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Small steps on the slippery road to life: molecular synthesis in astrophysical ices initiated by low energy electron impact

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Abstract

We report the synthesis and desorption of new chemical species from simple molecular surface ices irradiated by low energy (< 60 eV) electrons. For CD_4 ices we observe the formation and desorption of energetic ions such as D_3^+, CD_5^+, and $C_2D_n^+$ (n = 2 – 5), and three or four carbon containing chains, that are also observed to desorb from C_2D_2 films; for oxygen rich methane ices we observe the synthesis and desorption of H_2O^+, H_3O^+, as well as formaldehyde type cations, *viz.* H_nCO^+ (n = 1 -3), among others. The formation of all these pre-biotic molecular species, produced here by low-energy electron-impact-initiated cation-reactions in simple molecular films, suggests that similar mechanisms may lead to the synthesis of life's most basic molecular components in planetary, or astrophysical surface ices that are continuously subjected to the types of space radiations (UV, X-or γ-ray, or heavy ions) that can generate such low energy secondary electrons.

Introduction

The question of the origin for the building blocks of life, either synthesized here on earth, or in space [1], has been the subject of much debate, experimental investigation, or astronomical observation, much of it stimulated by the early experiments of Miller [2], and subsequent space radiation related variations thereof [3,4,5]. And while the precise details of the formation of even the simplest biomolecular elements that make up life on earth still remain shrouded in mystery, one of the notions that persist throughout the debate is that the building blocks of life, such as amino-acids, or even the components of RNA and DNA, where synthesized via radiolysis [6] either in the earths proto-atmosphere, its early oceans, or in the near interstellar space surrounding the early earth .

Here we provide experimental evidence for the hypothesis that the subsequent interactions of low energy secondary electrons and ions, formed during the radiolysis of solid or liquid media, with atoms and molecules in the medium, may have played, and may still play an important role in the chemical transformation of astrophysical or planetary surface ices [7], where they lead to the synthesis of more complex chemical species from less complex, naturally occurring components. It is not surprising that the contexts where such secondary electron and ion reactions occur are those wherever ionizing radiation deposits energy in matter, and thus range from radiation damage to DNA [8, 9], to the radiolysis of molecules at the surfaces of extraterrestrial icy grains or particles, or icy regions of some planets and their satellites [7], which are exposed to various space radiations. Many of the previous experiments have probed new products remaining in the films via methods of post irradiation analysis of the films, e.g. TPD-MS [10], or FTIR in ion irradiation studies [3], while some experiments have investigated the formation of new chemical products that desorb from films or surfaces during radiolysis [7, 11].

In this contribution, we present results of cation scattering in, and desorption from, molecular ices initiated by low energy electron (< 70 eV) impact. The thin ice layers studied here consist of several monolayer (ML) thick films consisting of various small molecules such as $^{16}O_2$, $^{18}O_2$, N_2, CD_4, and C_2D_2 condensed at 20 K under ultra high vacuum conditions, much like those found in interplanetary or interstellar space. The samples are irradiated directly with a low energy (E(e) $\leq$ 70 eV) electron beam emanating from a hemispherical monochromator (⊗E(e) ≈ 80 meV), and desorbing ionic species are mass selected with a high resolution mass spectrometer, and detected using standard charge sensitive electronics.

We find that low energy electron impact initiates a variety of cation fragment reactions at, or near, the surface of the molecular surface ices, all of which result in the formation and desorption of new, more complex chemical species than those that were initially deposited in the films. Therefore, we propose that similar cation reactions, initiated in planetary or astrophysical surface ices by the abundant secondary electrons generated by the various space radiations (UV, X-or γ-ray, or heavy ions) that impinge on them, can provide a mechanism not only for the formation of prebiotic molecules in various space environments, but also for their desorption into the vacuum of interstellar or interplanetary space.

Experimental Methods

The electron stimulated desorption (ESD) apparatus used in the present study has been described in great detail elsewhere **[**12**,** 13**]**. A monochromatic electron beam of about 2×10^{-9} A, with variable incident energy, and a resolution of about 80 meV fwhm, impinges onto a thin polycrystalline Pt foil press-fitted directly onto the tip of a closed cycle cryostat; the latter is held at 20 K during the sample preparation and experiments. The Pt substrate is cleaned by multiple resistive heating cycles at 900°C. Multilayer films are condensed on the clean Pt by means of a volumetric dosing procedure [14], with an accuracy of about ± 30 % and an overall repeatability of ± 0.2 monolayers (ML). The electron energy scale is calibrated to within ± 300 meV with respect to the vacuum level ($E_{vac} \equiv 0$ eV) by measuring the onset of the transmitted current through the film. Since energy shifts of the onset of current transmission relate to charging of the films, it is possible to verify that the present results where obtain from essentially un-charged samples. The entire system is housed in an ultra-high vacuum system held at 10^{-10} torr, and enveloped by a double μ-metal shield to eliminate stray magnetic fields.

Some of the cations produced during electron impact may desorb and enter an ion lens system (containing a set of retardation grids) which precedes a quadrupole mass spectrometer (QMS). The QMS system may be operated in (a) the *ion mass* mode, where the mass spectrum of desorbing ions is measured at a fixed incident electron energy, (b) the *ion yield* mode, where the signal of a particular desorbing ion species is monitored as a function of incident electron energy, E(e), or (c) the *ion energy mode*, where the desorbed cation signal is recorded versus the retardation voltage on the grids of the QMS lens system [13], at a fixed E(e) and ion mass to charge ratio.

The present experiments are performed on pure and heterogeneous multilayer films containing $^{16}O_2$, N_2, with stated purities of ca. 99.995 %, of 99% for CD_4 and C_2D_2, while the stated isotopic purity of $^{18}O_2$ was > 99%.

Results and Discussion

Starting with simple molecular films, we investigated electron impact initiated cation reactions in mixed films of O_2 and N_2. Shown in Figure 1 are the ESD yield functions for O^+, N^+, and NO^+ from a mixed film of O_2/N_2, while the inset shows the ESD mass spectrum of these ions. We observe that, while N^+ is only seen to desorb at electron energies above ca. 25 eV, both O^+

and NO^+ are desorbing at similar electron energies near 21 eV. Therefore, we propose that, based on the different desorption thresholds for these cations, the formation of NO^+ is most likely the result of O^+ scattering from N_2 in the mixed film, leading to the formation and desorption of NO^+ via the following reaction:

$$e^- + O_2 \rightarrow O_2^+ + e^- \rightarrow O^+ + O + e^- \quad \text{followed by}$$

$$O^+ + N_2 \rightarrow ON_2^+ \rightarrow NO^+ + N$$

Retardation analysis [13] of the O^+ ions desorbing from these films under electron impact, as shown in Figure 2, demonstrates that the O^+ fragments produced by low energy electron impact have sufficient kinetic energy to abstract N atoms from N_2 prior to desorption from the surface of the films. We note that the formation and desorption of both, O_2^+ and N_2^+, in these electron irradiated films is most likely already the result of electron initiated cation fragment reactions, as shown in Figure 3 for mixed $^{16}O_2/^{18}O_2$ films. Here the observation that similar intensities of $^{16}O_2^+$, $^{16}O^{18}O^+$, and $^{18}O_2^+$ are seen to desorb from the mixed films containing similar number densities of both isotopes, indicates efficient O atom abstraction reactions in the films, and suggests that at least the O_2^+ signal in the O_2/N_2 films is most likely attributable to O^+ reactive scattering in the films prior to desorption.

