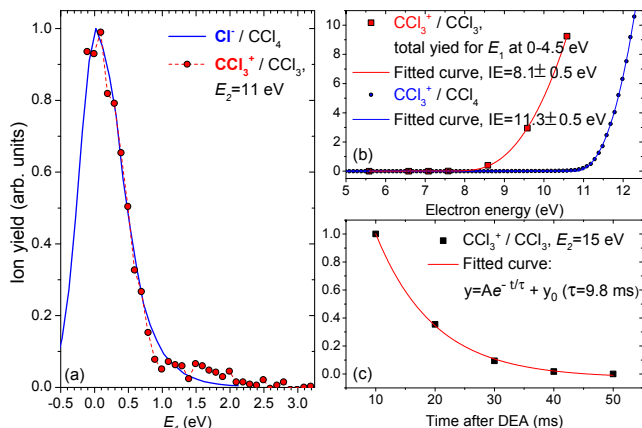


FIG. 2. Direct observation of CCl_3^+ radical from DEA to CCl_4 . (a) Normalized ion yield of Cl^- from the 1st-step acquisition (solid blue line) and CCl_3^+ from the 2nd-step acquisition, $E_2 = 11$ eV, (red circles) as a function of the 1st-step incident electron energy (E_1). (b) Total ion yield of CCl_3^+ obtained for E_1 between 0 – 4.5 eV (red squares) as a function of the 2nd-step incident electron energy (E_2), and ion yield of CCl_3^+ from EIF of CCl_4 as a function of incident electron energy, E_1 , (blue dots). (c) Ion yield of CCl_3^+ as a function of the time after the 1st-step DEA reaction.

To verify that the CCl_3^+ yield presented in Fig. 2(a) originated solely from the EI of CCl_3 , we repeated the acquisition scheme described above for different 2nd-step energies E_2 . Figure 2(b) presents the measured electron

impact ionization yield of CCl_3^+ for E_2 between 6 and 11 eV (red squares), for which we estimated the yield as the total CCl_3^+ yield for E_1 at 0 - 4.5 eV, i.e., the area under the red curve in Fig. 2(a). For comparison, in Fig. 2(b) we plotted the yield of CCl_3^+ formed by the electron impact dissociation of neutral CCl_4 measured in the 1st-step acquisition scheme under the same experimental conditions (blue dots). Based on a Wannier fit [18] to the experimental data obtained in the 2nd-step acquisition (Fig. 2(b), red curve), we determined the IE of CCl_3^+ to be at 8.1 ± 0.5 eV. This value closely matches previously reported experimentally-determined values of 8.11 eV [19] and 8.06 eV [20]. The uncertainty of the present IE is due to a low signal to noise ratio at the threshold and limited electron resolution. The calculated adiabatic IE of CCl_3^+ has been reported to be 7.954 eV [20]. Our calculations performed at the *ccsd(t)/aug-cc-pVTZ* level [21–24] with the Gaussian09 [25] package resulted in a vertical IE of 8.70 eV and an adiabatic IE of 8.02 eV. Note that a distinct separation between the IE of CCl_3^+ and the AE of CCl_3^+ from CCl_4 allows for a convenient choice of the 2nd-step energy E_2 to have a reasonably high cross section for CCl_3^+ ionization, thus making possible efficient detection while still avoiding any interference from CCl_4 molecules remaining in the target beam.

