

AN ABSTRACT OF THE THESIS OF

Benjamin J. Figard for the degree of Master of Science in Chemistry presented on December 16, 2004.

Title: The Analysis of Haloethylenes Using Resonance Electron Capture – Mass Spectrometry and Data Analysis Software.

Redacted for privacy

Abstract approved: _____

Max L. Deinzer

Resonance Electron Capture – Mass Spectrometry (REC-MS) is a sensitive experimental technique for the study of gas-phase compounds with positive electron affinity. This technique was used to study a class of compounds known as haloethylenes containing chlorine and bromine substitutions. Haloethylenes are an important class of compounds because ethylene is the simplest model system for studying resonance electron capture for larger π bond networks and the effects of substitution, both in position and type. Secondly, haloethylenes are environmental contaminants that result from large-scale industrial use thereby making it important to study methods that can produce additional specificity in environmental analysis and assist in unambiguously identifying the specific compound(s) present.

Through experimentation a correlation was found showing that increasing chlorine substitution resulted in a lowering of the effective yield maximum for Cl^- in chloroethylenes and that these chloroethylenes can be identified by the shape and maxima of the yield curves. Additional fragmentation channels not previously

observed were recorded and molecular ions (M^+) were observed for tetrachloroethylene and trichloroethylene, which were not previously known to exist. Higher energy fragmentations (6-10 eV) most likely result from Feshbach resonances involving the neutral (N) electronic to singlet (S) state transition. The effective yield maximum at 8 eV for production of the C_2Cl^+ from tetrachloroethylene represents a special case and may result from a Feshbach resonance at the ionization potential of the parent molecule.

Bromoethylenes have effective yield maxima that result from lower energy electron attachment for comparable fragmentation channels for chloroethylene species. A total of seven channels not having a maximum near zero eV were observed in bromoethylenes. No molecular ions were observed in any of the bromoethylenes studied.

Theoretical studies show that the vertical electron attachment energy of a compound is dependent upon the type, number, and location of substituents while the adiabatic electron affinity is dependent upon the type and number of substituents but not on the regiochemistry. Additional theoretical work has led to a new explanation for Cl^- fragment ions that occur with electrons of near to zero eV energy from tetrachloroethylene as possibly arising through a predissociation mechanism that allows for π^* and σ^* mixing in a non-coplanar structure of the negative ion.

Additional work was done to improve data analysis by developing a Visual Basic (VB) based software to parse data in output files. The program was entitled "Extractor" and resulted in a dramatic savings in time for data processing.

© Copyright by Benjamin J. Figard
December 16, 2004
All Rights Reserved

**The Analysis of Haloethylenes Using Resonance Electron Capture – Mass
Spectrometry and Data Analysis Software**

by

Benjamin J. Figard

A THESIS

submitted to

Oregon State University

**In partial fulfillment of
the requirements of the
degree of**

Master of Science

**Presented December 16, 2004
Commencement June 2005**

Master of Science thesis of Benjamin J. Figard presented on December 16, 2004.

APPROVED:

Redacted for privacy

Major Professor, representing Chemistry

Redacted for privacy

Chair of the Department of Chemistry

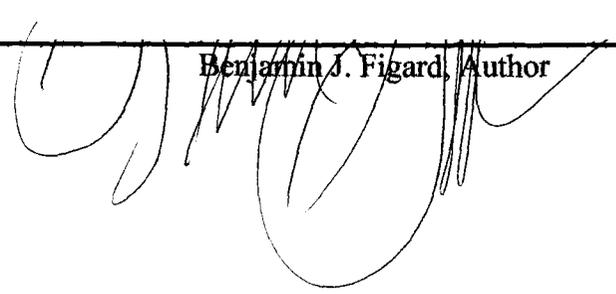
Redacted for privacy

Dean of Graduate School

I understand that my thesis will become a part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Redacted for privacy

Benjamin J. Figard, Author



ACKNOWLEDGEMENTS

The author would like to acknowledge the help and support of the members of the Mass Spectrometry and specifically Dr. Yuri Vasil'ev and Jeff Morr  who were invaluable during this work. I would also like to thank my friends, family, and the OSURFC for the support and at times, distraction. Lastly, I would like to thank Dr. Max Deinzer for giving me the opportunity to learn under his mentoring.

TABLE OF CONTENTS

	<u>Page</u>
1. Introduction.....	1
1.1 Resonance Electron Capture Mass Spectrometry.....	1
1.2 Instrument and Data Output.....	7
1.3 Haloethylenes	8
2. Materials and Experimental Procedure	17
2.1 Haloethylenes	17
2.1.1 Materials.....	17
2.1.2 Methods.....	17
2.2 Theoretical Calculations	17
2.3 Visual Basic Programming	19
3. Results.....	20
3.1 Haloethylene Experimental Observations.....	20
3.1.1 Tetrachloroethylene.....	20
3.1.2 Trichloroethylene.....	20
3.1.3 trans-1,2-Dichloroethylene.....	23
3.1.4 cis-1,2-Dichloroethylene.....	25
3.1.5 geminal-1,1-Dichloroethylene.....	25
3.1.6 Tribromoethylene.....	25
3.1.7 cis/trans-1,2-Dibromoethylene mixture.....	28
3.1.8 Vinyl Bromide.....	28
3.2 Theoretical Calculations.....	32

TABLE OF CONTENTS (Continued)

	<u>Page</u>
3.3 Data Analysis Software - Outline of Program.....	41
4. Discussion.....	52
4.1 Haloethylenes	52
4.2 Computational Data	58
4.3 Data Analysis Software	67
5. Conclusions.....	69
References.....	72
Appendix – Source Code for VB program Extractor.....	75

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1 Franck-Condon transition of a neutral molecule, AB, to a negative, excited radical ion, AB* ⁻	1
1.2 Franck-Condon transition of neutral AB to a negative radical ion, AB* ⁻ (arrow 1), and the autodetachment of an electron (arrow 2) resulting in a vibrationally excited neutral, AB*.....	2
1.3 Franck-Condon transition of neutral AB to a negative fragment, A ⁻ and a neutral radical, B [·] (2) or negative fragment, B ⁻ and neutral radical, A [·] (3).....	3
1.4 Franck-Condon transition of a neutral AB to long-lived molecular ion, AB ⁻	4
1.5 Effective interaction potential between incoming electron and a target that is generated in the case of a shape resonance (energy in arbitrary units on the y-axis and distance in Å on the x-axis); r ₁ to r ₂ is the width required for tunneling into and out of the potential well.	5
3.1 Effective yield curves of negative ions produced from tetrachloroethylene as functions of electron energy Insert for Cl ⁻ is a higher energy resolution spectrum of Cl ⁻ from different instrumental conditions optimized for better energy resolution	21
3.2 Effective yield curves of negative ions produced from trichloroethylene as functions of electron energy.....	22
3.3 Effective yield curves of negative ions produced from <i>trans</i> -1,2-dichloroethylene as functions of electron energy. Insert in Cl ⁻ effective yield curve shows peak without contaminants due to calibrant (CCl ₄).....	24
3.4 Effective yield curves of negative ions produced from <i>cis</i> -1,2-dichloroethylene as functions of electron energy.....	26
3.5 Effective yield curves of negative ions produced from <i>geminal</i> -1,1-dichloroethylene as functions of electron energy.....	27
3.6 Effective yield curves of negative ions produced from tribromoethylene as functions of electron energy. Inserts are expanded views of the curve near zero eV. Fine structure is due to instrument noise at low s/n.....	29
3.7 Effective yield curves of negative ions produced from <i>cis/trans</i> -1,2-dichloroethylene mixture as functions of electron energy.....	30

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
3.8	Effective yield curve for bromide ion produced from vinyl bromide a function of electron energy.....31
3.9	The energy difference between A and B is reported as the VEAE and the energy difference between point A and C is reported as the AEA.....33
3.10	A schematic explanation of the FIFE calculation. First, the geometry of the neutral molecule is optimized and the energy of the optimized geometry is $E_{\text{geo-opt}}$. The fragments are constructed and the geometry is optimized for each fragment. The energies are then added for the neutral radical and negative ion species to make E_{left} and E_{right} . E_{left} and E_{right} are then subtracted from $E_{\text{geo-opt}}$ to get the FIFE for the negative ions, $(\text{M-Cl})^-$ and Cl^-33
3.11	The regio-specific labeling used for differentiating the possible unique halogen losses from trihaloethylenes. The letters refer to the halogen lost for that specific fragmentation.....37
3.12	Lines 1 through 12 of a typical output file from the Oregon ToF program with line 4 indicated and the number of energy steps shown in a square.....41
3.13	Lines 14 and 200 of a typical output file from the Oregon ToF program with the mass values shown in larger font.....42
3.14	Output data of Extractor program in 2D array of Electron Energy and Intensity..43
3.15	Line 13 of a typical output file from the Oregon ToF program with the first and last values shown in larger font.....45
3.16	Output data of Extractor program in 2D array of m/z and Intensity.....46
3.17	Energy spectra from $m/z = 35$ for Cl^- from Glycine t-Butyl ester for manual peak selection (black), initial automated peak parsing (red), refined peak selection (blue), and additional peak selection refinement and background subtraction (green).....51
4.1	An expanded view of the Cl^- effective yield curve from tetrachloroethylene shown as Cl^- current (intensity) (y-axis) versus electron energy (x-axis).....53

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>	
4.2	An expanded view of the Cl ⁻ effective yield curve from tetrachloroethylene shown as Cl ⁻ current (intensity) times electron energy (y-axis) versus electron energy (x-axis). This view of the experimental data is direct comparison with data reported by Drexel et al ¹¹ and does not show the additional effective yield maxima of 0.7 eV, 0.9 eV, and 1.4 eV reported.....	54
4.3	The approximate electronegativities (χ) of fluorine and chlorine as function of charge (σ).....	56
4.4	Comparison of the VEAЕ for the chloroethylenes and bromoethylenes by halogenation (number of halogens on the compound) vs energy.....	60
4.5	Predicted geometric result of addition of an electron to either <i>cis</i> or <i>trans</i> dichloroethylene.....	62
4.6	Possible geometry result from energy minimization that does not result in global energy minimum for AEA of <i>cis</i> dichloroethylene.....	62
4.7	The non-equivalent carbons are shown as the carbanions for both possible negative ions for π^* orbital of <i>geminal</i> dichloroethylene.....	64
4.8	Both Equivalent radical negative ion structures from either <i>cis</i> or <i>trans</i> dichloroethylene.....	64

LIST OF TABLES

<u>Table</u>		<u>Page</u>
3.1	Calculated vertical electron attachment energy (VEAE) and adiabatic electron affinity (AEA) energy for chloroethylenes and bromoethylenes	33
3.2	Calculated Fragment Ion Formation Energy (FIFE) (eV) ^a for each unique Cl ⁺ and Cl [·] loss and Experimental Threshold Energy (ETE) (eV) for each experimentally observed ion	35
3.3	Calculated Fragment Ion Formation Energy (FIFE) (eV) ^a for each unique Br ⁺ and Br [·] loss and Experimental Threshold Energy (ETE) (eV) for each experimentally observed ion	36
3.4	Calculated Vertical Electron Attachment Energy (VEAE) for the <i>syn</i> and <i>anti</i> ^a constrained conformations of tetrachloroethylene with respect to the out-of-plane distortion angles (see structures below).....	38
3.5	Comparison of the lowest Vertical Electron Attachment Energy (VEAE) for ETS data, REC-MS (EAS) data, and theoretical calculations (Cal) for the fluoro-, chloro-, bromo-, and iodoethylenes. The data from the present study is denoted by "PW" for present work and all other values are referenced to the original work.....	39
3.6	Correlated values for lowest reported REC-MS (DEA) maxima and the associated ion(s) formed at this energy energy and compared by type of halogen (F, Cl, Br, and I) in the haloethylene. "PW" refers to the data from the present work and all other values are referenced to the original source.....	40

1. Introduction

1.1 Resonance Electron Capture Mass Spectrometry

Resonance Electron Capture-Mass Spectrometry (REC-MS) is simply described as the interaction between an electron and a neutral species wherein the resulting negative fragments, if any are produced, analyzed and detected by a mass spectrometer. A resonance can be thought of as the inelastic interaction of an electron and neutral species that results in an increase in the time that it takes the electron to travel past the neutral species.¹⁹ In the case of molecular systems, this interaction occurs as a vertical transition from the ground state of a molecule, AB, to the ground or an excited state of the corresponding negative ion, $AB^{\bullet-}$ (Fig 1.1).^{2, 25-28}

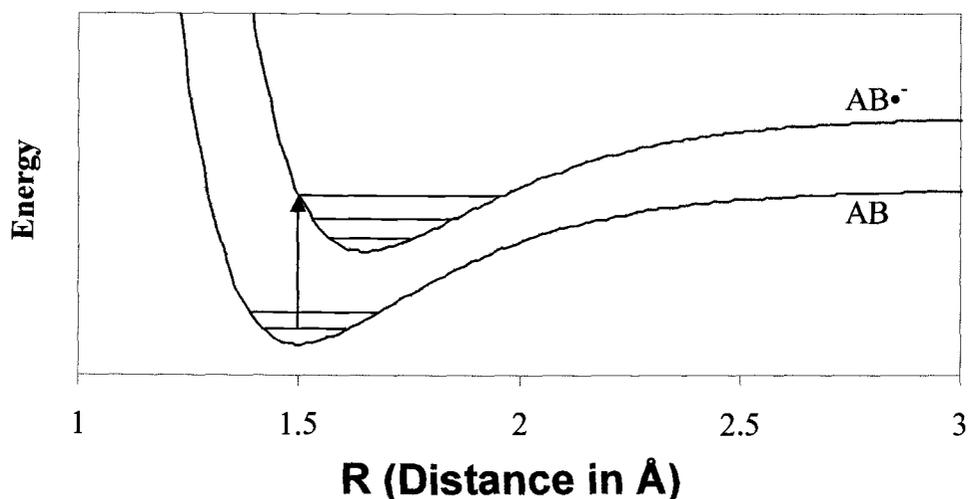
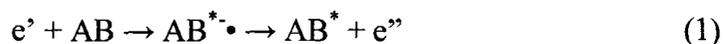


Figure 1.1 – Franck-Condon transition of a neutral molecule, AB, to a negative, excited radical ion, $AB^{\bullet-}$.

The interaction of the electron and the neutral species can occur via four processes.³ In all cases, the first step of the process is the same, an electron (e^-) interacts

with a neutral species (AB) forming a ground or excited radical negative ion ($AB^{\bullet-}$) via a vertical transition. At this point the processes proceed differently for each case. The most likely event is autodetachment of an electron resulting in an electron with a lower energy than the incident electron and a vibrationally excited neutral species.¹⁹



This can be visualized most clearly in a Franck-Condon diagram where arrow 1 represents the vertical transition (Fig 1.2). The intermediate resonant state, $AB^{\bullet-}$,

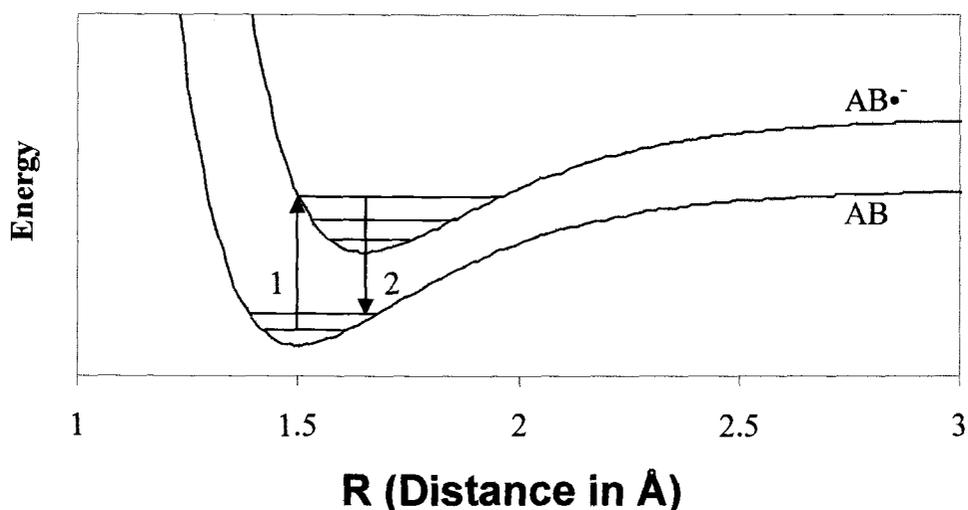


Figure 1.2 – Franck-Condon transition of neutral AB to a negative radical ion, $AB^{\bullet-}$ (arrow 1), and the autodetachment of an electron (arrow 2) resulting in a vibrationally excited neutral, AB^* .

then relaxes as the bond stretches from 1.5 Å to ~1.6 Å. Finally, autodetachment of the electron from the intermediate state proceeds.^{1,2} It is clear that the energy of the electron at autodetachment (Arrow 2, Fig 1.2) is different from the initial energy, given that the vertical transition starts at a lower energy level than the emission of the electron that results in the neutral species.

The second case involves fragmentation of the energetically excited radical species into a negative ion (A^-) and a neutral radical fragment (B^\bullet).



The third case involves formation of the complimentary ion (B^-) and the neutral radical (A^\bullet).



Both the second and third cases involve a vertical transition to a dissociative curve that relaxes into the fragments although the two cases rarely occur with the same energy (Fig1.3). In terms of molecular orbitals this can thought of as a vertical transition of an electron into an anti-bonding molecular orbital. The energetic considerations for fragmentation will be discussed later.