Moving on to pure hydrocarbon ices, we find that similar cation fragment reactions are likely responsible for the rich ESD mass spectrum observed for methane films, as shown in Figure 4 for 6 ML films of deuterated methane: in addition to cation reaction products such as D_3^+ or CD_5^+ (both of which are cations of great astrophysical relevance), we observe formation and desorption of species containing two carbon atoms, such as $C_2D_3^+$, and others. For many of the cation products, the electron energy desorption thresholds are found to be between 21 and 30 eV, as exemplified in Figure 5. Measurements from CH_4 multilayer films (not shown) illustrate that the lowest desorption thresholds are observed for CH_3^+ and H^+ near 20 - 21 eV, followed by about 25 eV for CH_2^+, CH_5^+, and $C_2H_3^+$, but about 33 – 34 eV for CH_4^+, $C_2H_4^+$, and $C_2H_5^+$. One of the more salient aspects of the present measurements is the observation that many of the desorbed cations have significant kinetic energies (KE). This is true, even for cations that are likely formed by cation fragment scattering within the films, e.g., $C_2D_3^+$, as shown in Figure 6 for CD_4 films. In the figure we see that at an incident electron energy of 54 eV, where the maximum KE of ion fragments such as D^+ may be as high as 6 – 8 eV, the maximum KE of ion fragment reaction products, such as $C_2D_3^+$, reaches 2 – 2.5 eV in the vacuum, despite having to overcome the local charge induced polarization barrier near the surface of the film (about 1 -1.5 eV), and/or scatter in the film prior to desorption. We note that similar reaction products have been observed to desorb from methane films during 1.5 keV electron impact [11]; however, in these cases their formation has been demonstrated to result from more violent Coulomb explosion, following C(1s) core-ionization induced Auger-cascades leading to multiple ionization of the molecules. Here, their formation at electron energies well below 30 eV certainly precludes such violent processes involving 1s core ionization / Coulomb explosion effects.

The notion that cation-fragment surface-scattering may be involved in the formation of the two carbon atom containing species from electron irradiated methane ices is demonstrated in Figure 7, where different amounts of CD_4 have been deposited on Kr substrates (condensed on Pt). We find that even for very small surface coverages of CD_4 on Kr, we still observe most of the cation reaction products, e.g., CD_5^+ and $C_2D_3^+$, even for 0.1 ML of CD_4 condensed on 5.5. ML Kr: here, assuming that the saturated, and thus relatively inert, methane molecules do not aggregate significantly on the Kr substrate, the formation of $C_2D_3^+$ from CD_4 molecules that are fairly isolated from each other on the rare gas substrate, suggests that they are the result of surface scattering events, involving the various cation fragments produced by the initial electron impact on the film. The fact that for medium concentrations of CD_4 on Kr substrates the relative signal of heavy cation products, such as $C_2D_3^+$ (as compared to lighter ones, e.g., CD_3^+) is significantly larger than for pure CD_4 films can be attributed to kinetic scattering effects. Here, light on heavy recoil collisions [13] between $C_2D_3^+$ (30 amu) and Kr (84 amu) prior to desorption, favor the desorption of the lighter $C_2D_3^+$, as compared to the heavy on light collisions in the case of $C_2D_3^+$ (30 amu) scattering in pure CD_4 (20 amu) films; the latter will favor momentum transfer to the lighter target CD_4, and thus lower the probability of $C_2D_3^+$ desorption. We note that, as the surface concentration of CD_4 decreases on the Kr substrate, an optimum condition is reached for formation and desorption of cation fragment scattering products such as $C_2D_3^+$, i.e. a compromise between CD_4 vs. Kr surface density is reached, i.e. somewhere near 0.5 ML of CD_4 on Kr, after which the intensity of reaction products such as $C_2D_3^+$ decreases, due to the decreasing number of CD_4 targets at the surface. The notion that reactive scattering of cation fragments might be responsible for the two carbon containing reaction products observed here is furthermore suggested by measurements involving either mixed heterogeneous films of CD_4/CH_4 (see supplement Figure 1), or for multilayer CD_4 films condensed on top of CH_4 substrates (see supplement Figure 2): here the fact that even for 3-6 ML of CD_4 deposited on 6 ML CH_4 we still observe reaction products such as CD_4H^+, or $C_2D_3H^+$, suggests that deuterium containing cation fragments have scattered into the film, reacted in the lower CH_4 substrate, and have scattered back out into the vacuum in order to be detected.

The most interesting effect is observed here when we mix methane and oxygen, as shown in Figure 8. As opposed to pure O_2 or CH_4 films, we observe the formation of water, i.e. H_2O^+, H_3O^+ (hydronium), as well as H_nCO^+ ($n = 1 – 3$), including formaldehyde, a molecule which has been tagged as energy/food source for the possible existence of extremophylic bacteria on Europa [15], where the formation of formaldehyde is proposed to be driven by radiation induced synthesis. As observed in other experiments (see supplement Figure 3), all of these products of the electron radiolysis of the mixed film are found to desorb at energies as low as 22 – 25 eV. The fact that here low energy electron interactions are able to synthesize biologically relevant molecules such as water, or carboxylic species, from two separate molecular constituents in condensed ices, provides support to the hypothesis that secondary electron driven processes at the surfaces of planetary ices, or interstellar icy grains, may likely have contributed to the synthesis of pre-biotic, or even biological molecules in the depths of space.