We note that CCl_3^+ is formed only in the first-step process through Reaction (1), because according to our calculations (again at the *ccsd(t)/aug-cc-pVTZ* level), the formation of CCl_3^+ from the direct C–Cl bond cleavage in CCl_4 , $\text{CCl}_4 \rightarrow \text{CCl}_3^+ + \text{Cl}$, requires an energy not less than 2.9 eV and the yield of CCl_3^+ seen in Fig. 2(a) appears mostly in the region $E_1 < 1$ eV. Consequently, the density of CCl_3^+ in the collision region should decrease in time after the completion of the first step. This was probed by the multistep SWES measurements. Figure 2(c) shows the time dependence of CCl_3^+ abundance, in which, after the first step in the DEA process, we set the electron energy at $E_2 = 15$ eV and recorded the intensity of CCl_3^+ as output every 10 ms. Note that E_2 was above $\text{CCl}_3^+/\text{CCl}_4$ AE (Fig. 2b) to ensure high-enough CCl_3^+ detection efficiency during a short acquisition time of secondary steps. However, CCl_3^+ produced directly from CCl_4 made a constant background which was subtracted. The quenching of CCl_3^+ is a consequence of several processes, which cannot be resolved in the present experiment. These processes include electron interaction (ionization and fragmentation); CCl_3^+ interaction with the target beam, the residual gas molecules, and surrounding surfaces; and the escape of neutral radicals due to their translational kinetic energy.

In addition to the resonant yield of the CCl_3 radical observed from DEA to CCl_4 (Fig. 2(a)), we also detected all the other positive ions that can possibly originate as neutrals from CCl_4 fragmentation. The gas-phase DEA to CCl_4 at incident electron energies close to 0 eV can proceed only by

Reaction (1). We probed the origin of these smaller ionic fragments by determining their AE as a function of the second-step energy E_2 (Figure 3). The measured yields of CCl_2^+ and CCl^+ cationic fragments demonstrate that their appearance thresholds fall between the IE of the corresponding neutrals and their AE from CCl_4 dissociative ionization (Figs. 3(a) and 3(b)). Therefore, these fragments can only appear from the electron impact dissociative ionization of CCl_3^+ formed in the DEA to CCl_4 , which offers the first opportunity to measure AEs of these fragments from the CCl_3 radical. Notably, the formation of Cl^+ and Cl_2^+ occurred close to energies of the IEs of their neutrals (Figs. 3(c) and 3(d)), therefore these two cations result from the ionization of Cl^\bullet and Cl_2 rather than the EIF of CCl_3 or CCl_4 . This is in accordance with the present calculations (Table I) showing that their AEs lay far above experimentally probed electron energy domain.

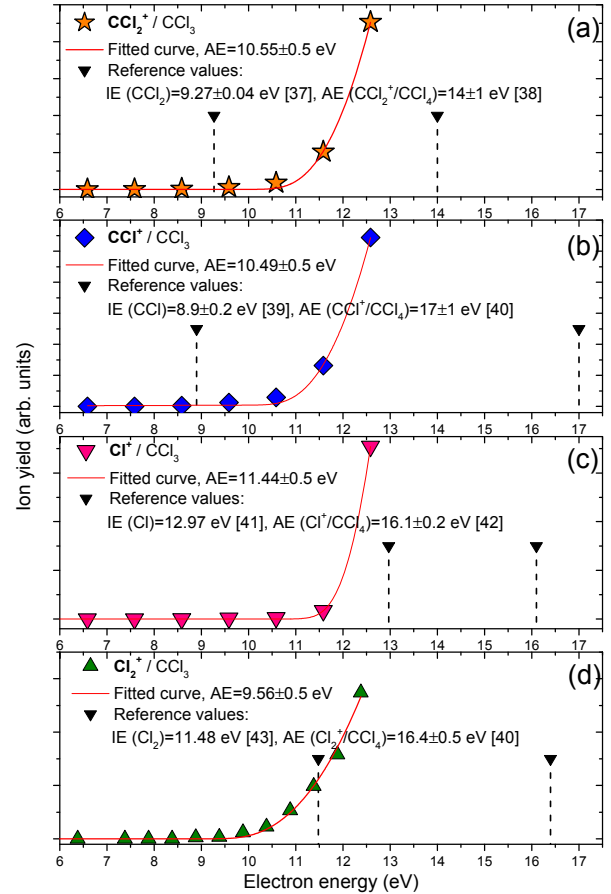


FIG. 3. Ion yields and appearance energies (AEs) of small cationic fragments from EIF of gas phase CCl_3^+ . Note: dashed lines represent experimentally determined IEs and AEs, as reported in given references.