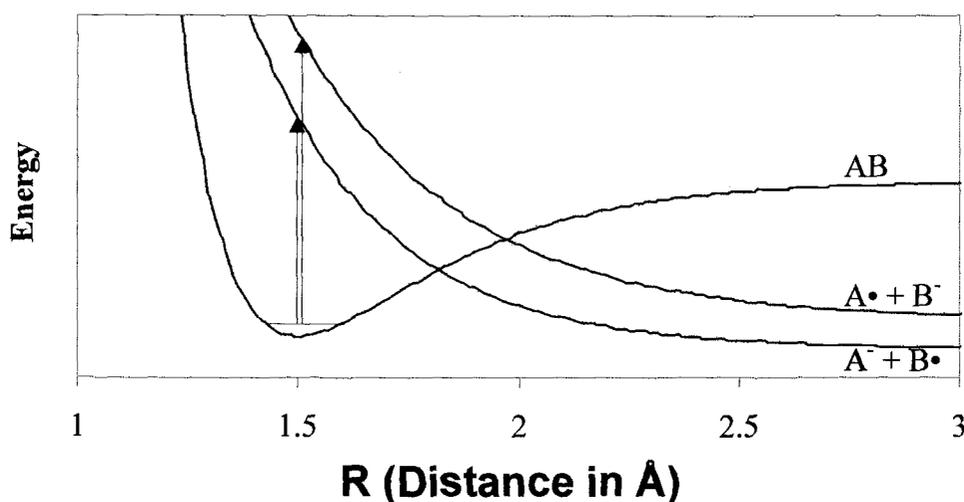
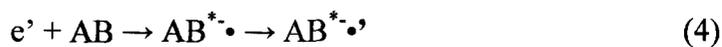


Figure 1.3 – Franck-Condon transition of neutral AB to a negative fragment, A^- and a neutral radical, B^\bullet (2) or negative fragment, B^- and neutral radical, A^\bullet (3).

Finally, there is the formation of a long-lived (lifetime longer than 1 μ s) molecular ion ($M^{*\bullet}$).



Typically this is accompanied by some relaxation of geometry resulting in a positive energy change for the species where $AB^{*\bullet}$, (4) represents this change of geometry from AB^{\bullet} . (Fig 1.4) These negative molecular ions may have lifetimes as long as 10^{-6} s or even greater for species with large positive electron affinity and are, therefore, detectable by mass spectrometry (MS). The long-lived negative molecular ion contrasts with the transient, negative ion intermediate that can undergo autodetachment in 10^{-14} to 10^{-15} s to μs ¹⁹ (1) or decomposition (pathways 2 & 3) in 10^{-12} to 10^{-14} s¹⁹ where the resulting fragment negative ions are also detected by MS.

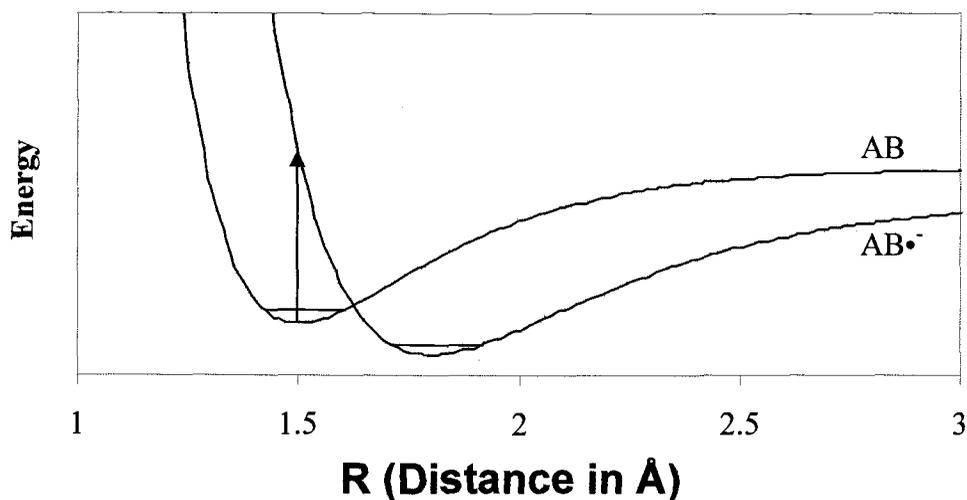


Figure 1.4 – Franck-Condon transition of a neutral AB to a long-lived molecular ion, AB^{\bullet} .

There are three types of resonances according to the classification of Bardsley and Mandl³⁸; these are shape, and electronically and vibrationally excited Feshbach resonances. Shape resonances occur when an electron is trapped in a potential well due to an energy barrier caused by the interaction of the electron and the target species (Fig. 1.5). The trapping potential barrier is due to the angular momentum of the electron in the centrifugal repulsive component of the electron/molecule interaction.⁵⁰ The lifetime of a

shape resonance is dependent on the height and width (r_1 to r_2) of the barrier trapping the electron.³⁸ There is reduced probability for electron tunneling into or out of the potential well for species with larger energy barriers.

In contrast to shape resonance, a Feshbach resonance has no energy barrier for trapping the electron.³⁸ The Feshbach resonance occurs when the electron transfers energy into the target leaving the electron without sufficient energy to escape from the attractive potential well. Generally, Feshbach resonances are associated with an excited vibrational or electronic state of the neutral species. These resonant ions are lower in energy than the corresponding parent neutral excited state.³⁷

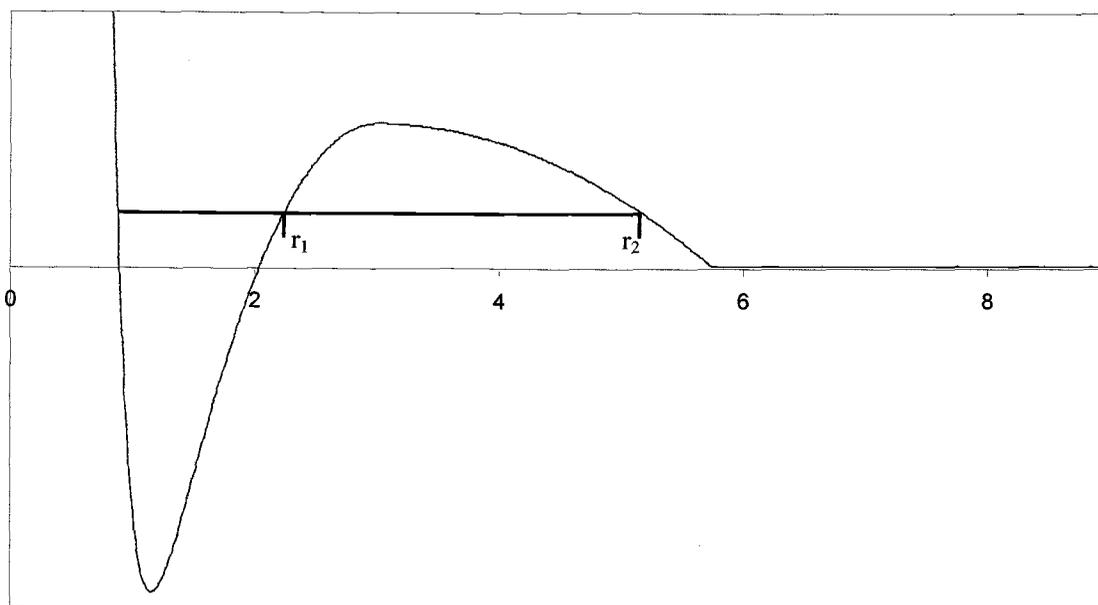


Figure 1.5 – Effective interaction potential between incoming electron and a target that is generated in the case of a shape resonance (energy in arbitrary units on the y-axis and distance in Å on the x-axis); r_1 to r_2 is the width required for tunneling into and out of the potential well.

REC-MS adds an additional level of information to the traditional mass spectrometric results. REC-MS uses a mono-energetic electron beam that allows the correlation between electron energy and the formation of a negative ion with specific

resonance energy. The correlation between electron energy and the resonance energy for the formation of a given ion allows for a more complete understanding of the physical properties of a decomposition pathway. However, the resulting effective yield curves, intensity vs. electron energy from REC-MS are not resonances. The effective yield curves show the electron energy resulting in a specific fragmentation from the resonance which may be one of many dissociative channels available. Put another way, the resonance interaction between an electron and a molecule is observed by ETS and leads to fragmentation of a molecule and the determination of effective yield curves by REC-MS. Lastly, molecular negative ions can be formed over a wide energy range from near to zero up to energies well exceeding the ionization threshold of neutral molecules, in which case ion pair formation, i.e. A^+ and B^- , results and the determination of effective yield curves for long-lived molecular ions is possible by REC-MS.

In contrast to negative, molecular ion formation, fragmentation or dissociative electron attachment (DEA) has a minimum energy requirement for the formation of the negative fragment ion.^{19,44} The minimum DEA energy, ϵ_1 , is related to the minimum heat of reaction for dissociation, ΔH_0 , and the excess energy lost as translational energy to the fragments, ϵ_x .

$$\epsilon_1 = \Delta H_0 + \epsilon_x \quad (5)$$

ΔH_0 in the simple molecular case of AB, is the bond dissociation energy (BDE) of AB minus the electron affinity (EA) of the radical species ($B\cdot$), that is the parent of the negative ion (B^-).

$$\Delta H_0 = D(AB) - EA(B\cdot) \quad (6)$$

The importance of the relationship governing ΔH_0 can be seen in a simple example. In the case of $C_2Cl_2F_2$, the EA of the chlorine atom is 3.61 eV and the BDE of a typical C-Cl bond is 3.58 eV.⁴⁵ The difference (-0.03 eV) in these energies provides the driving force for the formation of fragment negative ions from electron attachment to low-lying antibonding orbitals. As can be seen from this example, the electron energy necessary is near to zero eV, as are many of the resonance electron capture processes. If an electron is captured into a higher energy antibonding orbital, then the experimental attachment energy will be higher and the ion produced will have excess energy in vibrational, translational, or rotational levels, since the BDE and EA have not changed.

1.2 Instrument and Data Output

An instrument has been developed to study the details of REC-MS. Briefly, a trochoidal electron monochromator that produces a 15 nA electron beam with 100 meV or better energy resolution was interfaced with a reflectron time-of-flight mass spectrometer on a JEOL JMS-DX300 platform.^{4,5} The electron energy is ramped at a fixed rate from -1.7 to +25 eV and the ions resulting from the crossed electron and neutral molecule beams, are extracted orthogonally into the mass analyzer with a maximum frequency of 80 kHz corresponding to an upper mass limit of 500 amu. Given the molecular weight of the compounds studied, there is no need for a broader mass range in the present study but a larger mass range can be realized by lowering the extraction frequency to allow sufficient flight time for larger mass ions.

Data are acquired as large binary files requiring extensive data manipulation in order to be converted into a usable 2D data array. Typically, file sizes are on the order of tens of MB depending upon the mass range stored. The large file size makes utilizing the output files difficult on slower computer systems thus requiring a long time for processing. Extractor is a Visual Basic program written to parse data, or find and separate specific data output in large text files into two data columns (electron energy and intensity) for each mass spectrometric peak.²¹ Writing Extractor was necessary due to the amount of time required to manually separate and manipulate data to generate the energy spectra for each mass. Additional features of the software include output of a 2D mass spectrum (m/z vs intensity), generation of total effective yield curves (TEYC), energy calibration, and a mass peak table summarizing m/z , relative intensity (RI%), and energy peak maxima (E_{\max}). Removing the bottleneck due to data manipulation results in an increase in data analysis throughput.

1.3 Haloethylenes

Haloethylenes have been studied by a variety of experimental techniques including Electron Transmission Spectroscopy (ETS),^{18,29} Photoelectron Spectroscopy (PES),⁶ Electron Energy Loss Spectroscopy (EELS),^{7,8} Negative Chemical Ionization – Mass Spectrometry (NCI-MS),^{12,14,15} and Resonance Electron Capture-Mass Spectrometry (REC-MS).^{3,9-11} Each experimental technique contributes additional information regarding the electronic structure and reactivity of these compounds. ETS allows for the study of all resonances of any compound within the energy range of the

instrument. The ETS method can deal with resonances that have lifetimes before autodetachment that are significantly shorter than would be required for detection by other methods. However the information obtained does not include specific details on the dissociation of the resonances into negative fragment ions and the neutral counterparts.

Specific research has been carried out by Olthoff et al¹⁶ correlating ETS with REC-MS for vinyl halides and chloroethylenes among other halogen-containing compounds. For vinyl halides (vinyl fluoride, vinyl chloride, vinyl bromide, and vinyl iodide), ETS data show that increasing halogen atomic number results in a decrease in the attachment energy that results from electron capture into low-lying π^* and σ^* anti-bonding orbitals. In all cases, except for vinyl iodide, the π^* orbital is at least equal to if not lower in energy than the σ^* orbital. For vinyl bromide, the negative ion π^* resonance overlaps with the σ^* resonance that is thought to be on the high energy edge of the observed ETS band. Experimental attachment energies for capture of an electron into the π^* orbital are: vinyl chloride, 1.29 eV and vinyl bromide, 1.16 eV. Olthoff et al concluded that the electron capacity and not the electronegativity of the halogen is the important property for increased stabilization of the transient negative ions. Electron capacity or charge capacity of an atom is the “ability to donate or absorb electron density before its electronegativity changes too much for further electron transfer to take place.”³⁹ The electron capacity increases with increasing atomic size. By correlation with DEA for production of halide ions, ETS showed that DEA at electron energies below 7 eV is associated with the π^* resonance with the exception of vinyl iodide. In the case of vinyl iodide, halide ion formation is associated with both σ^* and π^* resonances because the σ^* orbital is lower in attachment energy than the π^* orbital in vinyl iodide.¹⁶

ETS data for chloroethylenes showed that the attachment energy of the π^* orbital is lower than it is for the σ^* orbital by 0.9 eV or more for all compounds. The electron energies required for attachment into low lying antibonding π^* orbitals are: 0.4 eV for tetrachloroethylene, 0.61 eV for trichloroethylene, 0.75 eV for *geminal*-1,1-dichloroethylene, 0.83 eV for *trans*-1,2-dichloroethylene, 1.12 eV for *cis*-1,2-dichloroethylene, and 1.28 eV for vinyl chloride. These values when correlated with halide negative ion formation seem to support the premise that DEA occurs via a π^* shape resonance. Furthermore, it is concluded that inductive stabilization of negative ion π^* resonances is greater in geminal substitution than it is for 1,2 substitution in dichloroethylenes. Simply put, geminal substitution leads to a lower energy resonance maximum than 1,2 substitution for chloroethylenes. Lastly, the formation of the halogen negative ions has been explained on the basis of an out-of-plane distortion that allows for a Franck-Condon overlap for a 0 eV transition. This hypothesis is in contrast to earlier theories about the tenths of an eV energy requirement for production of negative ions from tetrachloroethylene where ions produced at 0 eV were explained on the basis that the negative ion lifetime is inversely proportional to the energy of the electron and that, therefore, dissociation could effectively compete with autodetachment at near to zero energies.^{10, 17}

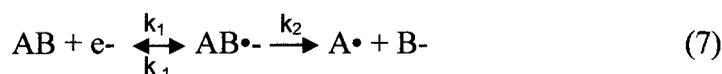
PES allows for the determination of the ionization potential of compounds.⁶ Unfortunately, no data exist for the bromoethylenes studied but there is comprehensive data on chloroethylenes. The first ionization energies of the chloroethylenes range from 9.5 to 11 eV and are, therefore, relevant to the present study of electron attachment as a potential source of parent states for Feshbach resonances.

EELS provides information on the electronic excitation including the energy of transition from the ground state (N) to triplet (T) and singlet (S) excited states.^{7,8} Again there are no data on bromoethylenes but extensive experimental results have been reported for chloroethylenes regarding the $N \rightarrow T$ and $N \rightarrow S$ transitions. The experimentally determined energies for these vertical transitions are 3.5 to 4.25 eV ($N \rightarrow T$) and 6 to 7 eV ($N \rightarrow S$), both of which are clearly relevant to the energy range in REMS, again as potential parent states for Feshbach resonances.

NCI-MS is the only experimental technique that has been used to study chloroethylenes and bromoethylenes other than the vinyl halides.¹³ It has been shown that the "branching effect," the relative ratio of fragmentation for a specific channel versus the dominant fragmentation channel due to the interaction with a thermal electron, is temperature and halogen substitution dependent. The specific experimental observations are that increasing temperature results in decreased formation of X_2^- and $(M-X)^-$ when compared with X^- formation and that the observed fragmentations show different ions, where M is the molecule and X is the halogen. In addition, the M^- is observed for *trans*-1,2-dichloroethylene and tribromoethylene but not for trichloroethylene. Of particular interest is the experimental observation that no $(M-Br)^-$ is formed from *cis*-1,2-dibromoethylene, but a temperature dependent Br_2^- fragment is produced. In direct contrast, no Br_2^- results from *trans*-1,2-dibromoethylene but a temperature dependent formation of $(M-Br)^-$ is observed. This observation is in contrast to the analogous *cis* and *trans* chloroethylenes, both of which show Cl_2^- but no $(M-Cl)^-$. These results led Nakagawa and Shimokawa³ to propose that chloroethylenes and bromoethylenes fragment via different mechanisms.