However, the absence of heavier multi-carbon containing species in these desorption experiments somewhat limits the notion that a secondary electron driven type of "chain reaction" might lead to the formation of increasingly larger hydrocarbon species from simple ingredients such as methane. Nonetheless, heavier hydrocarbon species, with their lower kinetic energy, will be less likely to overcome the charge induced polarization barrier at the film surface, and desorb as cations from the methane films; thus their relative intensity is likely to be too low for the present QMS based mass spectroscopy measurements. In order to investigate this aspect further, we have used a high resolution, high sensitivity, reflectron time of flight (TOF) mass spectrometer [16] in electron impact measurements on multilayer films of CD_4, as shown in Figure 9. Here, in addition to the previously observed reaction products, such as $C_2D_3^+$, or $C_2D_5^+$, we also observe small amounts of C_3D_3 and C_3D_5 cations. Considering the fact that these cations need at least 1 eV kinetic energy to desorb from the films, their small signals observed here suggests that in space environments most of them will likely remain at the surface where they may accumulate over time as the methane ice is continuously irradiated. As the concentration of intermediate radiolysis products, such as acetylene (here C_2D_2), that stabilize at or near the icy surface increases, so does the likelihood that they themselves might be converted to, and possibly desorbed as, more complex hydrocarbons. This is experimentally modeled here in the mass spectrum in Figure 10 (obtained with the QMS), where a small amount of C_2D_2 condensed on 5.5 ML Kr is irradiated with 36 eV electrons. We clearly observe the formation and desorption of three, four, and possibly even five carbon atom containing cation products. However, the present measurements provide no information on the structure of these multi-carbon containing radiolysis products, and the question weather or not they might form ring structures remains tantalizingly unanswered. However, preliminary results obtained with the reflectron TOF mass spectrometer on mixed methane/O_2 films (see supplement Figure 4) suggests that the formation and desorption of complex species such as C_2OH_x is possible by low energy electron interactions.

Summary and Conclusion

We have investigated the radiolysis of surface ices by low energy electron impact desorption mass spectroscopy. For pure CD_4 solids, reactions of CD_n^+ fragments with CD_4 lead to desorption of CD_4^+, CD_5^+, $C_2D_3^+$, and $C_2D_5^+$, and small traces of $C_2D_2^+$ (acetylene or vinylidene) and $C_2D_4^+$ (ethylene). Our measurements suggest that the more intense carbon chains with odd numbers of hydrogens are formed in surface reactions of CD_3^+ with CD_4, whereas those with even numbers of hydrogens are the result of CD_2^+ reactions with CD_4. For O_2/CH_4 solids, reactions of low energy O^+, with surface kinetic energies in the laboratory frame of less than 5 eV, lead to formation and desorption of H_2O^+, H_3O^+ (hydronium), OCH^+, OCH_3^+, and small quantities of OCH_2^+ (formaldehyde). Our results suggest that the abundant secondary electrons, formed at or within planetary or astrophysical surface ices by ionizing space radiations, can initiate subsequent ion reactions which result in the synthesis and desorption of new, more complex, organic chemical species. Thus, the synthesis of the most basic molecular elements of life may proceed via the very gradual and stepwise radiolysis of mixtures of ingredients with ever increasing complexity, the abundance of which certainly depends on the many different competing pathways, both physical and chemical, of formation and destruction. However, it is likely that ionizing radiation, while certainly able to destroy life, may also be a key ingredient for its creation.

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Figure Captions

Figure 1: Electron stimulated desorption (ESD) cation fragment yields as function of incident electron energy for a 5.5. monolayer (ML) mixed O_2/N_2 film (the curves have been displaced vertically for clarity), and the associated ESD mass spectrum obtained at 37 eV is shown in the inset.

Figure 2: Smoothed kinetic energy distributions (see ref. 13 for experimental details) for O^+ produced by ESD from a multilayer O_2 film at two different incident electron energies.

Figure 3: ESD cation mass spectrum, obtained at an electron energy of 36 eV for a pure 6 ML film of $^{18}O_2$, and a mixed $^{18}O_2$/$^{16}O_2$ film with mixing ration of 6:4, respectively. The curves have been displaced vertically for clarity, and the yield in the inset has been multiplied by 80.

Figure 4: ESD cation mass spectrum for a 6 ML film of CD_4 at an electron energy of 54 eV.

Figure 5: Selected ESD cation yields from a 6 ML film of CD_4 as a function electron energy. The curves have been displaced vertically for clarity.

Figure 6: ESD cation yields as function of retardation voltage on the QMS grids (see ref. 13 for details of the method) for cation products desorbing from a 6 ML film of CD_4 at an incident electron energy of 54 eV. The curves have been displaced vertically for clarity. The retardation

voltage is equivalent to the desorbed ion's kinetic energy in vacuum, and thus the retardation yield is an indication of the kinetic energy distribution of the respective cation fragments.

Figure 7: ESD cation mass spectra for a 6 ML film of pure CD_4, and for varying amounts of CD_4 condensed on a 5.5 ML Kr substrate, all obtained at an electron energy of 54 eV. The curves have been displaced vertically for clarity, and each mass spectrum is the result of a single QMS scan.

Figure 8: ESD cation mass spectra for a pure 5.5 ML film of CH_4, and a mixed O_2/CH_4 film (ratio of 1:1) of similar thickness. The curves have been displaced vertically for clarity, and each mass spectrum is the result of a single QMS scan at an electron energy of 36 eV.

Figure 9: ESD cation mass spectrum for a 4 ML film of CD_4 at an electron energy of 40 eV obtained here with a reflectron time-of-flight mass spectrometer (for details of the TOF apparatus, see ref. 16). The spectrum is a sum of four TOF spectra, each accumulated for 20 sec.

Figure 10: ESD cation mass spectrum for 0.4 ML C_2D_2 condensed on a 5.5 ML Kr substrate, obtained at an electron energy of 36 eV. This mass spectrum is obtained with the usual QMS method, as is all the data here, except for Fig. 9.