Considering electron interaction with radicals in the gas phase, to our knowledge, only those with fluorocarbon radicals have been investigated to date, including measurements of absolute elastic cross sections for CF_2 and

CF₃ [26,27] and DEA processes for CF₂ and C₂F₅ [28,29]. In the latter experiments, the target radical beam has been obtained by either pyrolysis or microwave discharge. With respect to the CCl₃ radical, the only relevant study was reported by Adams *et al.* [9], who used a flowing afterglow/Langmuir probe apparatus to measure a rate coefficient for a secondary process of DEA to CCl₃[•] formed in the primary DEA to CCl₄. Also, the CCl₃ radical has been studied, both theoretically and experimentally, using mass spectrometry, laser spectroscopy, and *ab initio* calculations [20,30–32]. From these calculations, electron impact IE and photon impact IE for CCl₃[•] were reported previously, but no data on the EIF of CCl₃[•] has been reported thus far.

Our calculations (at the ccscd(t)/aug-cc-pVTZ level) predicted the AEs of CCl₂⁺ and CCl⁺ from CCl₃[•] at 12.01 and 12.51 eV, respectively. These energies are about 1.5 eV above the experimentally measured thresholds of 10.55 ± 0.5 and 10.49 ± 0.5 eV for CCl₂⁺ and CCl⁺, respectively. The deviation between the measurement and the calculation might be explained by two reasons: the region close to the filament where the reactions occurred can be of very high temperature and the parent molecule CCl₃[•] resulting from the first-step DEA might be in an excited state. To estimate the effect of temperature, enthalpy changes for different pathways were calculated at various temperatures with complete basis set method CBS-QB3 [33,34] as listed in Table I. The increase in temperature from 300 to 2500 K lowers the enthalpy requirement by less than 0.2 eV, which could not explain the deviation observed in the experiment. Thus, it is more plausible the deviation is owing to an initial excited CCl₃[•] state. Previously, Popple *et al.* [5] reported the excess energy of Reaction (1) to be ~0.61 eV and concluded that there is an efficient redistribution of this excess reaction energy among the internal vibrational modes of the intermediate CCl₄[•] prior to dissociation, leaving only about 0.1 eV as a mean translational energy release.

TABLE I. Enthalpies calculated with CBS-QB3 method at 300 K and 2500 K for different reaction pathways.

M ⁺	ΔH		ΔH	
	M → M ⁺ + e ⁻		CCl ₃ [•] → M ⁺ + B + e ⁻	
	300 K	2500 K	300 K	2500 K
CCl ₂ ⁺	9.28	9.21	12.27	12.13
CCl ⁺	8.78	8.77	12.63	12.46
Cl ⁺	12.92	12.92	15.91	15.84
Cl ₂ ⁺	11.53	11.53	15.38	15.22

In conclusion, we designed a SWES method to probe the CCl₃ radicals resulting from gas-phase DEA to CCl₄ around zero eV. With this scheme, we measured the IE of CCl₃[•] as well as the lifetime of CCl₃[•] in vacuum conditions. We examined the cationic fragments resulted from EIF of CCl₃[•] by measuring the ion yield curves of the cation fragments as a function of electron energy. By comparing the AEs and

the calculated thresholds of different reaction pathways, we determined the AEs for CCl₂⁺ and CCl⁺ formed by the EIF of CCl₃[•]. The great advantage of this SWES methodology is that the production of the radicals and the subsequent ionization of the radicals can be performed in the same reaction compartment. In this way, we overcame the challenge of radical decay during transportation from the production site to the ionization site as reported in some other radical detection methods [35,36]. The method described here will have useful application in the investigation of radicals from the gas phase DEA, for which no studies have been reported. Obtaining a comprehensive picture of DEA processes has the potential to transform our understanding of the interactions of low-energy electrons with molecular systems, yielding basic science information which translates on variety biological and industrial applications.

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