Chen and coworkers ¹² have also used NCI-MS to determine the electron affinities of several compounds including those of tetrachloroethylene and trichloroethylene that showed electron affinities of 0.64 ± 0.03 eV and 0.40 ± 0.22 eV, respectively. In addition, it was shown that the electron detachment energy of the tetrachloroethylene and trichloroethylene molecular negative ions were 0.5 eV and 0.3 eV, respectively, with both ions having a 0.1 eV activation energy for thermal electron attachment. ¹⁴

Of particular relevance to REC-MS is work demonstrating the temperature dependence of the electron capture process. Given that k_1 is the rate constant of the forward reaction of the capture of a thermal electron by the molecule, k_{-1} is the rate constant of the electron autodetachment process, and k_2 is the dissociation rate constant forming the negative ion and neutral fragments, the equation (3) can now be expressed as follows:



It has been shown by Chen et al ¹² that in the temperature range $\sim 50^\circ$ C to 425° C, k_2 is small relative to k_1 . This makes the value of the experimentally observed rate, k_{ex} (8), dependent upon k_1 , k_{-1} , and k_N , where k_N (9) is defined as k_N' , the rate constant of charge neutralization (10), multiplied by the concentration of P^+ , the positive ions formed by the interaction of high energy electrons and cooling gas, plus the loss of ions by diffusion, $k_{diffusion}$ (11).

$$k_{ex} = k_1 / (k_{-1} + k_N) \quad (8)$$

$$k_N = k_N' [P^+] + k_{diffusion} \quad (9)$$



Because k_{-1} is temperature dependent and increases with increasing temperature and k_N is temperature independent, $k_{-1} \gg k_N$ at high temperature and therefore the expression for k_{ex} can be simplified (10).

$$k_{ex} = k_1 / k_{-1} \quad (12)$$

The experimental data show that the temperature where k_{-1} begins to dominate k_N is ~ 475 K (272° C) for tetrachloroethylene and at ~ 385 K (111° C) for trichloroethylene. This suggests that electron autodetachment is of real concern in the temperature range used in the ion source of the REC-MS for volatilization of these analytes. The temperature range for autodetachment may actually be lower given that under experimental conditions, REC-MS does not generate positive ions and, therefore, the loss of negative ions via charge neutralization is negligible, making $k_N = k_{diffusion}$. The lack of positive ions in REC-MS is explained by the electron energy being well below the ionization threshold for most electron-capturing compounds.

Lastly, Chen et al ¹⁵ using NCI-MS presented the C-Cl bond dissociation energy (BDE) for the formation of Cl^- and the counterpart radical, neutral species. The experimentally determined BDE values were 3.98 eV for tetrachloroethylene, 4.06 eV for trichloroethylene, 3.83 eV for *cis*-1,2-dichloroethylene, 3.84 eV for *trans*-1,2-dichloroethylene, and 4.05 eV for geminal-1,1-dichloroethylene. However, it is important to be aware that these BDEs are upper limits for fragmentation to Cl^- , since no measurements of the fragment ions' kinetic energies were performed. BDEs for C-Br bond dissociation were given for *cis*-1,2-dibromoethylene at 3.64 eV and *trans*-1,2-dibromoethylene at 3.62 eV. There are no other data for bromoethylenes.

REC-MS can be used to study resonance interactions between electrons and neutral molecules, but in addition the technique allows for correlating the electron energy with the resulting fragment and long-lived molecular negative ions. It is important to remember that the resulting negative ion effective yield curves, representing intensity vs. electron energy are not the total identity of the resonances themselves, but just indications of the resonances. Fragment negative ions are decay products of the resonances and molecular ions indicate what is left from the resonances after electron autodetachment in the typical mass spectrometric time scale.

In 1977 Johnson et al³ did the first studies on chloroethylenes applying REC-MS. Tetrachloroethylene, trichloroethylene, *cis*-1,2-dichloroethylene, *trans*-1,2-dichloroethylene, and 1,1-dichloroethylene fragmented to yield Cl^- , Cl_2^- , and $(\text{M}-\text{Cl})^-$ in addition to the molecular ion, M^- , that was observed in the case of tetrachloroethylene. In all cases the dominant ion was Cl^- , the production of which follows the order of decreasing energy from *trans*-1,2-dichloroethylene > *cis*-1,2-dichloroethylene > 1,1-dichloroethylene > trichloroethylene > tetrachloroethylene. In the cases of 1,1-dichloroethylene, trichloroethylene, and tetrachloroethylene there are two clear maxima with the one at 0.19 eV increasing in intensity with increasing chlorination. All other energy peaks reported were under 3 eV.

In 1984, Kaufel and coworkers published REC-MS data on chloroethylenes using an electron monochromator.⁹ Again, the Cl^- was the dominant species present for all compounds examined but there were three substantial differences between the two reports. First, the electron energy peaks for *cis*- and *trans*-1,2-dichloroethylene were different, with peak maxima at 1.05 eV and 1.1 eV, for the *cis*- and *trans*-1,2 dichloro

isomers respectively, in contrast with values of 1.35 eV and 0.95 eV reported by Johnson et al.³ The second important difference was the lack of multiple maxima in the electron attachment spectra of tetrachloroethylene, trichloroethylene, and 1,1-dichloroethylene. Simply put, there was only one clear maximum in each effective yield curve of Cl^- for the three aforementioned compounds. Lastly, additional fragmentation channels for tetrachloroethylene and *trans*-1,2-dichloroethylene were reported including three ions for tetrachloroethylene that had maxima in the 5-10 eV range. For tetrachloroethylene, four “new” fragmentation pathways were observed including those forming: $(\text{M}-\text{Cl})^-$, C_2Cl_2^- , CCl_2^- , and C_2Cl^- and for *trans*-1,2-dichloroethylene there were two “new” fragments, HCl_2^- and C_2HCl^- . The complete electron energy spectrum for tetrachloroethylene was also published by the same group and compared with mixed chloro- and fluoro-substituted ethylenes but no additional experimental data for chloroethylenes were presented.¹⁰

Recently, another report exclusively on tetrachloroethylene was published that agreed with Kaufel et al's results with only a few minor exceptions.¹¹ First, the relative intensity of ion formation differed between the reports. Second, while the overall Cl^- effective yield curves were in good agreement, the high energy resolution used by Drexel et al¹¹ helped to resolve four contributing resonances at: 0.4 eV, 0.7 eV, 0.9 eV and 1.4 eV. Lastly, a near to zero energy peak was observed in spectra when the effective yield energy maximum was not near to zero eV. This peak was proposed to be instrument geometry dependent resulting in fragmentation by interaction with autodetached electrons outside the ion source.

Several reports on aliphatic halocarbons have been published including comparisons of those bearing chlorine and bromine substituents^{20, 30-31} and mixed halogens.³⁶ These results show Br⁻ from dissociative electron attachment in the 0-2 eV energy range.

A more complete understanding of haloethylene negative ion formation and fragmentation was pursued in this work using an electron-monochromator mass spectrometer instrument with better sensitivity than was previously used.^{4, 5} A computational method was also developed that allowed for faster data reduction. Lastly, an effort was made to correlate theoretical results from high level calculations with experimental data.

2. Materials and Experimental Procedure

2.1 Haloethylenes

2.1.1 Materials

Reagents were purchased as liquids including *cis/trans* dibromoethylene mixture (98%) from Aldrich Chemical Co. (Milwaukee, WI), vinyl bromide 1.0 M in THF from Aldrich Chemical Co. (Milwaukee, WI), tribromoethylene (97%) from TCI (Portland, OR), and all other reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI) as neat liquids with a stated purity of 97% or better. Reagents were used without further purification.

2.1.2 Methods

Examination of haloethylenes was performed on a Resonance Electron Capture (REC) Time-Of-Flight (TOF) Mass Spectrometer (MS) instrument described recently.⁴ The instrument was calibrated for both mass and energy scales using CCl_4 ²² and SF_6 .²³²⁴ Haloethylene samples were introduced by injecting 2-3 μL into the reference sample inlet system and heated for volatilization. Data were acquired by proprietary software of Ionwerks (Houston, TX) and stored as binary files.

2.2 Theoretical Calculations

Calculation of physical properties for haloethylenes was performed on a Red Hat Linux v7.2 operating system with an AMD Athlon XP2100+ processor on the Jaguar v4.2 (Schrödinger, Inc., Portland, OR)³² program and Maestro v4.1 (Schrödinger, Inc., Portland, OR)³³ program for calculations and molecule construction, respectively. Calculations were performed using 6-31 G ** ++ B3LYP for all atoms except bromine where effective core potentials were used as defined in the LAV3P ** ++ B3LYP basis set. Using the LAV3P ** ++ B3LYP for the bromoethylenes results in 6-31 G ** ++ B3LYP characterization of all other atomic types used in these calculations. Once a molecule was constructed, geometry optimization was performed to determine the total energy minimum for the neutral molecule. From this geometry optimized model of the neutral molecule, the vertical electron attachment energy (VEAE) was calculated by adding an electron, changing the multiplicity from a singlet to a doublet, and freezing the molecular geometry. The difference in total energy between the neutral molecule and the negative ion doublet with the geometry of the neutral molecule was taken to be the vertical electron attachment energy or the vertical transition. The negative ion's geometry was then optimized to determine the adiabatic electron affinity by comparison of the total energy of the relaxed geometry of the negative ion to that of the neutral molecule. Finally, threshold energies for fragmentation processes were calculated for each unique halogen loss and both possible complimentary negative ions were calculated for each unique bond dissociation. The total energy of each complimentary ion and its neutral counterpart were compared with the total energy of the original neutral molecule to determine the minimum energy required for each fragmentation process.³⁴

In order to test the effects of non-planarity on the vertical transition energy, the dihedral bond angles of the four chlorine atoms of tetrachloroethylene were constrained to 1, 2, 5, 10, and 20 degrees from planarity with both *syn* and *anti* arrangements. The geometries for these new structures were optimized for all other variables (all bond lengths and other non-dihedral bond angles) and VEAEs calculated as described above.

2.3 Visual Basic Programming

The program entitled “Extractor” (see Appendix for source code) was written using Microsoft Visual Basic (VB) from the Microsoft Visual Studio 6.0 Professional Edition.^{21, 35} The program was run on a Microsoft Windows 2000 operating system⁴ and within the VB editor using a full compilation of the program prior to use. Running the program in this manner allows for any programming bugs to be examined when they occur but improves speed of execution of the program.

3. Results

3.1 Haloethylenes

3.1.1 Tetrachloroethylene

REC-MS results for C_2Cl_4 (Fig 3.1) are in good agreement with previously reported results by Drexel et al¹¹ and Kaufel et al,⁹ both of which are basically identical in the location of resonance maxima. The spurious peaks at near to 0 eV mentioned by Drexel et al were not observed reaffirming that these peaks are probably due to the ion extraction geometry specific to their instrument. In addition to good agreement with the overall resonance shapes of Drexel et al and Kaufel et al, the relative intensities of the ions differ somewhat but are overall in good agreement with all previously published reports.^{3,9,11} The data obtained in the present studies show no fine structure on the Cl^- resonance as recently suggested.¹¹

3.1.2 Trichloroethylene

There exists more limited data on C_2HCl_3 in the literature with Johnson et al³ reporting only three fragment ions; $(M-Cl)^-$, Cl_2^- , and Cl^- , from the compound and Kaufel et al⁹ reporting only Cl^- formation. The present results (Fig 3.2) show six ions including the aforementioned, $C_2Cl_2^-$, C_2Cl^- , and the molecular ion, M^- , that has also been mentioned by Chen and Wentworth using NCI-MS.¹² It is believed that this is the first

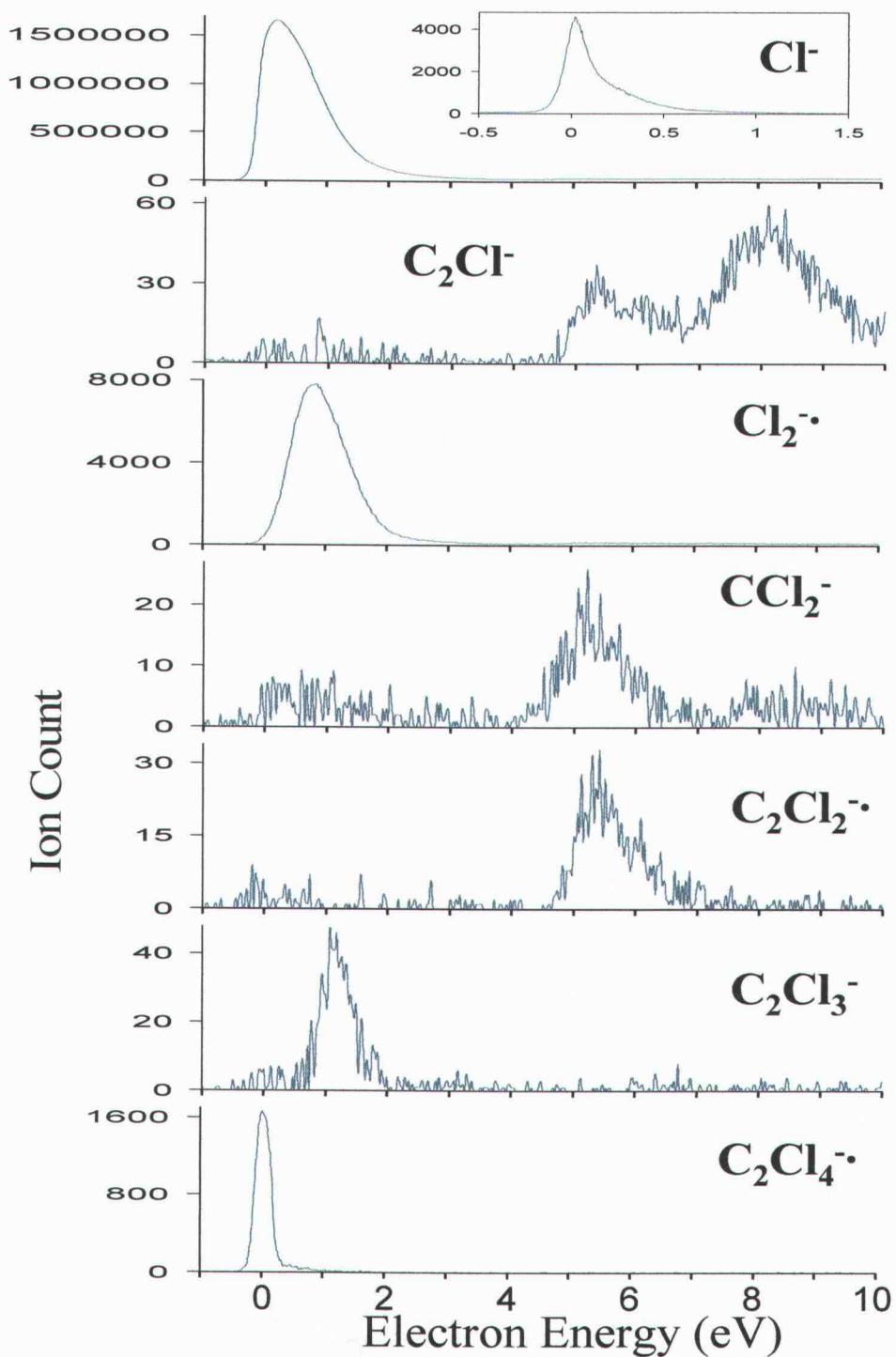


Fig 3.1 – Effective yield curves of negative ions produced from tetrachloroethylene as functions of electron energy. Insert for Cl^- is a higher energy resolution spectrum of Cl^- from different instrumental conditions optimized for better energy resolution.

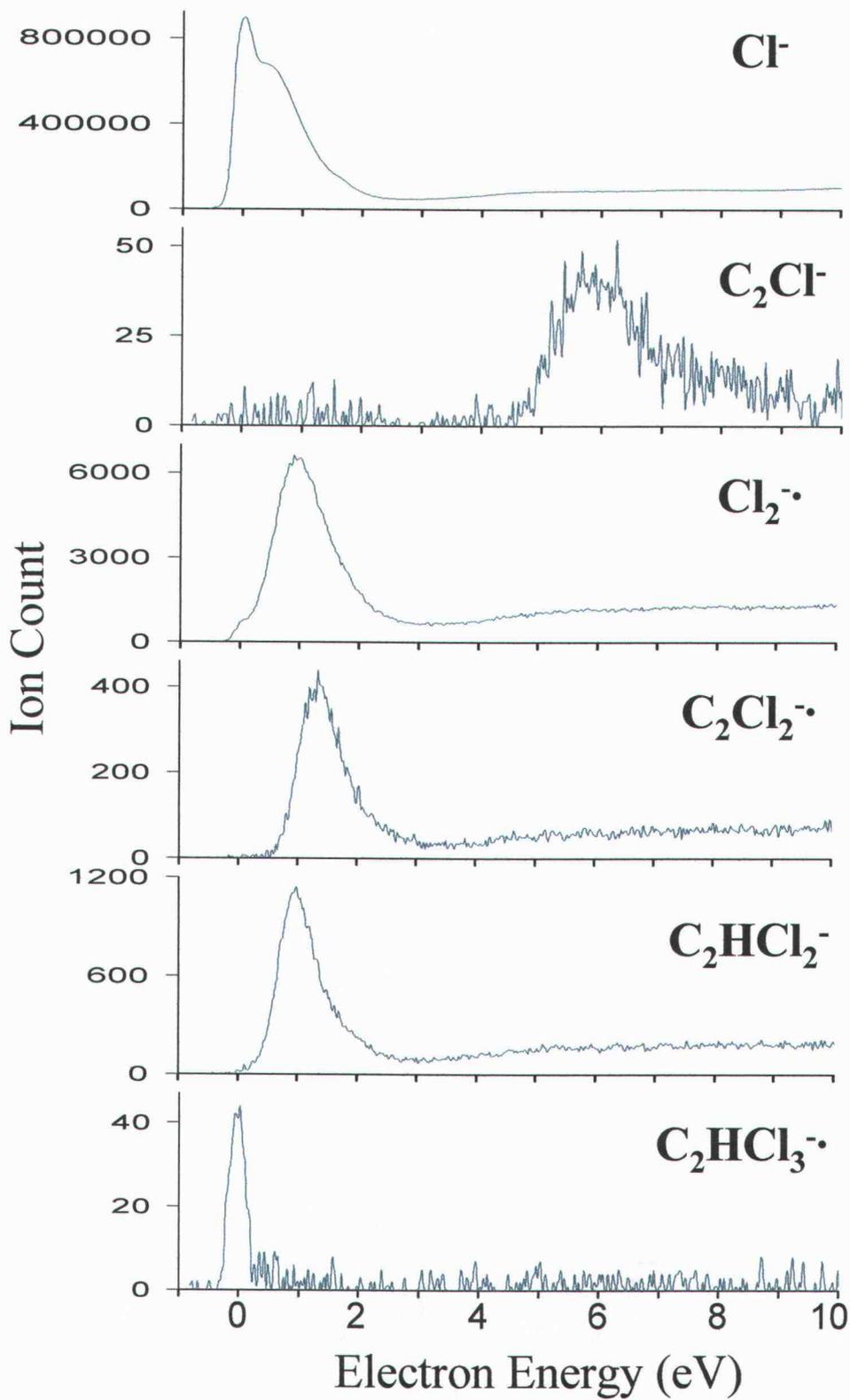


Fig 3.2 – Effective yield curves of negative ions produced from trichloroethylene as functions of electron energy.

report of the negative molecular ion of trichloroethylene observed by REC-MS at an energy near to 0 eV. The present data are in relatively good agreement with the previous results reported by Johnson et al in both positions of the ion yield maxima and the relative intensities of the ions. The intensities of the two resonances for the Cl^- are inverted in intensity with the near to 0 eV resonance dominating the higher one. Finally, the C_2Cl^- from C_2HCl_3 shows only one resonance at ~ 6 eV in contrast to the same ion, C_2Cl^- , from C_2Cl_4 that shows an additional resonance at ~ 8 eV.