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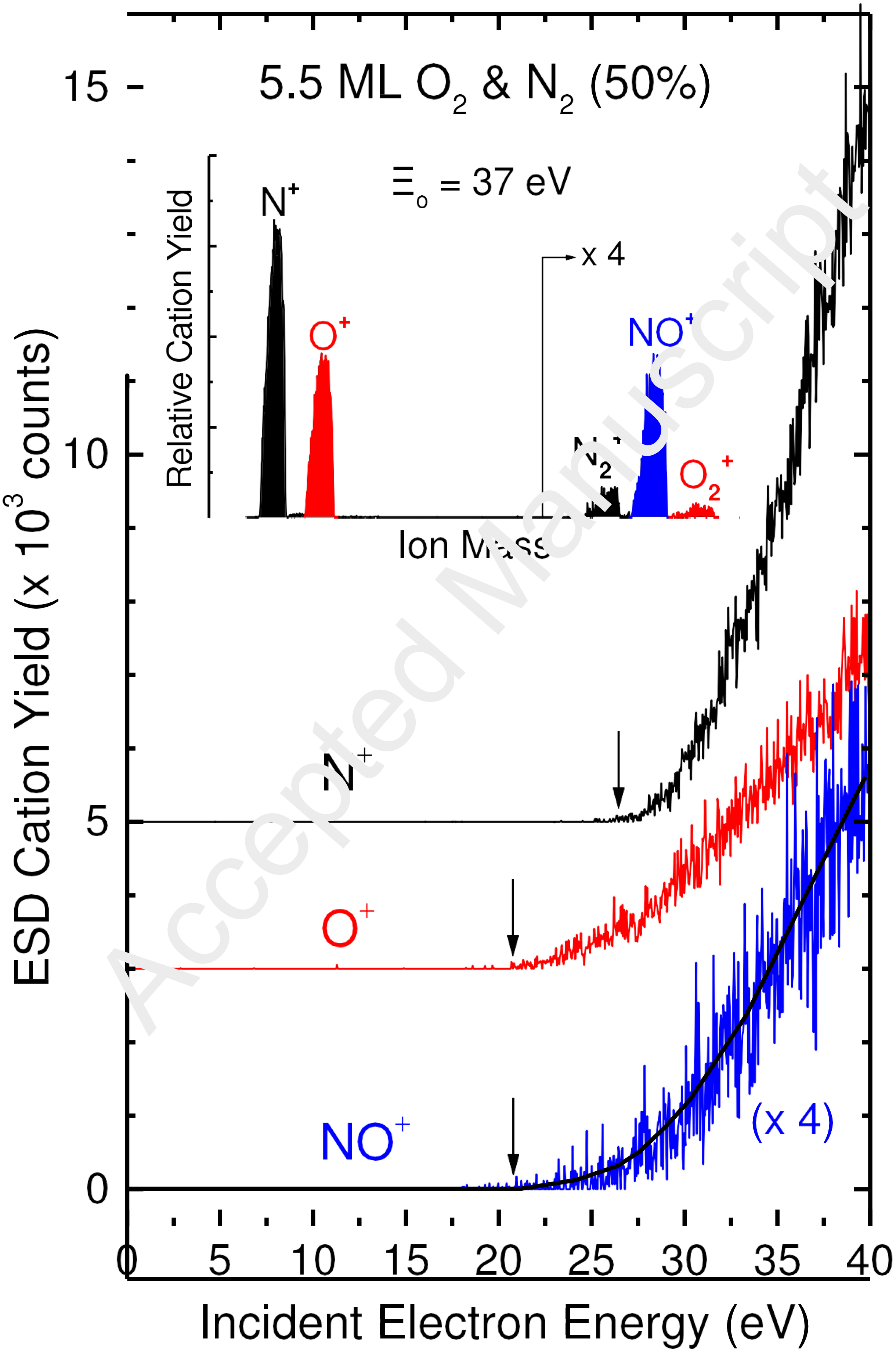
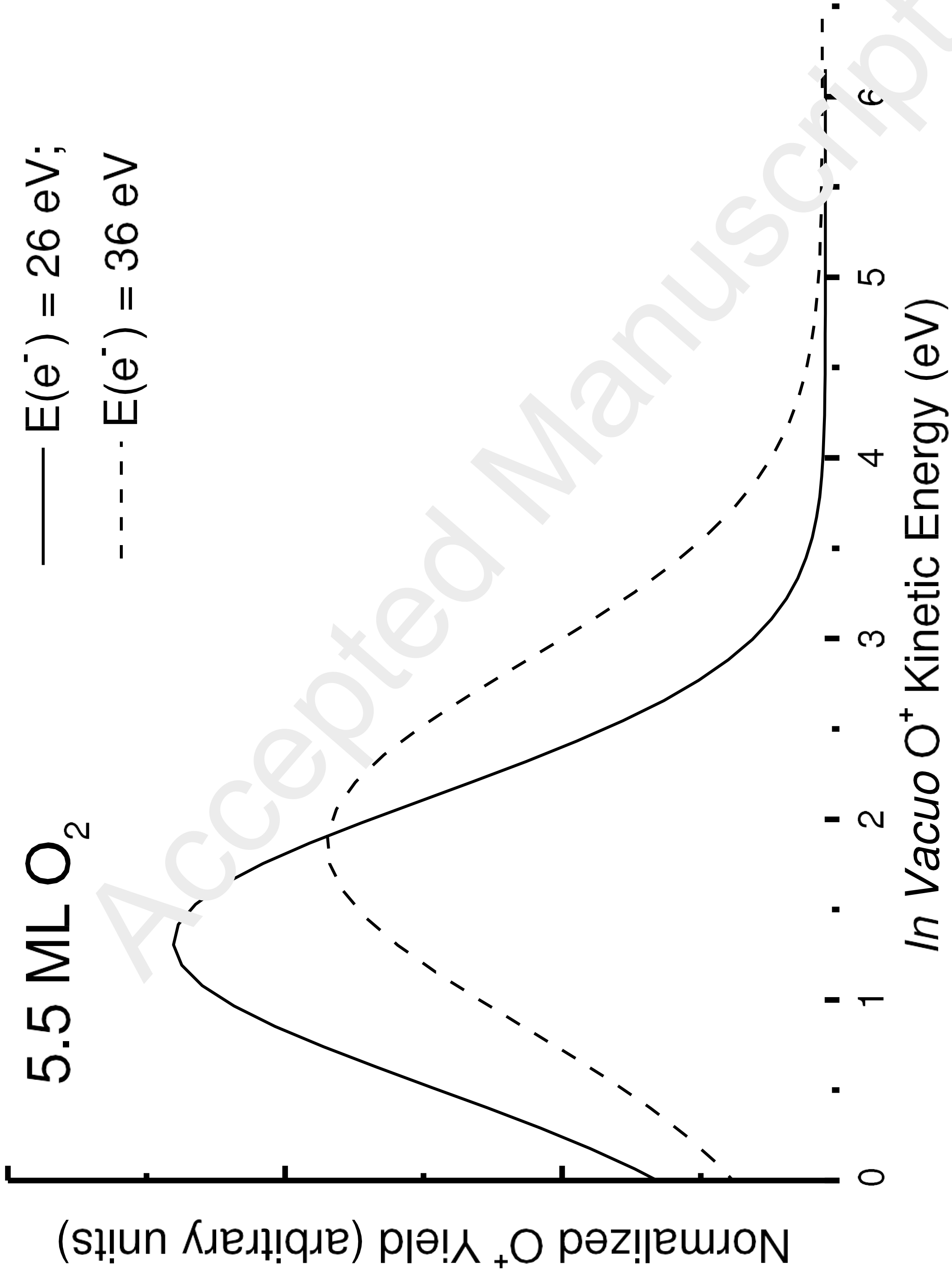