3.1.3 *trans*-1,2-Dichloroethylene

Data from *trans*-1,2-dichloroethylene differ from results reported by Kaufel et al⁹ and Johnson et al.³ The most obvious differences are the lack of the HCl_2^- peak in the present mass spectrum that was observed by Kaufel and the additional fragment ion of $(\text{M}-\text{HCl})^-$ that was not observed by Johnson (Fig 3.3). The Cl^- spectra agree better with Johnson et al's reported value of 0.95 eV but in addition show a higher energy resonance in each case not reported in either of the previous studies. The higher peak in the Cl^- effective yield curve and a near to zero peak are due to the calibrant CCl_4 and are not seen in the insert spectrum that came from experimental data uncontaminated by the calibrant. In addition to the previously reported resonances, broadening at the high energy side was observed for fragment ions m/z 35, m/z 61, and m/z 71 which contrasts with Johnson et al's data, who reported low energy broadening and Kaufel et al who reported symmetric resonances.

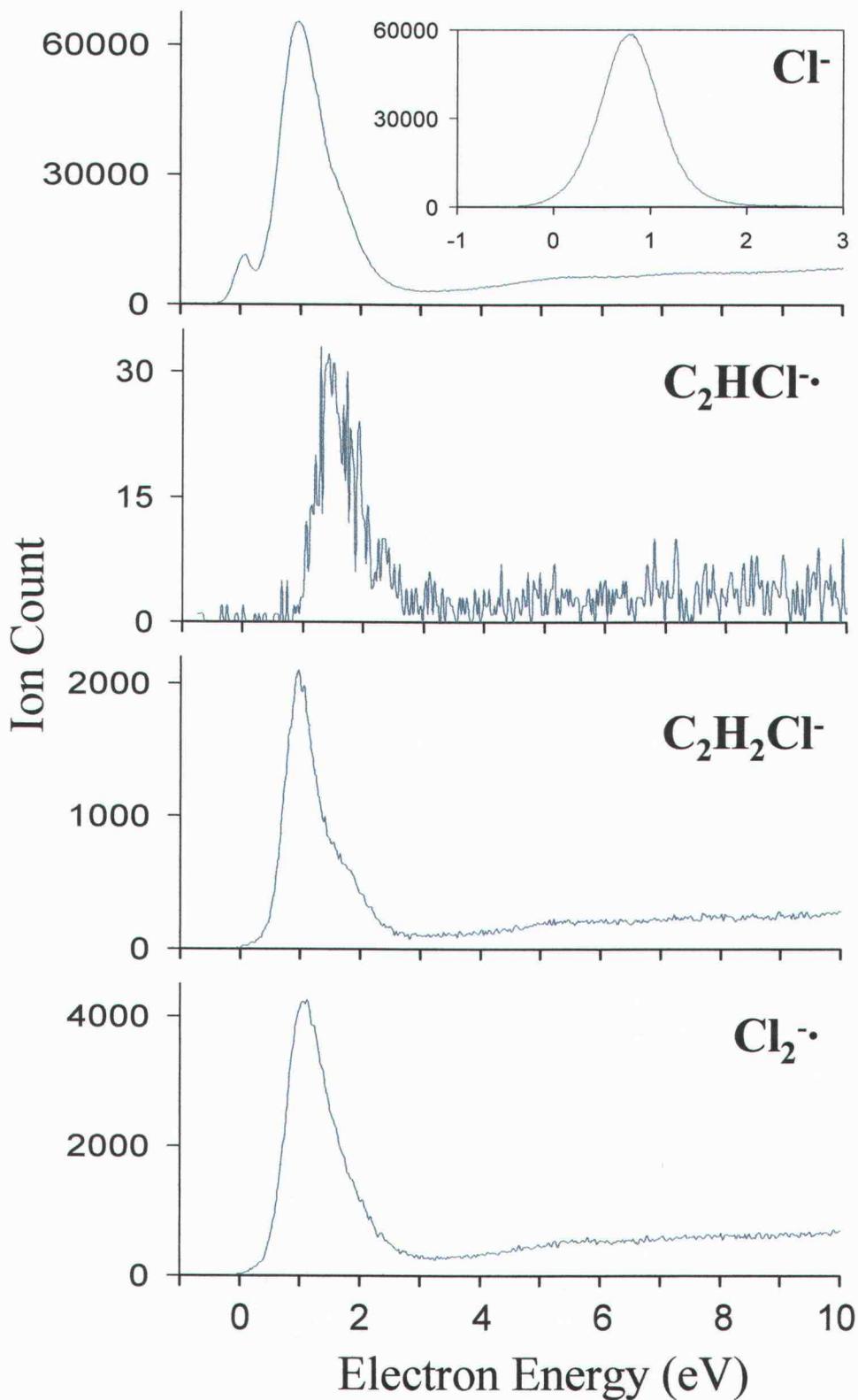


Fig 3.3 – Effective yield curves of negative ions produced from *trans*-1,2-dichloroethylene as functions of electron energy. Insert in Cl^- effective yield curve shows peak without contaminants due to calibrant (CCl_4).

3.1.4 *cis*-1,2-Dichloroethylene

There are only three ions reported for *cis*-1,2-dichloroethylene: $(M-Cl)^-$, Cl_2^- , and Cl^- . The present results (Fig 3.4) show good agreement with the reported value for the Cl^- resonance of 1.05 eV by Kaufel et al.⁹ and the resonance of 1.25 eV for Cl_2^- reported by Johnson et al.³ Also the $(M-Cl)^-$ resonance has a maximum at 1.0 eV, results that are lower than the previously reported value of 1.25 eV. In addition the resonances of three previously unreported ions which were observed here include, $(M-HCl)^-$, C_2H^- , and C_2^- at 1.5 eV, 5.8 eV, and 5.9 eV, respectively.

3.1.5 *geminal*-1,1-Dichloroethylene

The three previously reported mass peaks and associated resonances by Johnson et al.³ were observed for *geminal*-1,1-dichloroethylene. These are $(M-Cl)^-$, Cl_2^- , and Cl^- . In agreement with the previously reported values for the Cl^- resonance of 0.65 eV⁹ and 0.75 eV³ a maximum of 0.65 eV (Fig 3.5) was observed in the present studies. Also the $(M-Cl)^-$ and Cl_2^- were observed at ~1.0 eV which is lower in both cases than that reported by Johnson et al.³ Surprisingly the second most intense resonance observed, after that of Cl^- , was the previously unreported $(M-HCl)^-$ or C_2HCl^- (Fig 3.5) at 1.6 eV. Three other weak resonances were observed for the fragment anions; $(M-HCl-H)^-$, C_2H^- and C_2^- all in the 6 eV range.

3.1.6 Tribromoethylene

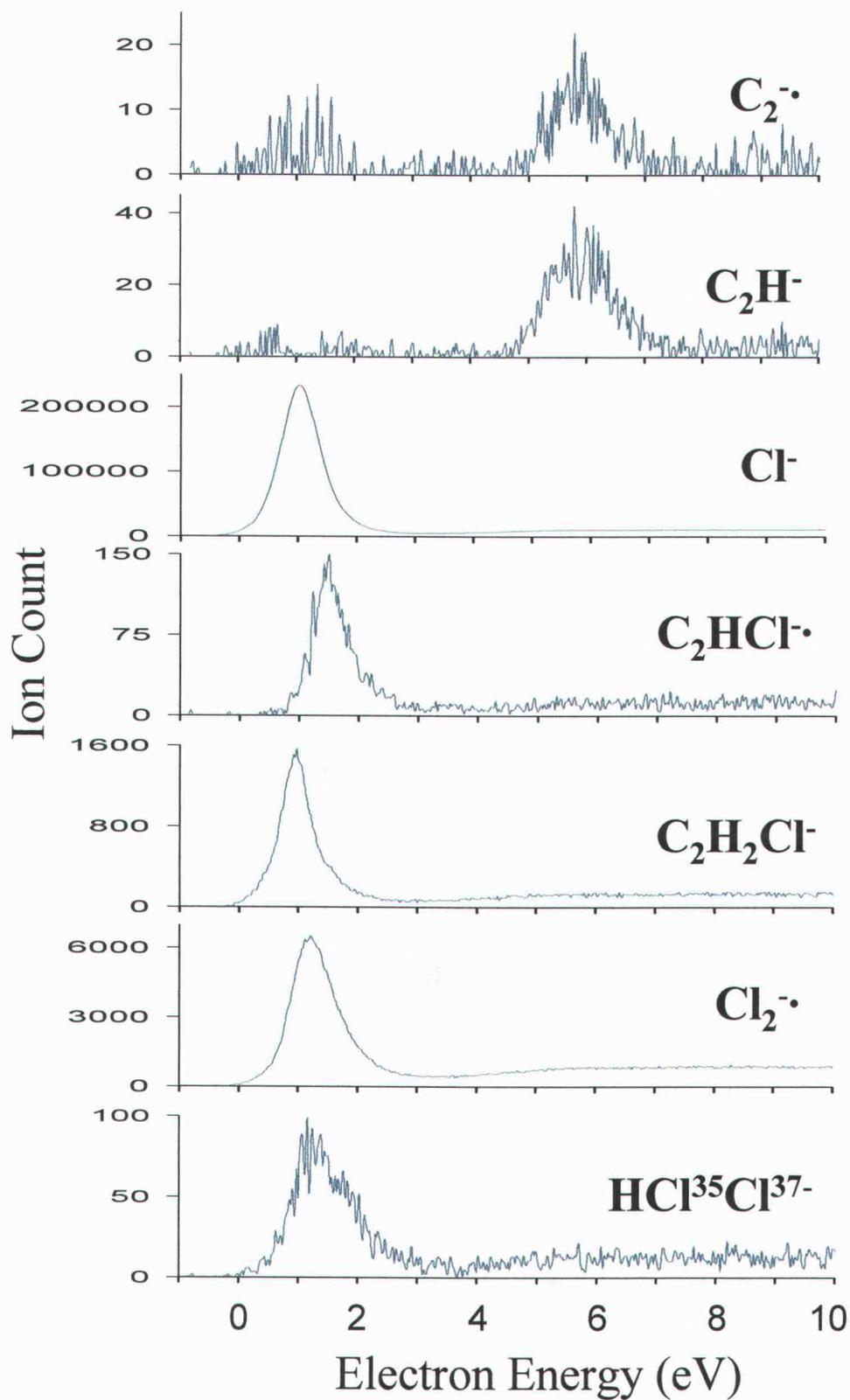


Fig 3.4 – Effective yield curves of negative ions produced from *cis*-1,2-dichloroethylene as functions of electron energy.

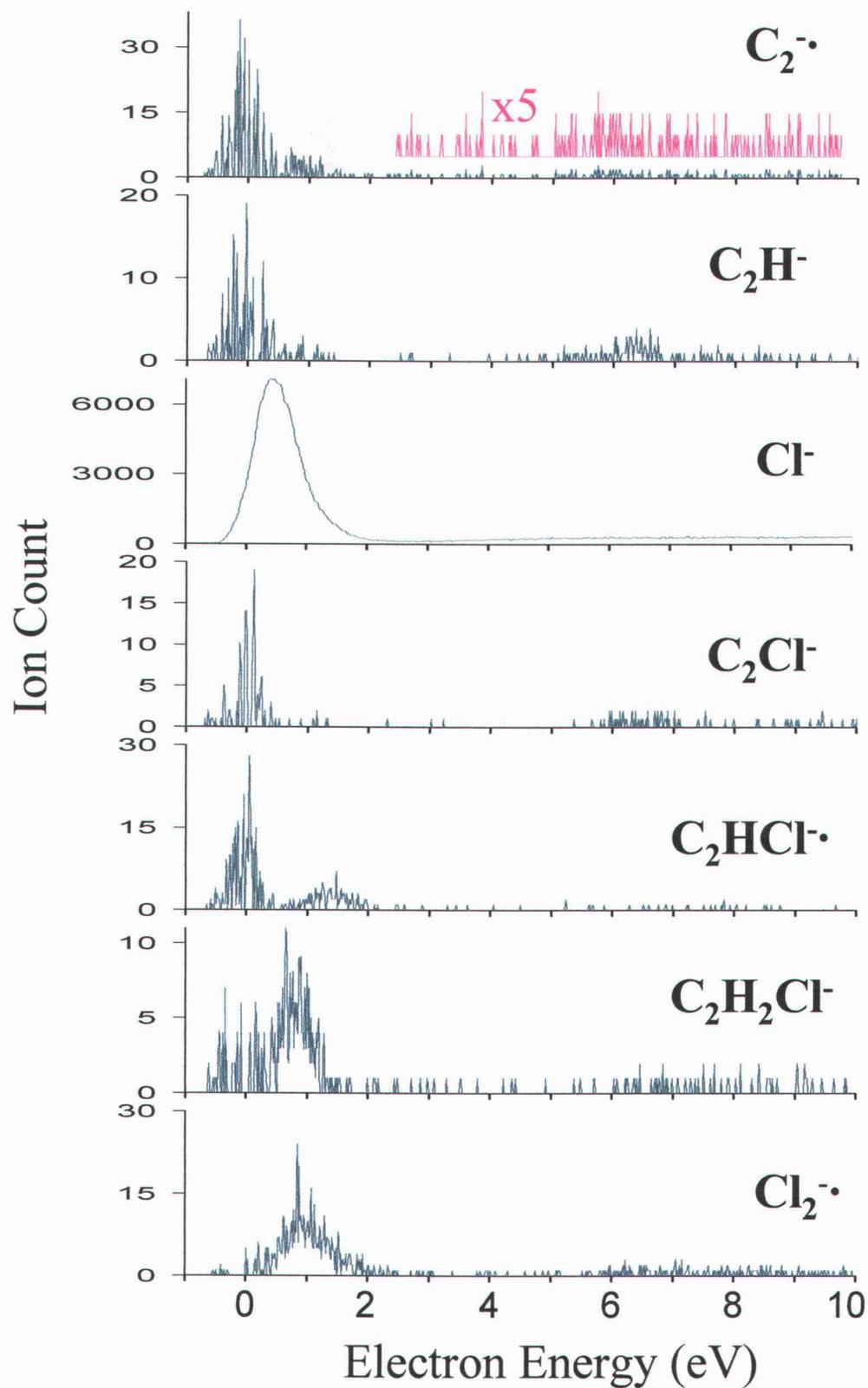


Fig 3.5 – Effective yield curves of negative ions produced from *geminal*-1,1-dichloroethylene as functions of electron energy.

Three resonances were observed for tribromoethylene and these are $(M-Br)^{\cdot-}$, $Br_2^{\cdot-}$, and $Br^{\cdot-}$ (Fig 3.6). All resonances are near to 0 eV and show strong isotopic peaks all of which have the same resonance capture maxima.

3.1.7 *cis/trans*-1,2-Dibromoethylene mixture

There are six masses with associated resonance structures observed for the *cis/trans*-1,2-dibromoethylene mixture (Fig 3.7). Consistent with the chloroethylenes, the $(M-X)^{\cdot-}$, $X_2^{\cdot-}$, and $X^{\cdot-}$ species are observed, where X in this case is bromine. Also observed are $(M-HBr)^{\cdot-}$, $C_2H^{\cdot-}$, and $C_2^{\cdot-}$ with resonance energy maxima at 1.5 eV, 6.0 eV, and 5.9 eV, respectively. $(M-Br)^{\cdot-}$, $Br_2^{\cdot-}$, and $Br^{\cdot-}$ have two obvious resonance energy maxima while all other resonances have only one apparent maximum. $(M-Br)^{\cdot-}$ effective yield maxima differ from the $Br_2^{\cdot-}$ and $Br^{\cdot-}$ effective yield maxima due to the considerably weaker higher maximum at ~1.2 eV for $(M-Br)^{\cdot-}$.

3.1.8 Vinyl Bromide

Only one resonance was observed for vinyl bromide and this was for the production of $Br^{\cdot-}$ at ~1.1 eV (Fig 3.8).