Huels, et al., Figure 1



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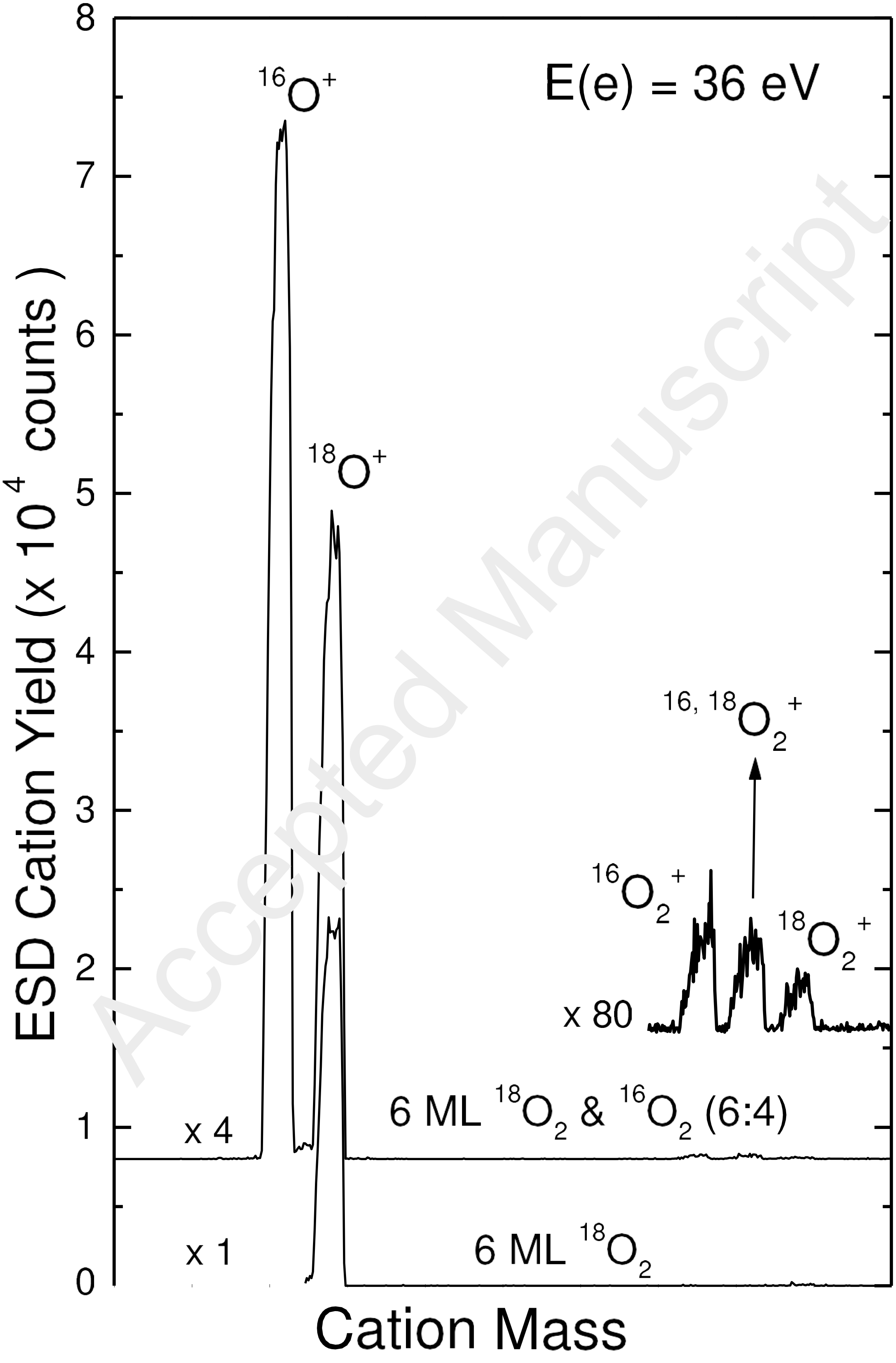
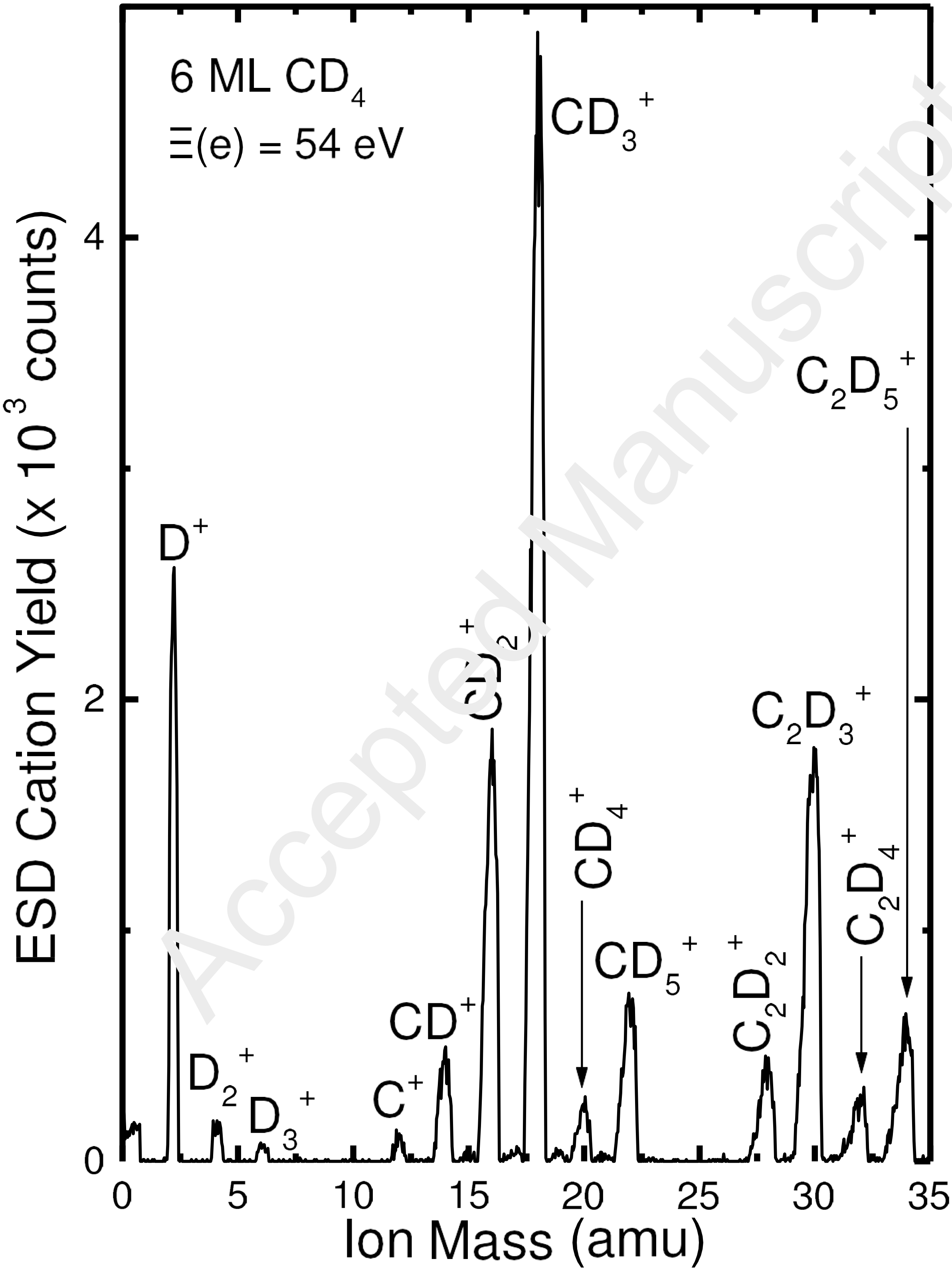
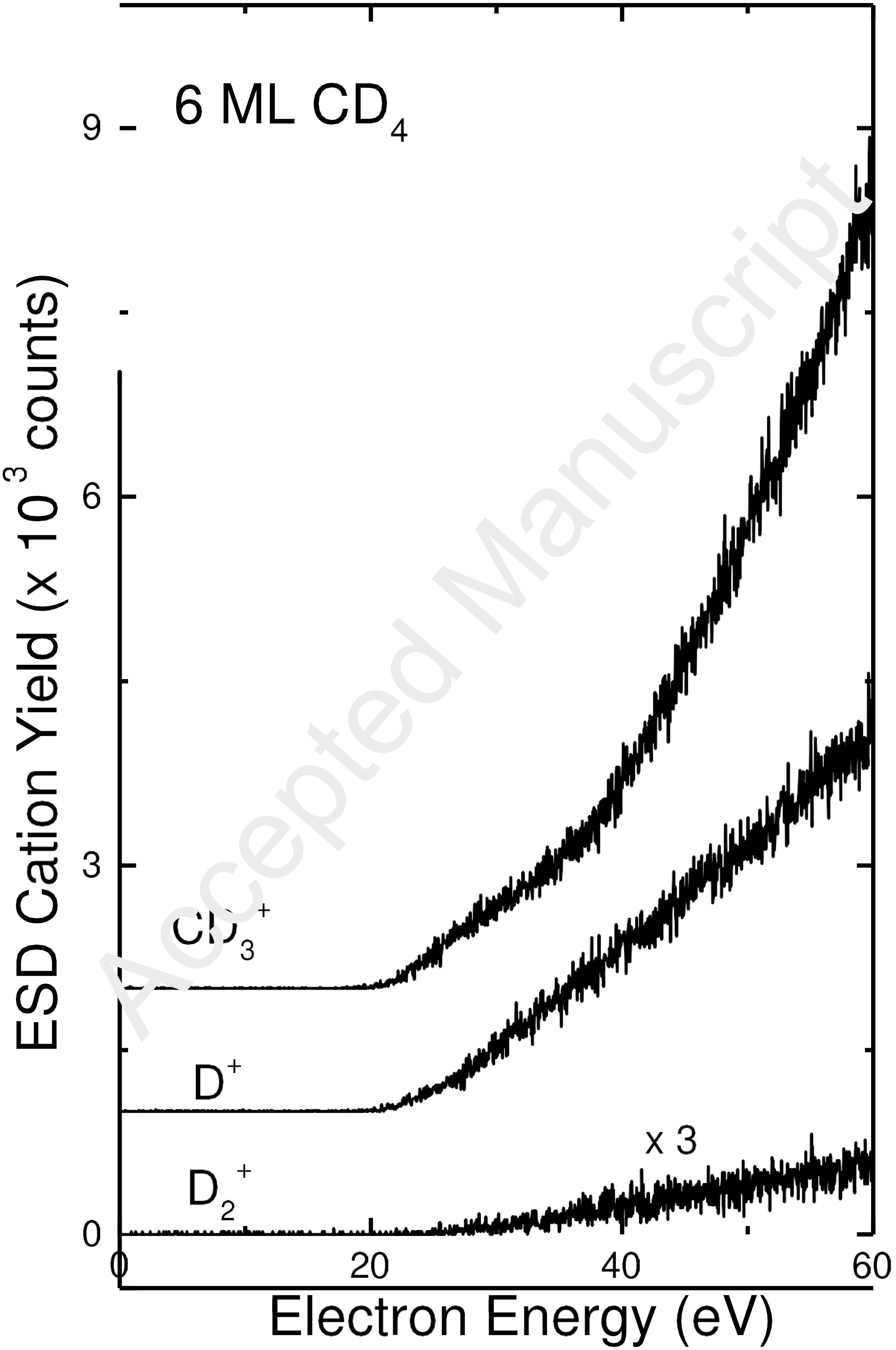