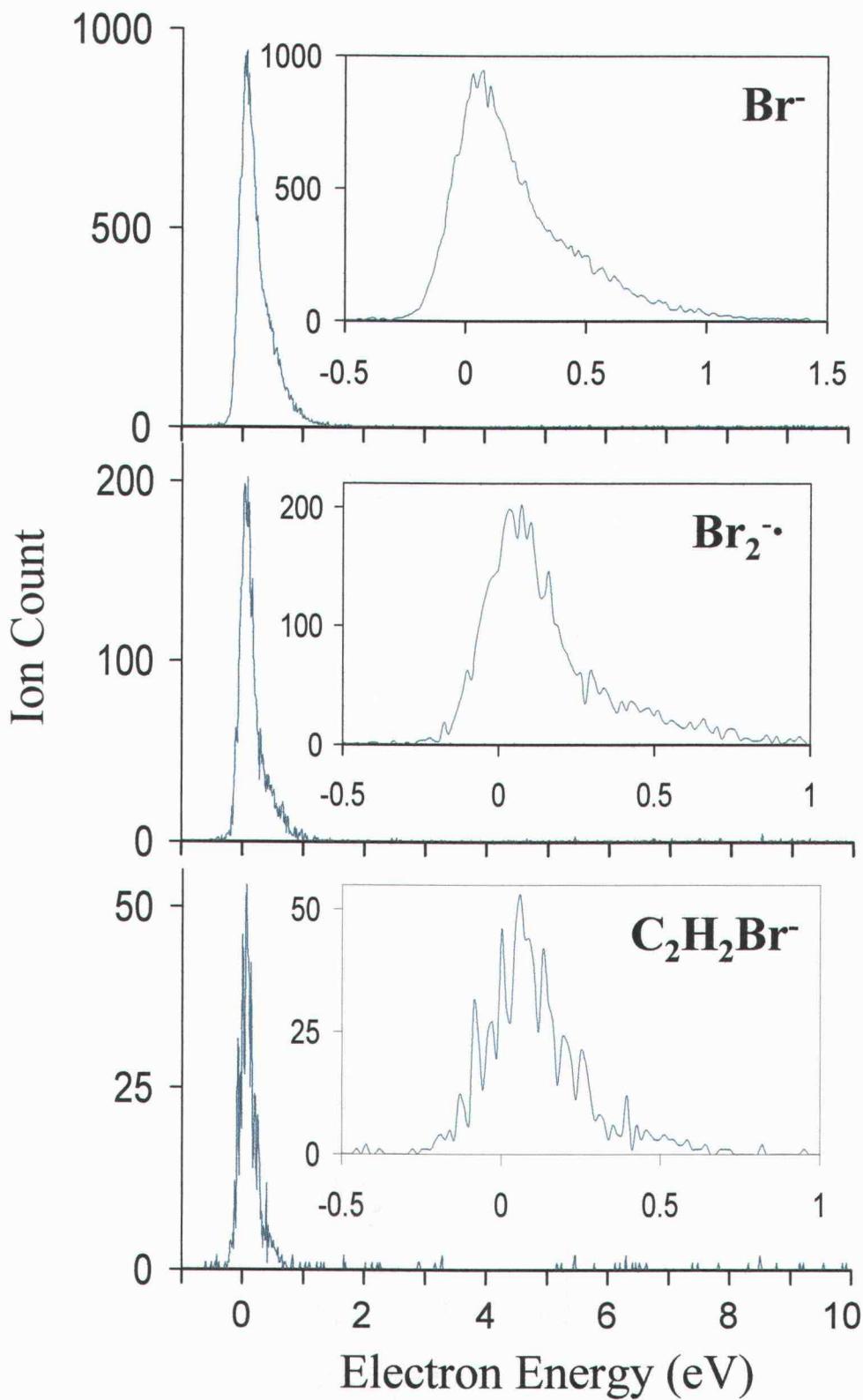


Fig 3.6 – Effective yield curves of negative ions produced from tribromoethylene as functions of electron energy. Inserts are expanded views of the curve near zero eV. Fine structure is due to instrument noise at low s/n.

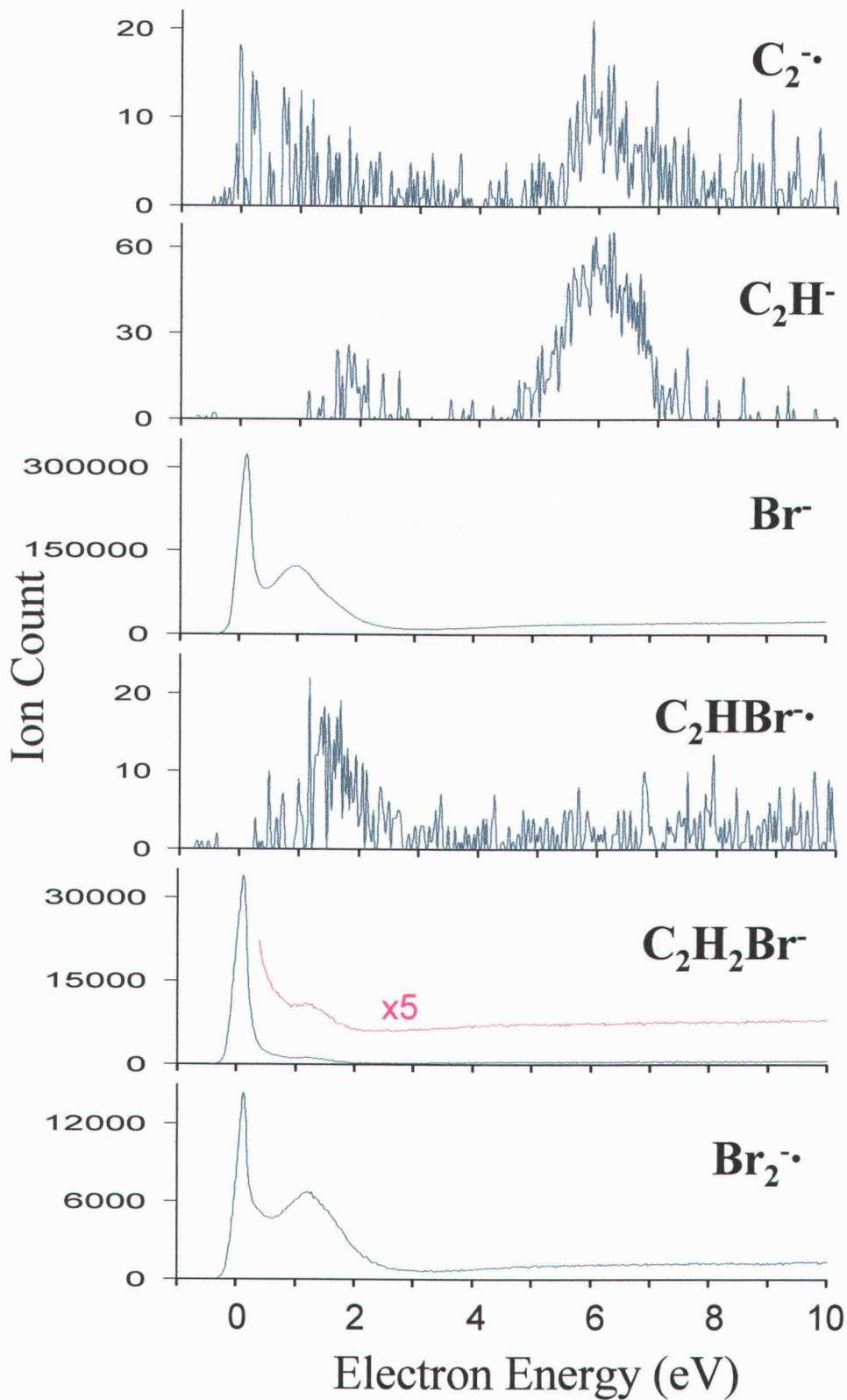


Fig 3.7 – Effective yield curves of negative ions produced from *cis/trans*-1,2-dichloroethylene mixture as functions of electron energy.

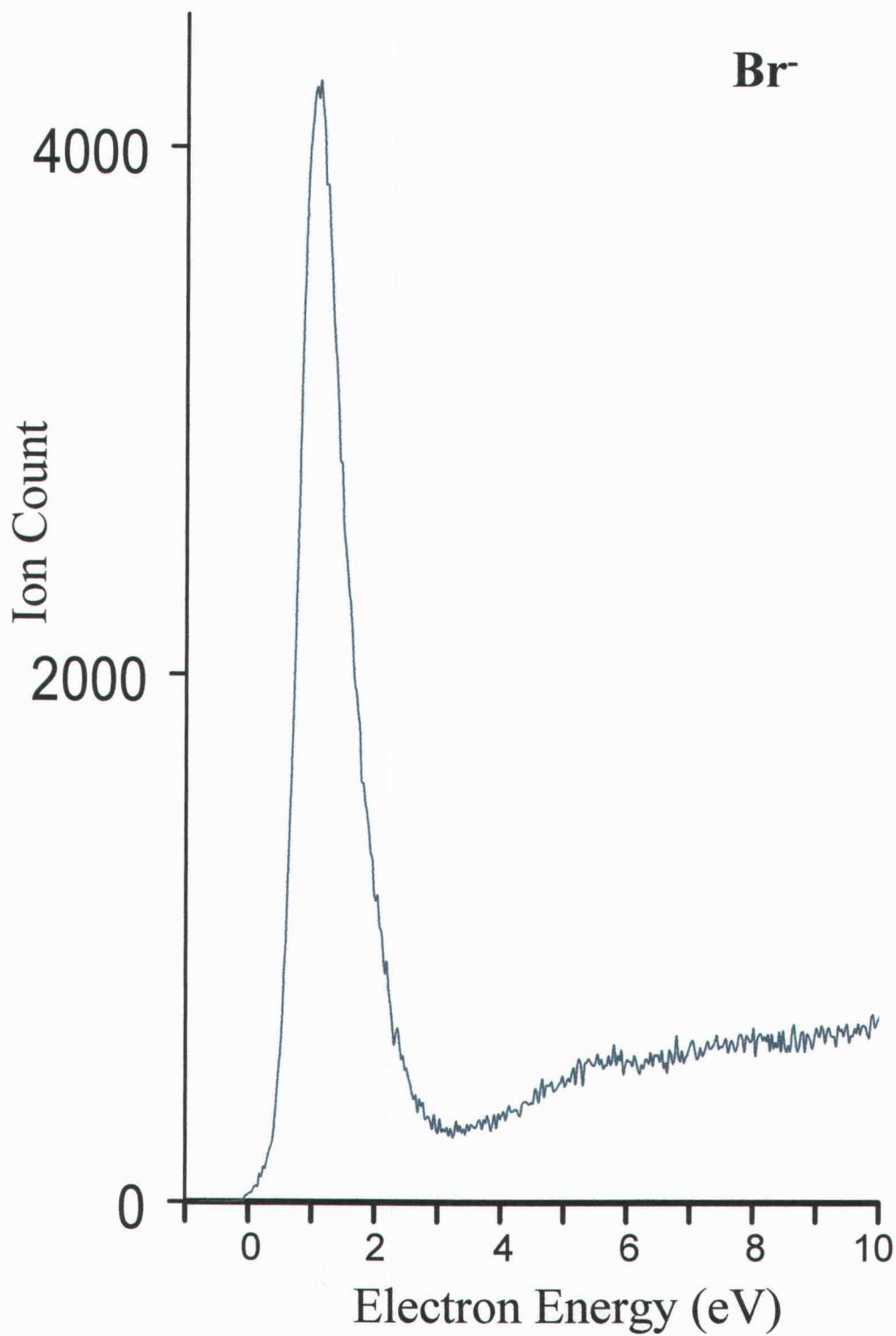


Fig 3.8 – Effective yield curve for bromide ion produced from vinyl bromide as a function of electron energy.

3.2 Theoretical Calculations

The vertical electron attachment energies yielding negative ions of haloethylene molecules and the adiabatic electron affinities (AEA) (Fig 3.9) were calculated in hartrees and converted to electron volts (eV) for interpretation and better understanding of the experimental results (Table 3.1). The calculated thermochemical threshold or fragment ion formation energy (FIFE) (Fig 3.10) for each unique loss of halogen from chloroethylenes (Table 3.2) and bromoethylenes (Table 3.3) as well as the complimentary ion results from the difference between the initial calculated energy of the whole molecule and the total energy of the resulting fragment. The position labels for the tri-halogenated compounds are in reference to the loss of halogen relative to hydrogen (Fig 3.11). The out-of-plane angle calculations for 1, 2, 5, 10, and 20 degrees are shown in both *syn* and *anti* confirmations (Table 3.4). Lastly, a comparison of all experimental data and the present theoretical data are shown (Table 3.5) and the results are correlated with formation of fragment ions (Table 3.6).

Table 3.1: Calculated vertical electron attachment energy (VEAE) and adiabatic electron affinity (AEA) energy for chloroethylenes and bromoethylenes.

Compound	VEAE (eV)	AEA (eV)	Difference (eV) ^a
Tetrachloroethylene	-0.628	0.505	1.133
Trichloroethylene	-0.656	0.656	1.312
<i>geminal</i> -dichloroethylene	-0.957	0.461	1.418
<i>trans</i> -dichloroethylene	-1.083	0.522	1.605
<i>cis</i> -dichloroethylene	-1.322	0.176	1.498
Vinyl Chloride	-1.389	-0.212	1.177
Tetrabromoethylene	0.013	1.551	1.538
Tribromoethylene	-0.329	1.174	1.503
<i>geminal</i> -dibromoethylene	-0.509	1.267	1.776
<i>trans</i> -dibromoethylene	-0.764	1.299	2.063
<i>cis</i> -dibromoethylene	-0.669	0.979	1.648
Vinyl Bromide	-1.447	0.159	1.606

(a) Difference (eV) between VEAE and the ground state energy of the geometry optimized negative molecular ion.

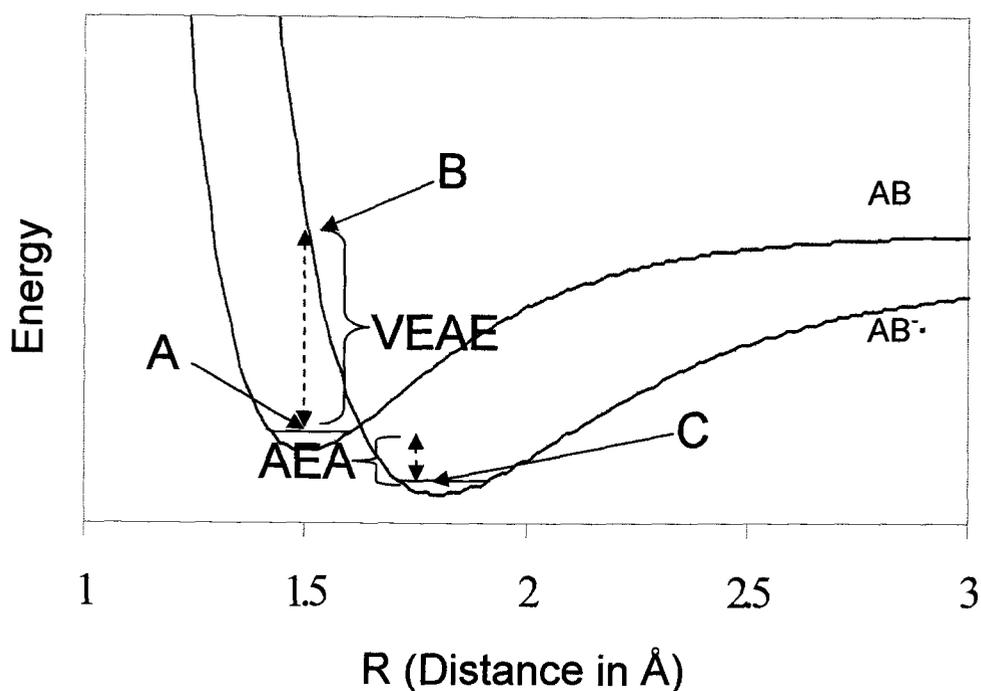


Figure 3.9 – The energy difference between A and B is reported as the VEAE and the energy difference between point A and C is reported as the AEA.