Huels et al. Figure 3



Huels et al, Figure 4



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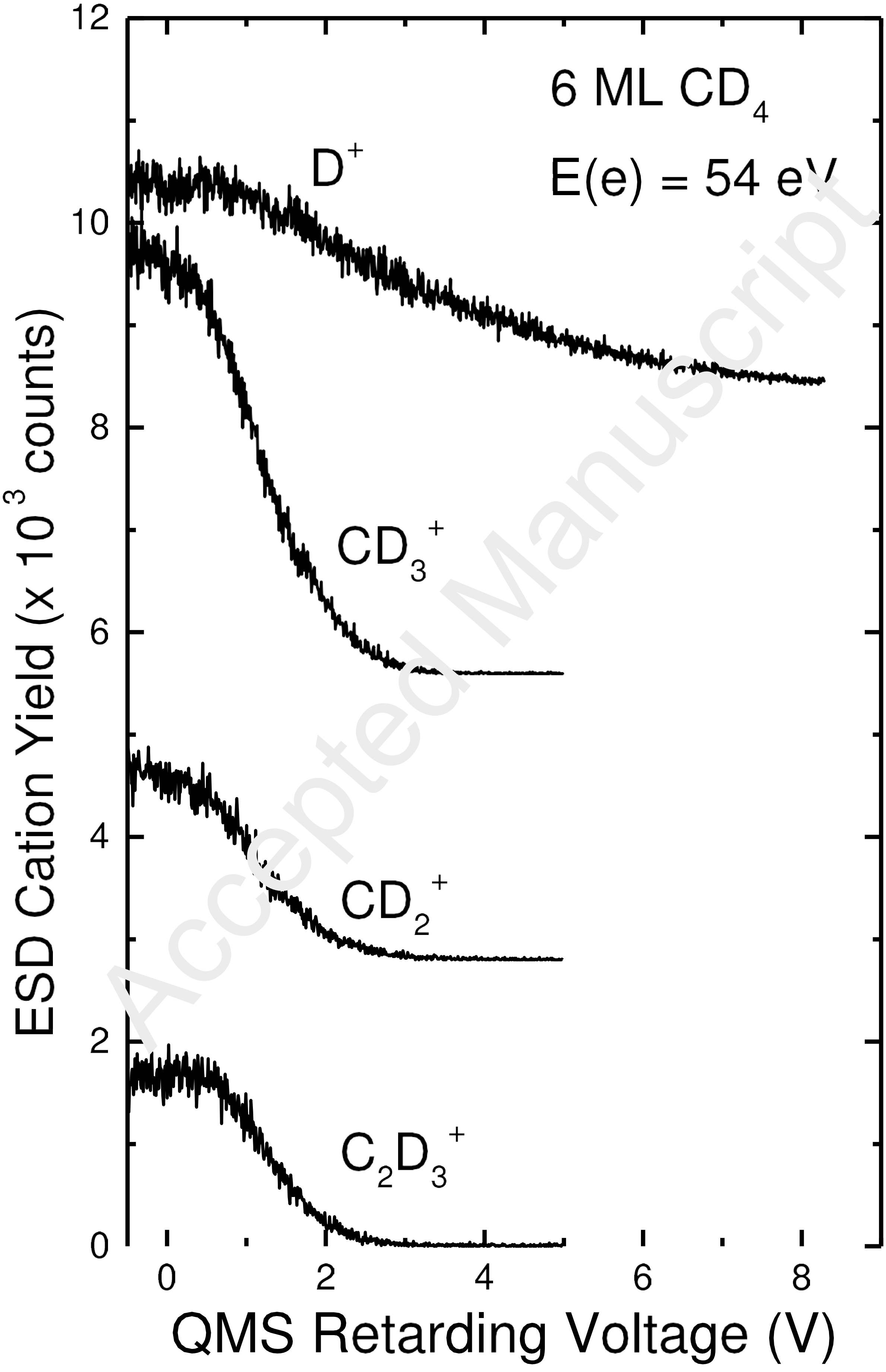

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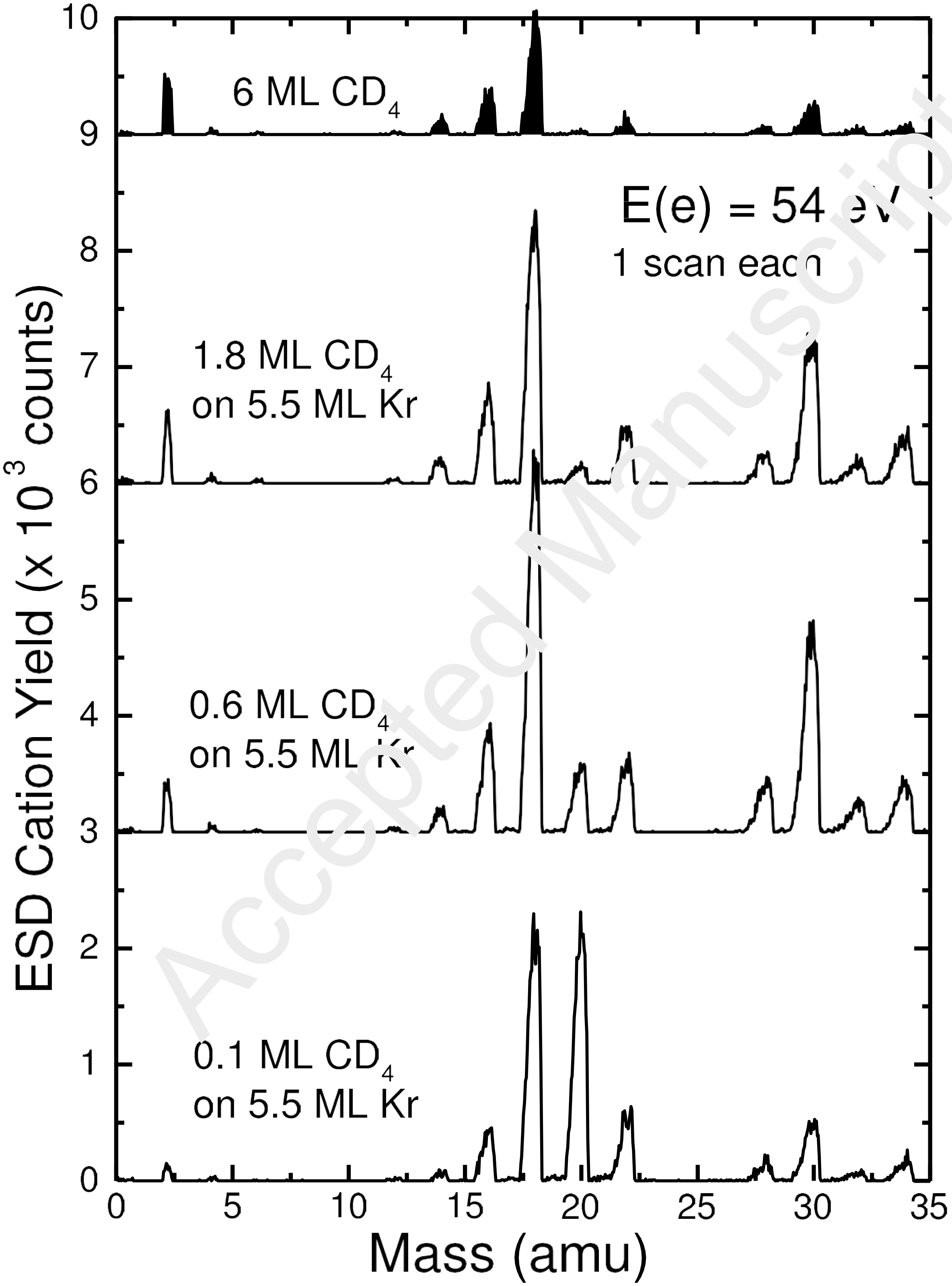