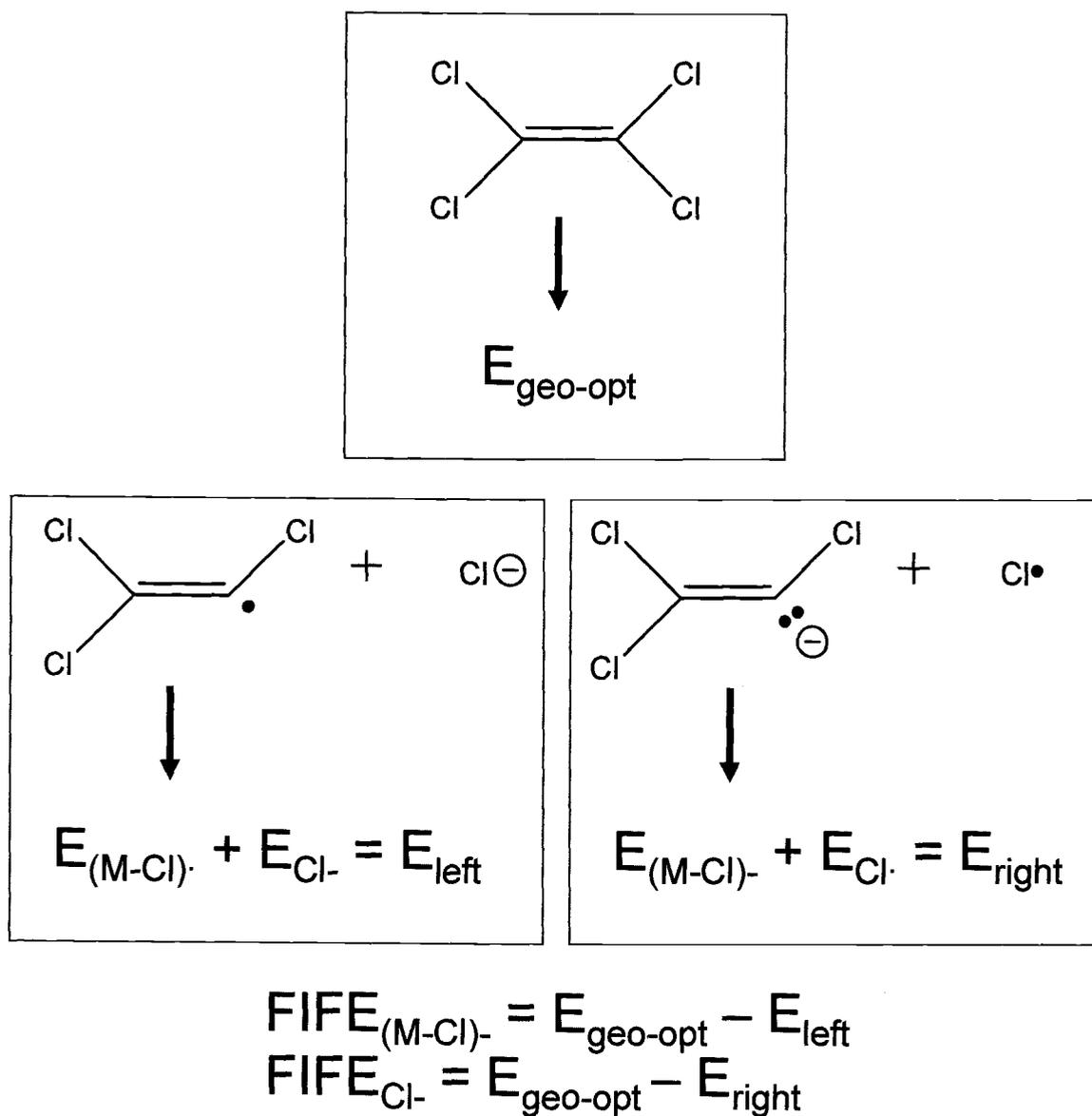


Figure 3.10 – A schematic explanation of the FIFE calculation. First, the geometry of the neutral molecule is optimized and the energy of the optimized geometry, $E_{\text{geo-opt}}$ is calculated. The fragments are constructed and the geometry is optimized for each fragment. The calculated energies are then added for the neutral radical and negative ion species to make E_{left} and E_{right} . E_{left} and E_{right} are then subtracted from $E_{\text{geo-opt}}$ to get the FIFE for the negative ions, $(M-Cl)^-$ and Cl^- .

Table 3.2: Calculated Fragment Ion Formation Energy (FIFE) (eV)^a for each unique Cl⁻ and Cl· loss and Experimental Threshold Energy (ETE) (eV) for each experimentally observed ion.

Compound	FIFE (eV)	ETE (eV)
Tetrachloroethylene (M) ⁻		0.01
(M-Cl) ⁻	-3.868	0.55
Cl ⁻	-0.430	0.00
Trichloroethylene (M) ⁻		~0
A - (M-Cl) ⁻ ^b	-1.346	0.38
A - Cl ⁻ ^b	0.049	-0.02
B - (M-Cl) ⁻ ^b	-1.147	
B - Cl ⁻ ^b	-0.148	
C - (M-Cl) ⁻ ^b	-1.346	
C - Cl ⁻ ^b	0.049	
<i>cis</i> -dichloroethylene (M) ⁻		
(M-Cl) ⁻	-0.870	0.77
Cl ⁻	-0.170	0.67
<i>geminal</i> -dichloroethylene (M) ⁻		
(M-Cl) ⁻	-1.884	
Cl ⁻	0.065	0.17
<i>trans</i> -dichloroethylene (M) ⁻		
(M-Cl) ⁻	-0.903	0.56
Cl ⁻	-0.159	0.58
Vinyl Chloride (M) ⁻		
(M-Cl) ⁻	-3.314	
Cl ⁻	-0.256	

- (a) FIFE is calculated by comparing the energy of the geometry optimized neutral molecule with the negative ion listed and the neutral complimentary fragment. Values are scaled according to convention: negative values being higher in energy than that of the initial neutral, and positive values being lower in energy.
- (b) The labels A, B, and C are for the specific loss of each unique halogen and refer to data in Fig 3.10.

Table 3.3: Calculated Fragment Ion Formation Energy (FIFE) (eV)^a for each unique Br⁻ and Br[•] loss and Experimental Threshold Energy (ETE) (eV) for each experimentally observed ion.

Compound	FIFE (eV)	ETE (eV)
Tetrabromoethylene (M) ⁻		
(M-Br) ⁻	0.169	
Br ⁻	0.021	
Tribromoethylene (M) ⁻		0.00
A - (M-Br) ^{-b}	-0.251	0.00
A - Br ^{-b}	0.060	0.01
B - (M-Br) ^{-b}	-0.200	
B - Br ^{-b}	-0.043	
C - (M-Br) ^{-b}	-0.251	
C - Br ^{-b}	0.060	
<i>cis</i> -dibromoethylene (M) ⁻		
(M-Br) ⁻	0.140	0.05
Br ⁻	-0.176	0.03
<i>geminal</i> -dibromoethylene (M) ⁻		
(M-Br) ⁻	-0.847	
Br ⁻	0.023	
<i>trans</i> -dibromoethylene (M) ⁻		
(M-Br) ⁻	0.230	0.05
Br ⁻	-0.087	0.03
Vinyl Bromide (M) ⁻		
(M-Br) ⁻	-2.484	
Br ⁻	-0.269	0.72

- (c) FIFE is calculated by comparing the energy of the geometry optimized neutral molecule with the negative ion listed and the neutral complimentary fragment. Values are scaled according to convention: negative values being higher in energy than that of the initial neutral, and positive values being lower in energy.
- (d) The labels A, B, and C are for the specific loss of each unique halogen and refer to data in Fig 3.10.

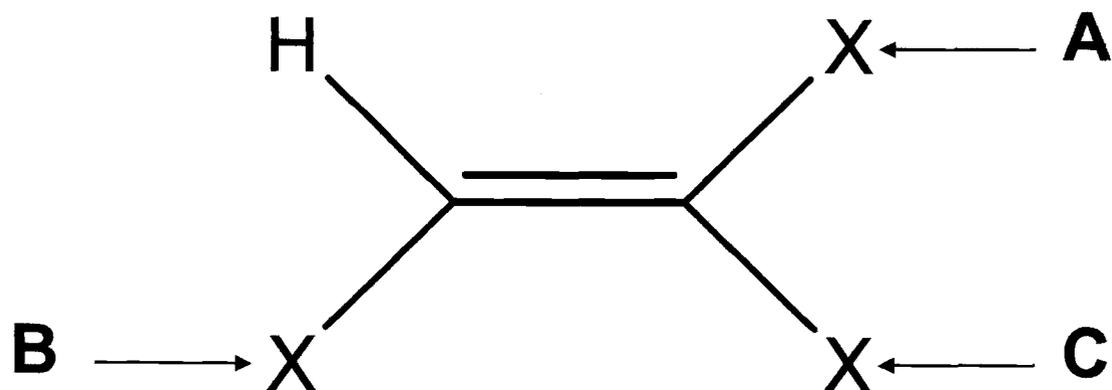


Figure 3.11 - The regio-specific labeling used for differentiating the possible unique halogen losses from trihaloethylenes. The letters refer to the halogen lost for that specific fragmentation.

Table 3.4: Calculated Vertical Electron Attachment Energy (VEAE) for the *syn* and *anti*^a constrained conformations of tetrachloroethylene with respect to the out-of-plane distortion angles (see structures below).

VEAE energy <i>syn</i> conformation		
Distortion angle ^b	Energy (eV)	Change in Energy (eV) ^c
0	-0.63	-
1	-0.623	0.0005
2	-0.606	0.002
5	-0.52	0.0128
10	-0.34	0.0516
20	0.059	0.2077
VEAE energy <i>anti</i> conformation		
Distortion angle ^b	Energy (eV)	Change in Energy (eV) ^c
0	-0.63	-
1	-9.667	0.0004
2	-0.586	0.0016
5	-0.523	0.0097
10	-8.666	0.039
20	-18.977	0.1557

- (a) *syn* and *anti* conformations are defined as shown below:
 (b) Distortion angle relative to the plane formed by the C=C bond.
 (c) Change in energy is between the neutral 0 degree distortion angle structure and the neutral structure with the given distortion angle.

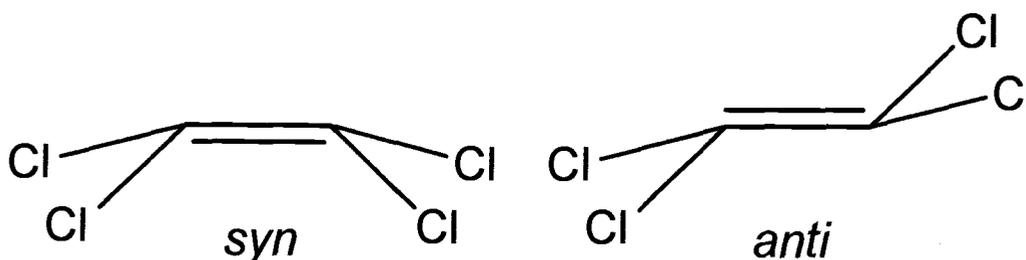


Table 3.5: Comparison of the lowest Vertical Electron Attachment Energy (VEAE) by ETS data, REC-MS (EAS) data, and theoretical calculations (Cal) for the fluoro-, chloro-, bromo-, and iodoethylenes. The data from the present study is denoted by "PW" for present work and all other values are referenced to the original work.

Compound	ref. 40	ref. 41,42	ref. 16	ref. 16	PW	PW	ref. 16	ref. 16
	F ETS	F EAS	Br ETS	Br EAS	Br EAS	Br Cal	I ETS	I EAS
Vinyl halide	1.91	2.05	1.16	~1.0	~1.1	1.45	0.5	~0.3
geminal Halide	2.39	2.4	-	-	-	0.51	-	-
cis dihaloethylene	2.18	2.2	-	-	0.04	0.67	-	-
trans dihaloethylene	1.84	1.95	-	-	0.1	0.76	-	-
trihaloethylene	2.45	2.65	-	-	0	0.33	-	-
tetrahaloethylene	3	3	-	-	-	-0.01	-	-

Compound	ref. 43	ref. 16	ref. 16	ref. 3	ref. 9	ref. 11	PW	PW
	Cl ETS	Cl ETS	Cl EAS	Cl EAS	Cl EAS	Cl EAS	Cl EAS	Cl Cal
Vinyl halide	1.28	1.28	~1.28	-	1.2	-	-	1.39
geminal Halide	0.76	0.75	~0.75	0.75	0.65	-	0.63	0.96
cis dihaloethylene	1.11	1.12	~1.12	1.35	1.05	-	1.09	1.32
trans dihaloethylene	0.8	0.83	~0.83	0.95	1.1	-	0.85	1.08
trihaloethylene	0.59	0.61	~0.61	0.19	0.45	-	0.34	0.66
tetrahaloethylene	0.3	0.4	~0	0.18	0.15	0.4	0.05	0.63

Table 3.6: Correlated values for lowest reported REC-MS (EAS) maxima and the associated ion(s) formed at this energy and compared by type of halogen (F, Cl, Br, and I) in the haloethylene. "PW" refers to the data from the present work and all other values are referenced to the original source.

Compound	ref. 41,42		ref. 16		PW		ref. 16			
	F	Fragment	Br	Fragment	Br	Fragment	I	Fragment		
Vinyl halide	2.05	F ⁻	~1.0	Br ⁻	~1.1	Br ⁻	~0.3	I ⁻		
geminal dihaloethylene	2.4	F ⁻	-		-		-			
cis dihaloethylene	2.2	F ⁻	-		0.04	Br ⁻ , Br ₂ ⁻	-			
trans dihaloethylene	1.95	F ⁻	-		0.1	Br ⁻ , Br ₂ ⁻	-			
trihaloethylene	2.65	F ⁻	-		0	Br ⁻ , Br ₂ ⁻ , (M-Br) ⁻	-			
tetrahaloethylene	3	F ⁻	-		-		-			
Compound	ref. 16		ref. 3		ref.9		ref. 11		PW	
	Cl	Fragment	Cl	Fragment	Cl	Fragment	Cl	Fragment	Cl	Fragment
Vinyl halide	~1.28	Cl ⁻	-		1.2	Cl ⁻	-		-	
geminal dihaloethylene	~0.75	Cl ⁻	~0.2/0.75	Cl ⁻ / Cl ⁻	0.65	Cl ⁻	-		0.63	Cl ⁻
cis dihaloethylene	~1.12	Cl ⁻	1.35/1.25	Cl ⁻ / Cl ₂ ⁻ , (M-Cl) ⁻	1.05	Cl ⁻	-		1.09	Cl ⁻ , (M-Cl) ⁻
trans dihaloethylene	~0.83	Cl ⁻	0.95	Cl ⁻ , Cl ₂ ⁻ , (M-Cl) ⁻	1.1	Cl ⁻	-		0.85	Cl ⁻ , Cl ₂ ⁻ , (M-Cl) ⁻
trihaloethylene	~0.61	Cl ⁻	0.19	Cl ⁻	0.45	Cl ⁻	-		0.34 / 0	Cl ⁻ / M ⁻
tetrahaloethylene	~0	Cl ⁻	~0.0/0.18	M ⁻ / Cl ⁻	0.15 / 0	Cl ⁻ / M ⁻	~0.0	Cl ⁻ , M ⁻	0.05	

3.3 Data Analysis Software - Outline of Program

Initial input files are generated as text files by the Oregon ToF program and are typically 35 MB or larger. Consequently, they are not easily utilized except on modestly powerful computers (~1 GHz or better) with large amounts of RAM. The input files are formatted into a 13-line header and a line for each mass point (Fig 3.12). The latter is a mass value followed by a list of the intensities at each energy step (Fig 3.13, line 200). Therefore, the number of elements in each line after the header equals the number of energy steps in each energy scan plus one for the associated mass. The header has two particularly useful features. On line 4, the number of energy steps into the time-of-flight analyzer is explicitly defined for the file. Additionally, from line 12 (which is a list of the values of each energy step) the range of the energy scan can be determined by subtracting the first value on the line from the last value on the line. Dividing the total energy range

```
OregonTOF v1.0 compiled Jun 18 2003 15:26:37
This data was saved on 08/23/03 12:12:08
ID: ID:
Line # 4 → # of Extractions = 830 ; # of Interleaves = 1
TDC Resolution: 0.625 nsec
TDC Active Time: 2.520 usec
Drift Time = 0.000 msec
Histogram length: 20416 cells
TOF start delay = 2.3 usec
Extraction Frequency = 60 kHz
Extraction Pulse Width = 1.00 usec
Laser Frequency = 20 Hz
```

Figure 3.12 – Lines 1 through 12 of a typical output file from the Oregon ToF program with line 4 indicated and the number of energy steps shown in a square.

by the number of energy steps determines the energy increment per step. The first set of data in the final output array (Fig 3.14) is generated by multiplying the energy increment per step by all integers from 1 to the number of energy steps listed on line 4 of the header. The energy scaling can be “corrected” or calibrated using the energy scale read from line 13 (Fig 3.15) and is done by reading the starting value in the first position of line 13 and then incrementing it by the energy step. This method for generating the energy scale has one clear advantage over reading the calibrated energy values from line 13 in that it removes rounding errors for each energy step as output in the file. However, this assumes that the user has calibrated the energy scale in the output file while using the Oregon ToF program.

The selection and reading of the intensities is more complicated. Extractor provides for two forms of peak selection either by manual input or by an automated peak finder. A text box is provided for manual input; it accepts entries in the format of “Mass1, Mass2, Mass3”. Automated peak selection works by defining a “threshold” or multiplier of the background. To simplify the calculation and reduce the time required, finding the background level of each line presently works by summing all of the ion counts for the first fifty mass points and dividing by 50. If this calculated background value is less than 1, then 1 is used which is typically the case. Returning to the discussion of automated peak selection, Extractor compares the “MS” array (Fig 3.16) to the “background” value multiplied by the “threshold.” If the ion count is higher than the established level (“background” value multiplied by the “threshold”) the associated mass is compared to the “mass of interest” array to make sure a mass is not in the array more than once. If the mass is not in the “mass of interest” array, it is added to the array and a counter is

<u>Energy</u>	<u>Intensity</u>
-0.25	11
-0.2357952	0
-0.2215904	0
-0.2073855	2
-0.1931807	10
-0.1789759	22
-0.1647711	16
-0.1505663	26
-0.1363614	21
-0.1221566	24
-0.1079518	26
-9.374698E-02	28
-7.954216E-02	27
-6.533735E-02	31
-5.113252E-02	27
-0.0369277	32
-2.272289E-02	38
-8.518065E-03	38
5.686754E-03	33
1.989157E-02	32
3.409639E-02	37
4.830121E-02	29
6.250603E-02	37
7.671085E-02	34
9.091567E-02	25
0.1051205	26
0.1193253	28
0.1335301	29
0.147735	30
0.1619398	31
0.1761446	44
0.1903494	29
0.2045542	30
0.218759	34
0.2329639	29
0.2471687	32
0.2613735	35
0.2755783	30
0.2897831	33
.	.
.	.
.	.

Figure 3.14 – Output data of Extractor program in 2D array of Electron Energy and Intensity.

Line # 13

```

-0.25 -0.24 -0.22 -0.21 -0.19 -0.18 -0.16 -0.15 -0.14 -0.12 -0.11
-0.09 -0.08 -0.07 -0.05 -0.04 -0.02 -0.01 0.01 0.02 0.03 0.05 0.06
0.08 0.09 0.11 0.12 0.13 0.15 0.16 0.18 0.19 0.20 0.22 0.23 0.25 0.26
0.28 0.29 0.30 0.32 0.33 0.35 0.36 0.38 0.39 0.40 0.42 0.43 0.45 0.46
0.48 0.49 0.50 0.52 0.53 0.55 0.56 0.57 0.59 0.60 0.62 0.63 0.65 0.66
0.67 0.69 0.70 0.72 0.73 0.75 0.76 0.77 0.79 0.80 0.82 0.83 0.84 0.86
0.87 0.89 0.90 0.92 0.93 0.94 0.96 0.97 0.99 1.00 1.02 1.03 1.04 1.06
1.07 1.09 1.10 1.11 1.13 1.14 1.16 1.17 1.19 1.20 1.21 1.23 1.24 1.26
1.27 1.29 1.30 1.31 1.33 1.34 1.36 1.37 1.38 1.40 1.41 1.43 1.44 1.46
1.47 1.48 1.50 1.51 1.53 1.54 1.56 1.57 1.58 1.60 1.61 1.63 1.64 1.66
1.67 1.68 1.70 1.71 1.73 1.74 1.75 1.77 1.78 1.80 1.81 1.83 1.84 1.85
1.87 1.88 1.90 1.91 1.93 1.94 1.95 1.97 1.98 2.00 2.01 2.02 2.04 2.05
2.07 2.08 2.10 2.11 2.12 2.14 2.15 2.17 2.18 2.20 2.21 2.22 2.24 2.25
2.27 2.28 2.29 2.31 2.32 2.34 2.35 2.37 2.38 2.39 2.41 2.42 2.44 2.45
2.47 2.48 2.49 2.51 2.52 2.54 2.55 2.56 2.58 2.59 2.61 2.62 2.64 2.65
2.66 2.68 2.69 2.71 2.72 2.74 2.75 2.76 2.78 2.79 2.81 2.82 2.84 2.85
2.86 2.88 2.89 2.91 2.92 2.93 2.95 2.96 2.98 2.99 3.01 3.02 3.03 3.05
3.06 3.08 3.09 3.11 3.12 3.13 3.15 3.16 3.18 3.19 3.20 3.22 3.23 3.25
3.26 3.28 3.29 3.30 3.32 3.33 3.35 3.36 3.38 3.39 3.40 3.42 3.43 3.45
3.46 3.47 3.49 3.50 3.52 3.53 3.55 3.56 3.57 3.59 3.60 3.62 3.63 3.65
3.66 3.67 3.69 3.70 3.72 3.73 3.74 3.76 3.77 3.79 3.80 3.82 3.83 3.84
3.86 3.87 3.89 3.90 3.92 3.93 3.94 3.96 3.97 3.99 4.00 4.02 4.03 4.04
4.06 4.07 4.09 4.10 4.11 4.13 4.14 4.16 4.17 4.19 4.20 4.21 4.23 4.24
4.26 4.27 4.29 4.30 4.31 4.33 4.34 4.36 4.37 4.38 4.40 4.41 4.43 4.44
4.46 4.47 4.48 4.50 4.51 4.53 4.54 4.56 4.57 4.58 4.60 4.61 4.63 4.64
4.65 4.67 4.68 4.70 4.71 4.73 4.74 4.75 4.77 4.78 4.80 4.81 4.83 4.84
4.85 4.87 4.88 4.90 4.91 4.92 4.94 4.95 4.97 4.98 5.00 5.01 5.02 5.04
5.05 5.07 5.08 5.10 5.11 5.12 5.14 5.15 5.17 5.18 5.20 5.21 5.22 5.24
5.25 5.27 5.28 5.29 5.31 5.32 5.34 5.35 5.37 5.38 5.39 5.41 5.42 5.44
5.45 5.47 5.48 5.49 5.51 5.52 5.54 5.55 5.56 5.58 5.59 5.61 5.62 5.64
5.65 5.66 5.68 5.69 5.71 5.72 5.74 5.75 5.76 5.78 5.79 5.81 5.82 5.83
5.85 5.86 5.88 5.89 5.91 5.92 5.93 5.95 5.96 5.98 5.99 6.01 6.02 6.03
6.05 6.06 6.08 6.09 6.10 6.12 6.13 6.15 6.16 6.18 6.19 6.20 6.22 6.23
6.25 6.26 6.28 6.29 6.30 6.32 6.33 6.35 6.36 6.38 6.39 6.40 6.42 6.43
6.45 6.46 6.47 6.49 6.50 6.52 6.53 6.55 6.56 6.57 6.59 6.60 6.62 6.63
6.65 6.66 6.67 6.69 6.70 6.72 6.73 6.74 6.76 6.77 6.79 6.80 6.82 6.83
6.84 6.86 6.87 6.89 6.90 6.92 6.93 6.94 6.96 6.97 6.99 7.00 7.01 7.03
7.04 7.06 7.07 7.09 7.10 7.11 7.13 7.14 7.16 7.17 7.19 7.20 7.21 7.23
7.24 7.26 7.27 7.28 7.30 7.31 7.33 7.34 7.36 7.37 7.38 7.40 7.41 7.43
7.44 7.46 7.47 7.48 7.50 7.51 7.53 7.54 7.56 7.57 7.58 7.60 7.61 7.63
7.64 7.65 7.67 7.68 7.70 7.71 7.73 7.74 7.75 7.77 7.78 7.80 7.81 7.83
7.84 7.85 7.87 7.88 7.90 7.91 7.92 7.94 7.95 7.97 7.98 8.00 8.01 8.02
8.04 8.05 8.07 8.08 8.10 8.11 8.12 8.14 8.15 8.17 8.18 8.19 8.21 8.22
8.24 8.25 8.27 8.28 8.29 8.31 8.32 8.34 8.35 8.37 8.38 8.39 8.41 8.42
8.44 8.45 8.46 8.48 8.49 8.51 8.52 8.54 8.55 8.56 8.58 8.59 8.61 8.62
8.64 8.65 8.66 8.68 8.69 8.71 8.72 8.74 8.75 8.76 8.78 8.79 8.81 8.82
8.83 8.85 8.86 8.88 8.89 8.91 8.92 8.93 8.95 8.96 8.98 8.99 9.01 9.02
9.03 9.05 9.06 9.08 9.09 9.10 9.12 9.13 9.15 9.16 9.18 9.19 9.20 9.22
9.23 9.25 9.26 9.28 9.29 9.30 9.32 9.33 9.35 9.36 9.37 9.39 9.40 9.42
9.43 9.45 9.46 9.47 9.49 9.50 9.52 9.53 9.55 9.56 9.57 9.59 9.60 9.62
9.63 9.64 9.66 9.67 9.69 9.70 9.72 9.73 9.74 9.76 9.77 9.79 9.80 9.82
9.83 9.84 9.86 9.87 9.89 9.90 9.92 9.93 9.94 9.96 9.97 9.99 10.00
10.01 10.03 10.04 10.06 10.07 10.09 10.10 10.11 10.13 10.14 10.16
10.17 10.19 10.20 10.21 10.23 10.24 10.26 10.27 10.28 10.30 10.31
10.33 10.34 10.36 10.37 10.38 10.40 10.41 10.43 10.44 10.46 10.47
10.48 10.50 10.51 10.53 10.54 10.55 10.57 10.58 10.60 10.61 10.63
10.64 10.65 10.67 10.68 10.70 10.71 10.73 10.74 10.75 10.77 10.78
10.80 10.81 10.82 10.84 10.85 10.87 10.88 10.90 10.91 10.92 10.94
10.95 10.97 10.98 11.00 11.01 11.02 11.04 11.05 11.07 11.08 11.10
11.11 11.12 11.14 11.15 11.17 11.18 11.19 11.21 11.22 11.24 11.25
11.27 11.28 11.29 11.31 11.32 11.34 11.35 11.37 11.38 11.39 11.41
11.42 11.44 11.45 11.46 11.48 11.49 11.51 11.52 11.54

```

Figure 3.15 – Line 13 of a typical output file from the Oregon ToF program with the first and last values shown in large font.

<u>m/z</u>	<u>Intensity</u>
10.349	3
10.355	0
10.362	0
10.368	0
10.374	0
10.38	0
10.386	0
10.393	0
10.399	0
10.405	0
10.411	0
10.417	0
10.424	0
10.43	0
10.436	0
10.442	0
10.448	0
10.455	0
10.461	0
10.467	0
10.473	0
10.48	0
10.486	0
10.492	0
10.498	0
10.504	0
10.511	0
10.517	0
10.523	0
10.529	0
10.536	0
10.542	0
10.548	0
10.554	0
10.561	0
10.567	0
10.573	0
10.579	0
10.586	0
.	.
.	.
.	.

Figure 3.16 – Output data of Extractor program in 2D array of m/z and Intensity.

advanced by one to keep track of the number of masses in the array.

An understanding of the data management scheme is necessary to understand the program since Extractor uses several arrays to control the data parsing process. First, a 2 by 30,000 element array is created of mass values from the lines in the input file and the total intensity for each mass that comes from summing the intensities at each energy step. (Fig 3.14) Put another way, a Mass Spectrum (MS) is created by Extractor and for the purposes of discussion, will be referred to as the "MS" array. The second array created is the "mass of interest" array. This array consists of 1000 elements where the mass peaks that have energy spectra to be parsed are stored as discussed above.

There are several more arrays that deal specifically with the energy spectra. First is the "final output" array that has been introduced above and contains elements in a 2D array by the number of energy steps (Fig 3.12, Line 4). The first set of elements is the incremented energy steps as mentioned above which do not change after being written to the array. The second set of elements in the "final array" is the energy spectra for a given mass defined in the "mass of interest" array. The background and energy spectra arrays have elements equal to the number of ion extractions (Fig 3.12, Line 4) and are overwritten while summing each energy spectrum. Additional energy arrays are created to record the total effective yield curves (TEYCs) and are similar to the energy spectrum array as described in detail below.

After completing the "mass of interest" array both the manual and automated mass input methods follow the same procedure. First, the local maximum of the mass peak for each "mass of interest" is determined. Next, in order to find the start of the peak the program compares the MS intensity for each previous mass starting at the local

maximum until it reaches the background/threshold limit but not moving more than 20 mass points prior to the maximum. In the simplest data parsing situation, Extractor defines this point as the “start line” for reading the peak. When the user selects background subtraction the “start line” is moved up in the text file equal to the number of lines to be read and compiled to make the energy spectra. This is best explained with a simple example. If the maximum intensity for a mass peak is at line 200 of the text file, the program would examine preceding lines until it finds the first line with intensity less than the background/threshold, at most moving 20 mass points before the maximum. In this example let’s assume that this point is at line 185 and that the user has selected to compile 30 lines to generate the energy spectra for this mass. If the background subtraction is not used, then intensities for each of the energy steps in lines 185 to 215 are read into memory and processed (summed) into the energy spectra for this mass. On the other hand, if background subtraction is used, then intensities for each of the energy steps in lines 155 to 185 are summed into the “background” array and the intensities for each of the energy steps in lines 185 to 215 are summed into the “energy spectra” array.

Once the data has been read in, the “background” spectrum or array is subtracted from the “energy spectra” array and the resulting spectrum is stored in the “final array.” The final array is then written to a file and given a name either manually selected by the user or by using the input file name and, in both cases, titled with the selected name plus “_XX” (Fig 3.14), where “XX” is the m/z of the ion that produces the energy spectrum. Extractor then repeats the input, processing, and output for each mass in the “mass of interest” array. The final step before Extractor is ready for processing a new text file, is to

fill all of the arrays generated with null characters to prevent data “carry over” from one input file to another.

Extractor contains several additional output file options that can be user selected in any execution of the program. First, the user can create a sub-directory using the name of the output file. This makes keeping track of output files easier and more straightforward. Second, an MS file can be output from the “MS” array discussed earlier. Third, a TEYC can be drawn for all peaks above a specific m/z . This output comes in two varieties, one that uses only peaks above the threshold multiplied by background limit, and another that uses all the energy spectra recorded for all m/z values above the user defined limit. Next, the user can decide to apply the energy calibration from the Oregon TOF program to the output file with a calibrated energy scale.

The last functionality of Extractor is the generation of a peak table. This is a table of m/z , RI%, and the E_{\max} ideally for each resonance, output in a format easily imported into spreadsheet software such as Excel. Presently the RI% is calculated using the most intense energy channel in the entire output file, excluding those from Cl^- , compared with the most intense energy channel for each mass. Cl^- is excluded from the RI% because it used for calibration of energy and mass scales from CCl_4 in this study and therefore the intensity of the Cl^- is not indicative of the ratio of Cl^- formation to other ions. The associated energy for the intensity maximum is recorded and output along with the E_{\max} for the three adjacent energy value maxima ($n-1$, n , $n+1$) and five adjacent energy value maxima ($n-2$, $n-1$, n , $n+1$, $n+2$). For both E_{\max} for the 3 adjacent values and the 5 adjacent values the energy recorded corresponds to the center value, n .

Presently Extractor can effectively generate equivalent peak selection and data extraction compared to manual peak selection and data manipulation in approximately 10 seconds (program) versus 2 minutes (manual) at best for each individual spectrum. (Fig 3.17) The residual Cl^- from the Fischer esterification reaction which uses HCl in the procedure of glycine to the t-butyl ester was used because it was the most intense peak in the mass spectrum of this compound. "Real" data (i.e. not test data) with a mass range of 500 amu require ~10 minutes to completely process. This provides a dramatic time savings for data manipulation.

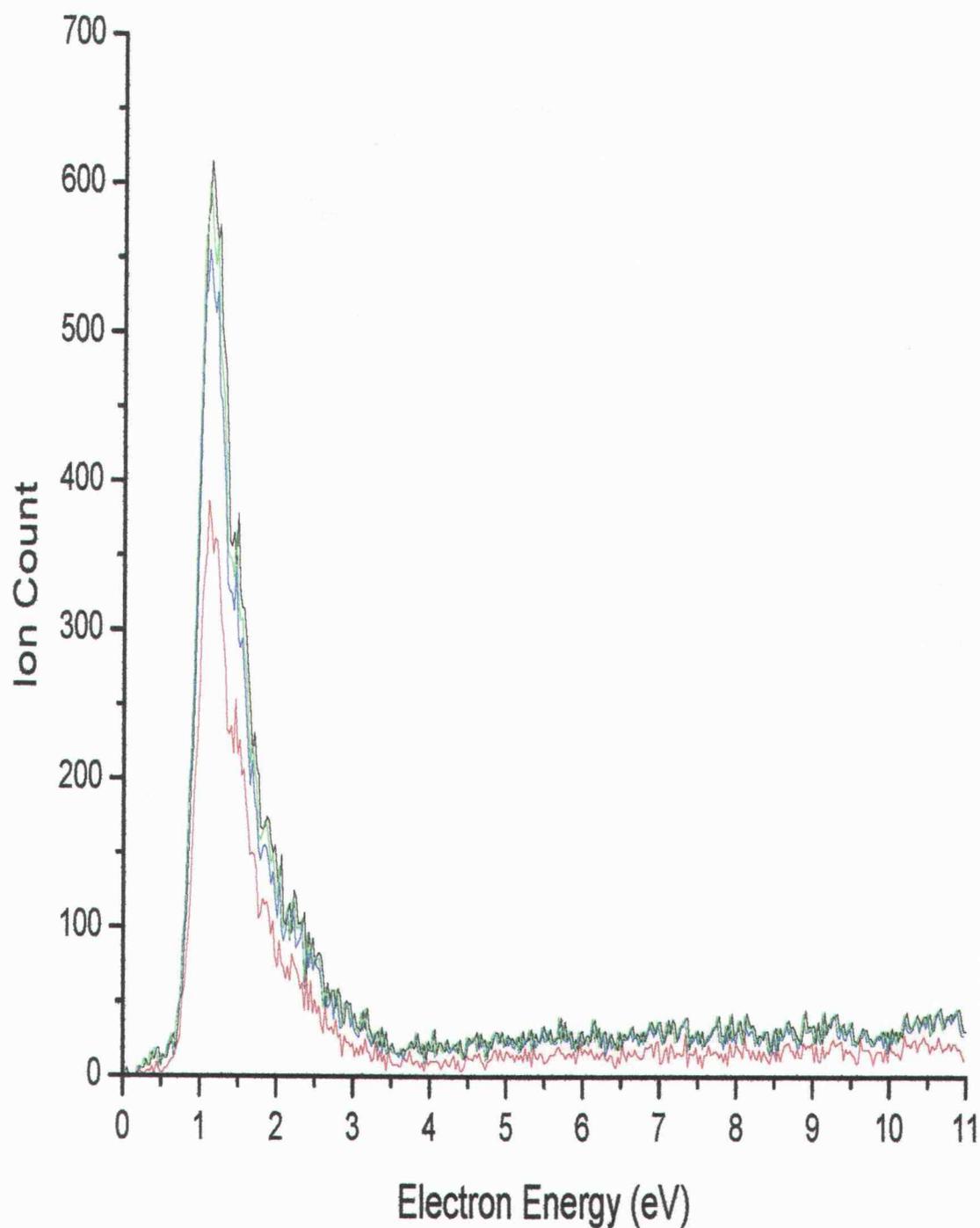


Figure 3.17 – Effective yield curve for $m/z = 35$ of residual Cl^- of Fischer esterification by t-butyl alcohol of glycine. Colors refer to manual peak selection (black), initial automated peak parsing (red), refined peak selection (blue), and additional peak selection refinement and background subtraction (green).

4. Discussion

4.1 Haloethylenes

There are three subsections of the results for haloethylenes to consider. First is an explanation for the apparent difference from previously reported results. Second is the correlation of these results to other experimental observations to achieve a more holistic understanding of the system. Lastly is the determination of theoretically based trends for the haloethylene series.