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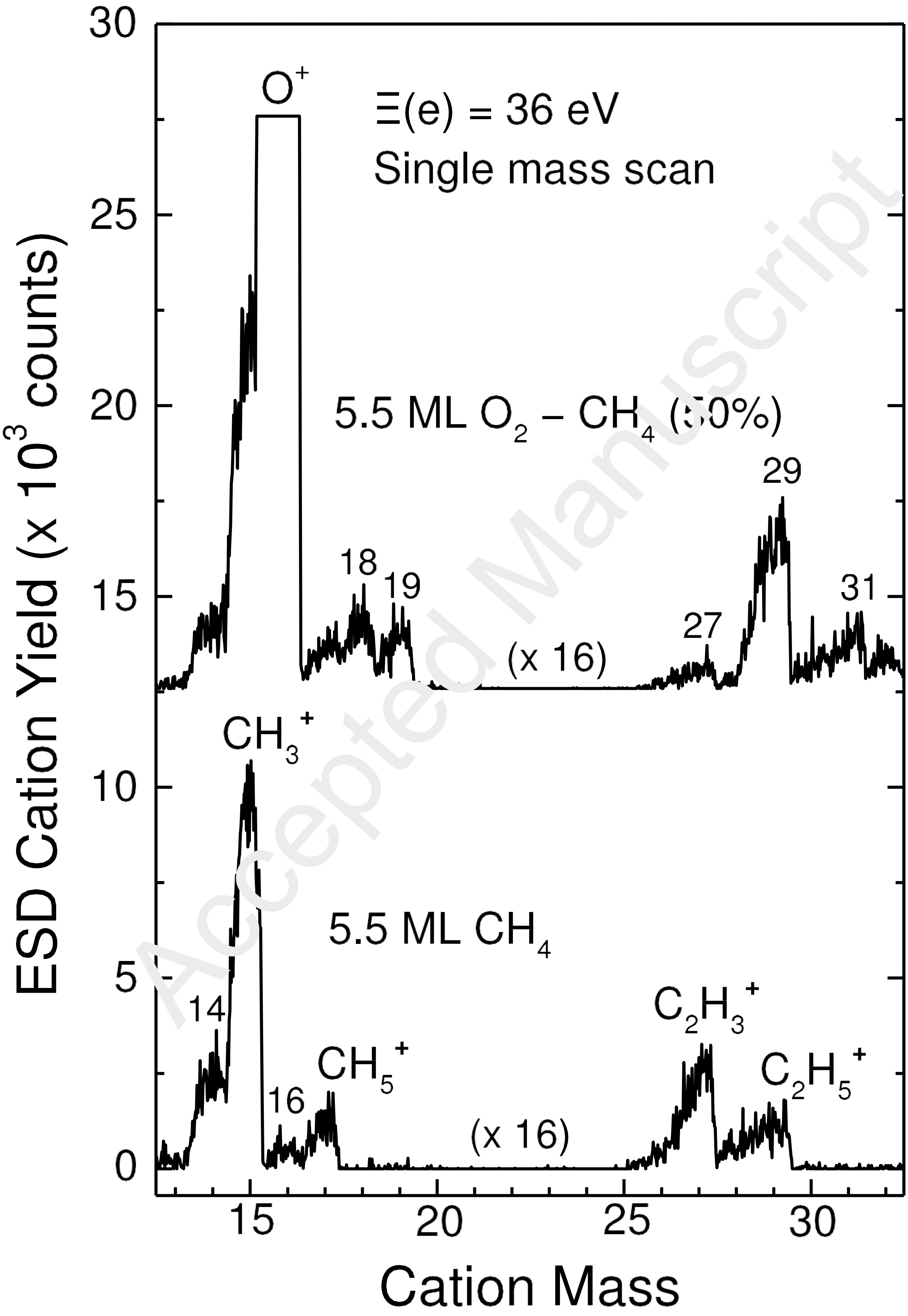

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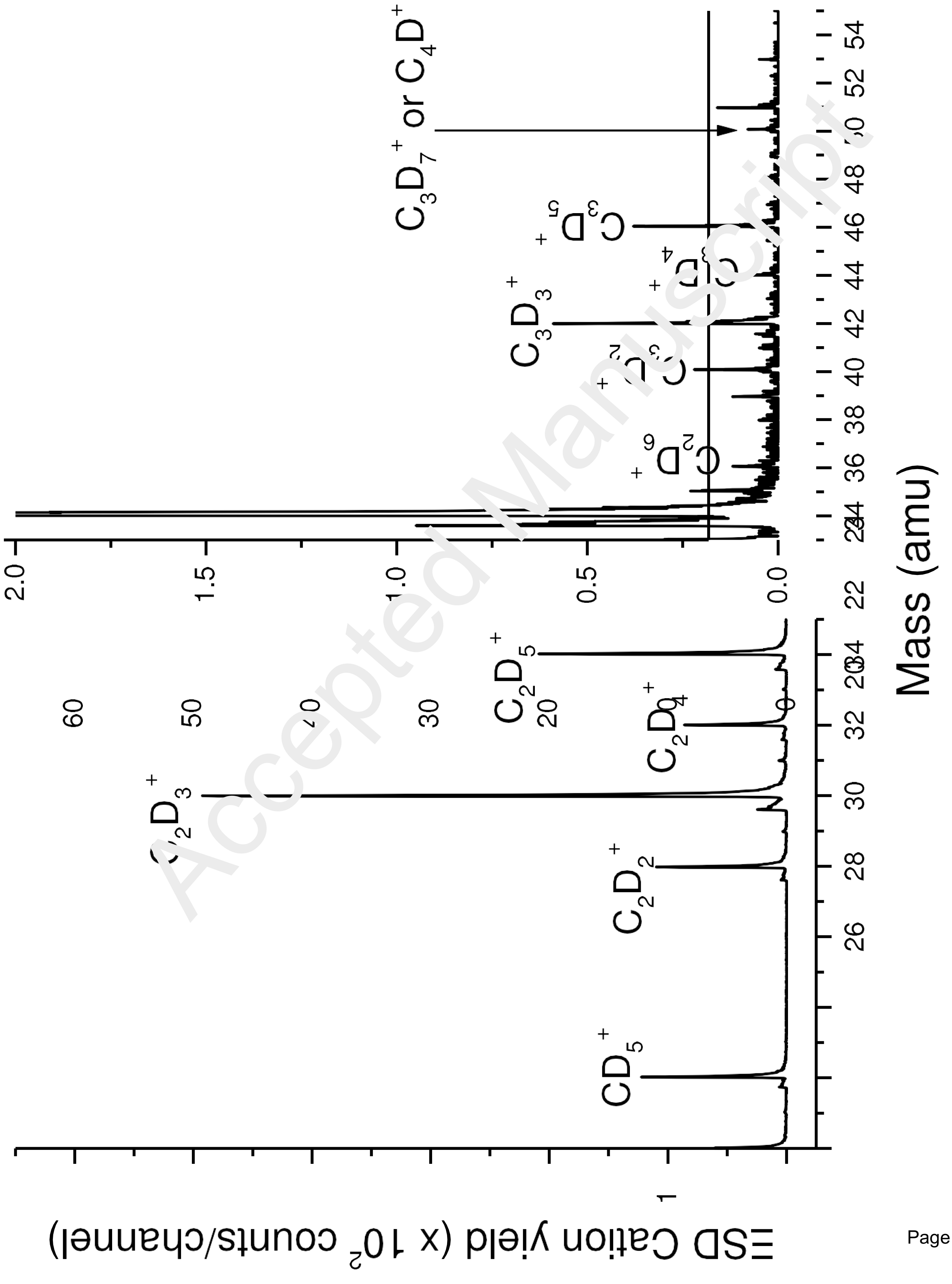

Huels et al., Figure 9

Huels, et al, Figure10