In comparison with the work by Johnson et al³ on chloroethylenes the present results show additional peaks that have not been reported previously. This may be ascribed to better sensitivity or dwell time of the present instrument.^{4,5} Of primary importance may be the time taken to acquire each REC-MS spectrum. Several spectra were taken over a time period of an hour or greater, resulting in an opportunity to record ions with very low probability of formation. This is certainly assisted by the excellent signal to noise ratio provided by the present instrument design and advances in electronics.

While there are several new results in the present data set, it is important to examine the differences between the experimental data and that from the literature. In contrast to previous reports for the Cl⁻ resonance from C₂Cl₄, the present data show a much simpler peak structure.^{3,9,11} A single dominant resonance peak at near to zero eV (Fig 4.1) with a higher resonance at ~0.4 eV are observed. Only these two peaks are observed because of the lower energy resolution used in the present experiments in

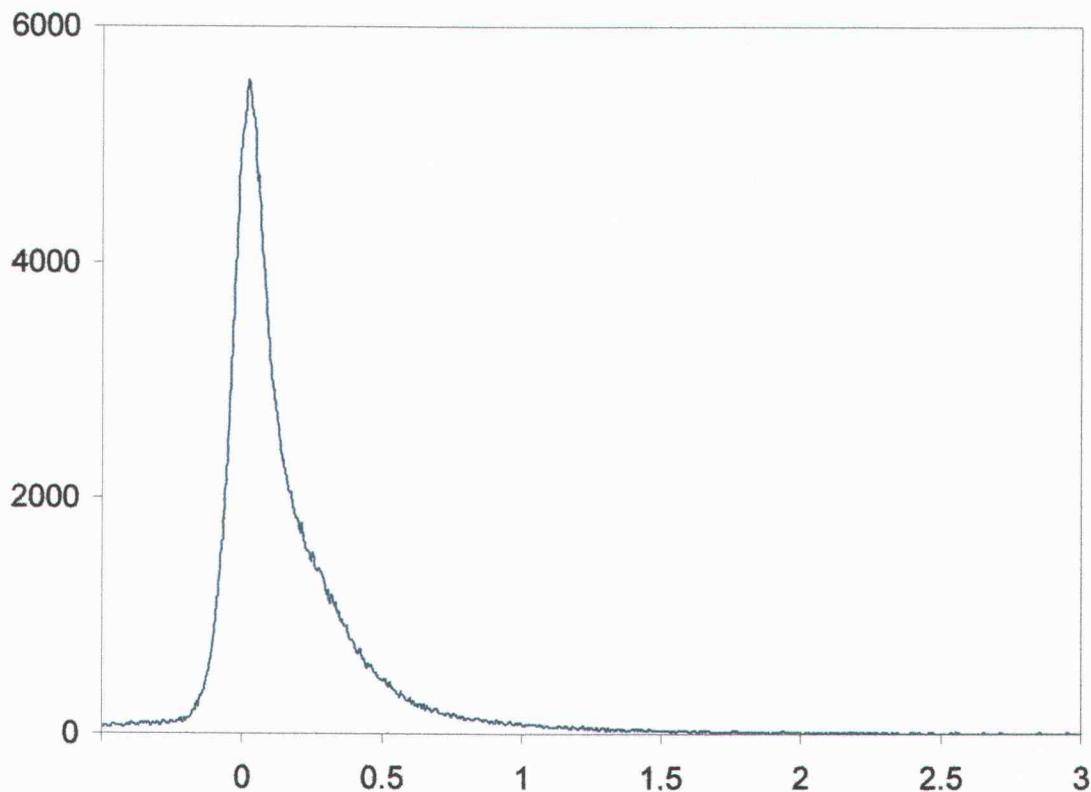


Figure 4.1 – An expanded view of the Cl^- effective yield curve from tetrachloroethylene shown as Cl^- current (intensity) (y-axis) versus electron energy (x-axis).

comparison with recently reported studies.¹¹ Drexel et al¹¹ reported that as well as a maximum intensity of near to zero eV for Cl^- , there were four effective yield maxima at 0.4 eV, 0.7 eV, 0.9 eV, and 1.4 eV. The data can be viewed as a graph of Cl^- current times electron energy versus electron energy to remove the contribution of s-wave capture of an electron at near to zero energy (Fig 4.2) and allowed for the determination of the aforementioned effective yield maxima.¹¹ The inability of the present instrumentation to observe the additional resonances reported with higher resolution (Fig 4.2) can be assigned to optimizing the tuning setting of the instrument for ion detection and not energy resolution. In addition, other compounds within this family do not show a complex resonance peak except for trichloroethylene for which the

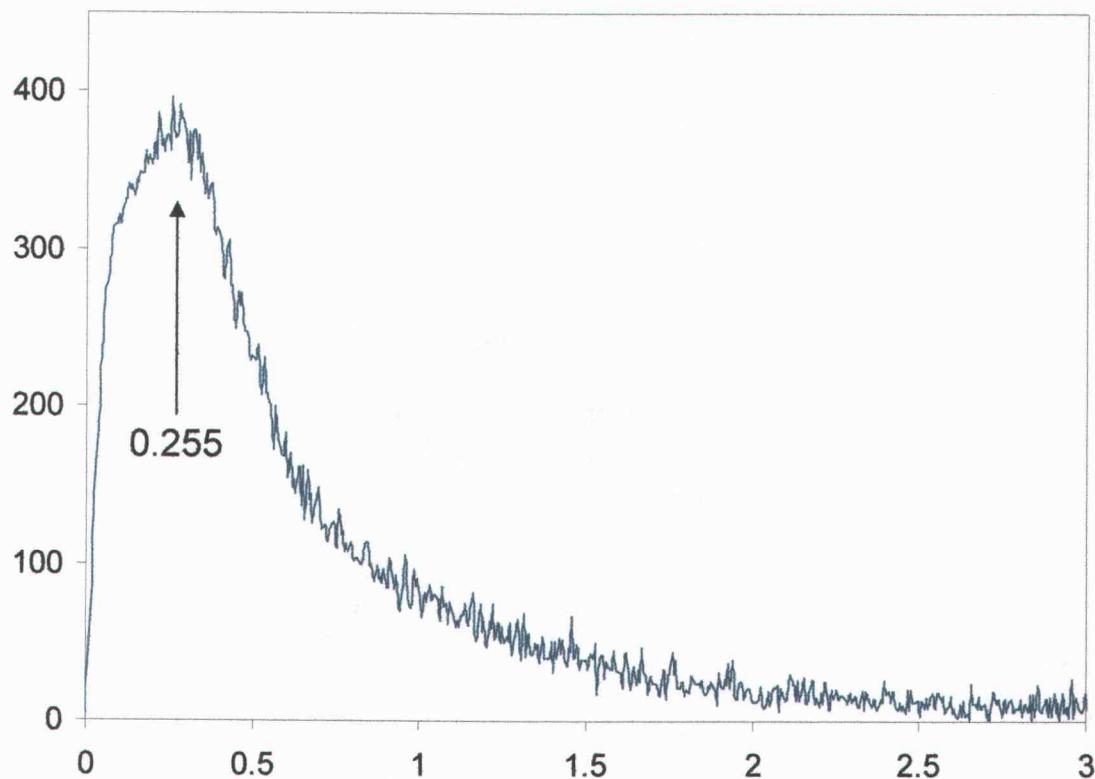


Figure 4.2 - An expanded view of the Cl^- effective yield curve from tetrachloroethylene shown as Cl^- current (intensity) times electron energy (y-axis) versus electron energy (x-axis). This view of the experimental data is direct comparison with data reported by Drexel et al.¹¹ and does not show the additional effective yield maxima of 0.7 eV, 0.9 eV, and 1.4 eV reported.

experimental data show two resonance maxima at near to zero eV and ~ 0.75 eV as previously reported by Johnson et al.³

Resonances that have been almost wholly unreported but were observed in the present study are those in the range 5 to 10 eV. In the present study, there were six compounds for which resonances were observed in this range and these have been compared with results from other experimental techniques. In the case of C_2Cl_4 (Fig 3.1), three ions, C_2Cl_2^- m/z 94 (~ 5.5 eV), CCl_2^- m/z 82 (~ 5.5 eV), and C_2Cl^- m/z 59 (~ 5.5 eV and ~ 8 eV), formed from “high” energy resonances have been reported^{9,11} and the present results are in good agreement with these findings. From a comparison of the

resonance at ~ 5.5 eV that decays by dissociation into the aforementioned ions with data from electron energy loss spectroscopy (EELS), one can conclude that there is a correlation of the resonant state with an excited state of neutral C_2Cl_4 observed for an $N \rightarrow S$ transition at 6.21 eV in EELS.^{7,8} In other words, the resonance at 5.5 eV is an electronically excited Feshbach resonance for which the parent state is the neutral excited state at 6.21 eV. There is another higher energy resonance that produces the C_2Cl^+ in the reported spectra^{9,11} of C_2Cl_4 with a maximum at ~ 8 eV. The energy for this fragment ion is lower than the reported value of 9.58 eV for the ionization potential of C_2Cl_4 as determined by photoelectron spectroscopy.⁶ One may suggest that the corresponding Rydberg state of the neutral molecule can be a parent state for a Feshbach resonance that decomposes into C_2Cl^+ .

In the other five compounds (C_2HCl_3 , *cis*- $C_2H_2Cl_2$, *geminal*- $C_2H_2Cl_2$, and the *cis/trans*- $C_2H_2Br_2$ mixture) where higher energy resonances have been observed, none of them have resonances above 8 eV. For the chloroethylenes, there is good correlation between the EELS and REC-MS data showing that Feshbach resonances have their genealogical origin from the corresponding $N \rightarrow S$ transition. In the case of the *cis/trans* dibromoethylene mixture it is unclear whether these "higher" energy resonances are due to one or both of the compounds.

The results for bromoethylenes indicate that bromination has the effect of lowering the resonance state for almost all analogous resonances so that they are within experimental error of 0 eV (Table 3.5). Of the seven resonances not near to zero (eV), two from the *cis/trans* dibromoethylene mixture (Fig 3.7), C_2^+ m/z 24 (~ 6 eV) and C_2H^+ m/z 25 (~ 6 eV), can be tentatively classified as Feshbach resonances of the $N \rightarrow S$

transition type by extension from the results for chloroethylenes. But, as there are no EELS spectra for these compounds the $N \rightarrow S$ transition cannot be substantiated. The ions $C_2H_2Br^-$ and C_2HBr^- both have maxima at ~ 1.2 eV but in the case of $C_2H_2Br^-$ this is in conjunction with a near to zero resonance. The other three non-zero resonances consist entirely of bromine species (Br^- and Br_2^-). For vinyl bromide it is not surprising that the Br^- has a higher energy resonance (~ 1.1 eV) than the more highly brominated compounds given the ETS data (Fig 3.8). In the cases of the remaining two resonances, Br^- m/z 79 (~ 1 eV) and Br_2^- m/z 158 (~ 1.2 eV), both are from the *cis/trans* mixture and are in conjunction with a near to zero resonance (Fig 3.7).

The experimental data showing molecular ions and fragment ions at near to zero energies are an important observation given that these experimental results were not completely resolved by previous ETS work showing that the π^* orbitals are the primary origin of dissociative electron attachment for chloroethylenes. This discrepancy will be discussed further in conjunction with the computational data below.

The overall trends for haloethylenes from the experimental data remain consistent with the explanations put forth by Olthoff et al.¹⁶ First, the dominate property for the experimentally observed resonance states is the electron capacity of the halogen. Increased electron capacity results in increased stabilization, relative to ethylene, of the π^* and σ^* orbitals in the order iodo- > bromo- > chloro- substituents for the halogenated vinyl compounds. In fluorinated compounds the results show an increase of energy of the π^* orbital relative to ethylene that is related to the lower charge capacity of the fluorine atom compared to the other halogens. The effect of lower charge capacity can be examined in the context of electronegativity as a function of charge (Fig 4.3) where at a

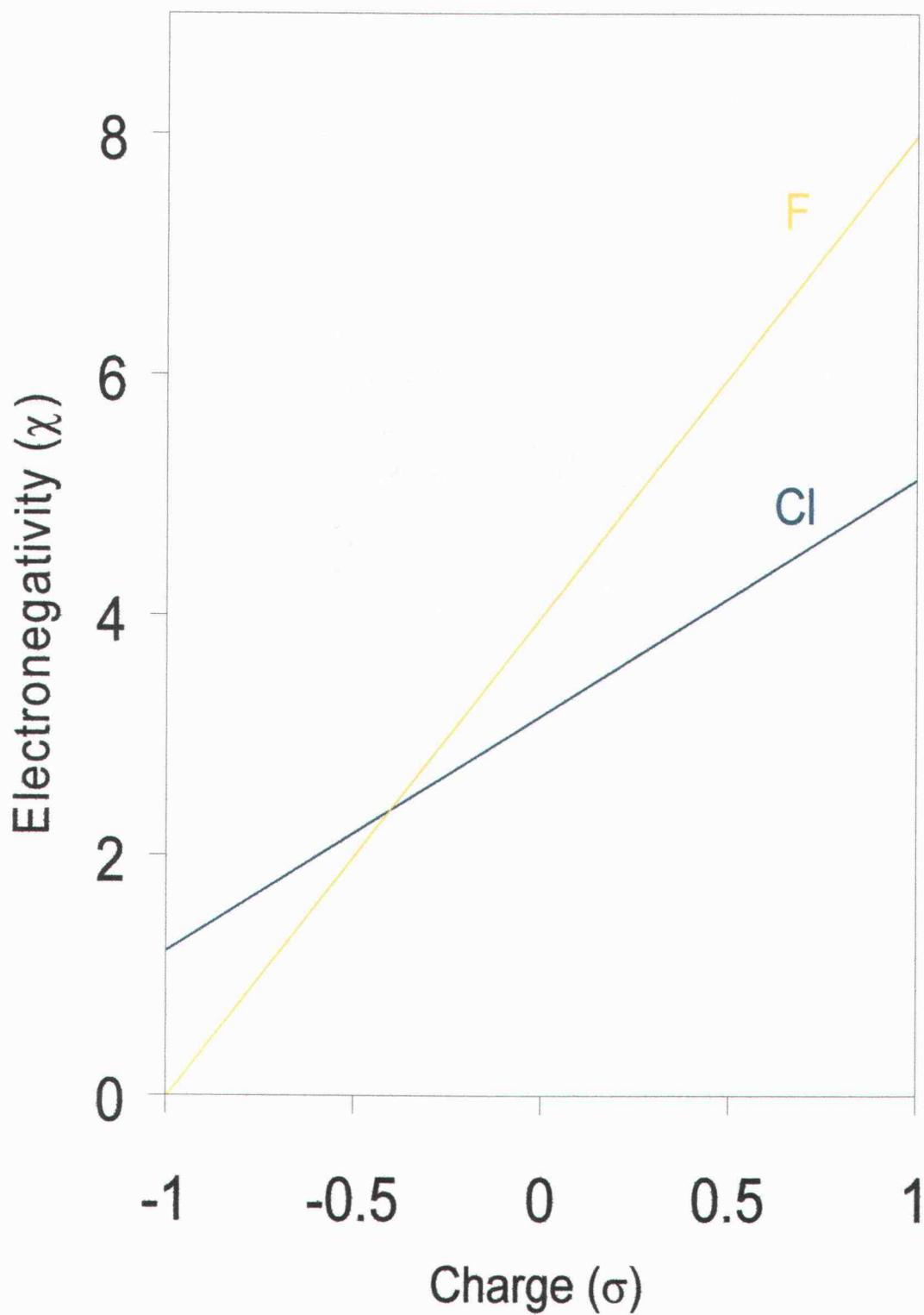


Fig 4.3 – The approximate electronegativities (χ) of fluorine and chlorine as a function of charge (σ).

~-0.4 charge fluorine becomes less electronegative than chlorine.³⁹ The slope corresponds to the inverse of the charge capacity of the atom as given by the following:

$$\chi = a + b\sigma \quad (13)$$

where χ is the electronegativity, a is the neutral atom electronegativity, b is the inverse of the charge capacity, and σ is the partial charge of the atom.³⁹

Another factor in understanding fluorine's differences compared to the other halogens is the overlap between the fluorine and the ethylene antibonding orbitals due to both carbon and fluorine being in same row of the periodic table and therefore having the same atomic valence orbitals. The result of this increased interaction would be the destabilization of the orbitals that would require additional energy for the attachment of an electron. The other halogens would have lower antibonding orbital overlap and therefore less destabilization of the antibonding orbitals due to having different atomic valence orbitals. Furthermore, the data on the series of fluoroethylenes, chloroethylenes, and bromoethylenes (Table 3.5) show that the inductive effect of an individual halogen substituent and its effect upon the observed resonance states, is continued with increasing halogenation but that the effect is regio-specific and not merely additive.

4.2 Computational Data

The calculated values for the vertical transition vertical electron attachment energy (VEAE) (Table 3.1) seem to agree with experimental resonance energies previously reported. The general trend of increasing halogenation results in decreasing VEAE as is evident from the results (Table 3.1) and that can be seen for both

chloroethylenes and bromoethylenes (Fig 4.4). The lowering of the VEAEs results from lowering of the energies of the anti-bonding orbitals because the π^* orbital is the lowest unoccupied molecular orbital in the ethylene molecule. For both sets of compounds the stabilization by geminal halogens is greater than it is for either 1,2 *cis* or *trans* arrangement. In all cases the relaxation of the negative ion geometry results in at least ~1 eV stabilization in energy and all compounds, except vinyl chloride, show positive adiabatic electron affinities for the optimized geometries (Table 3.1). From these results it

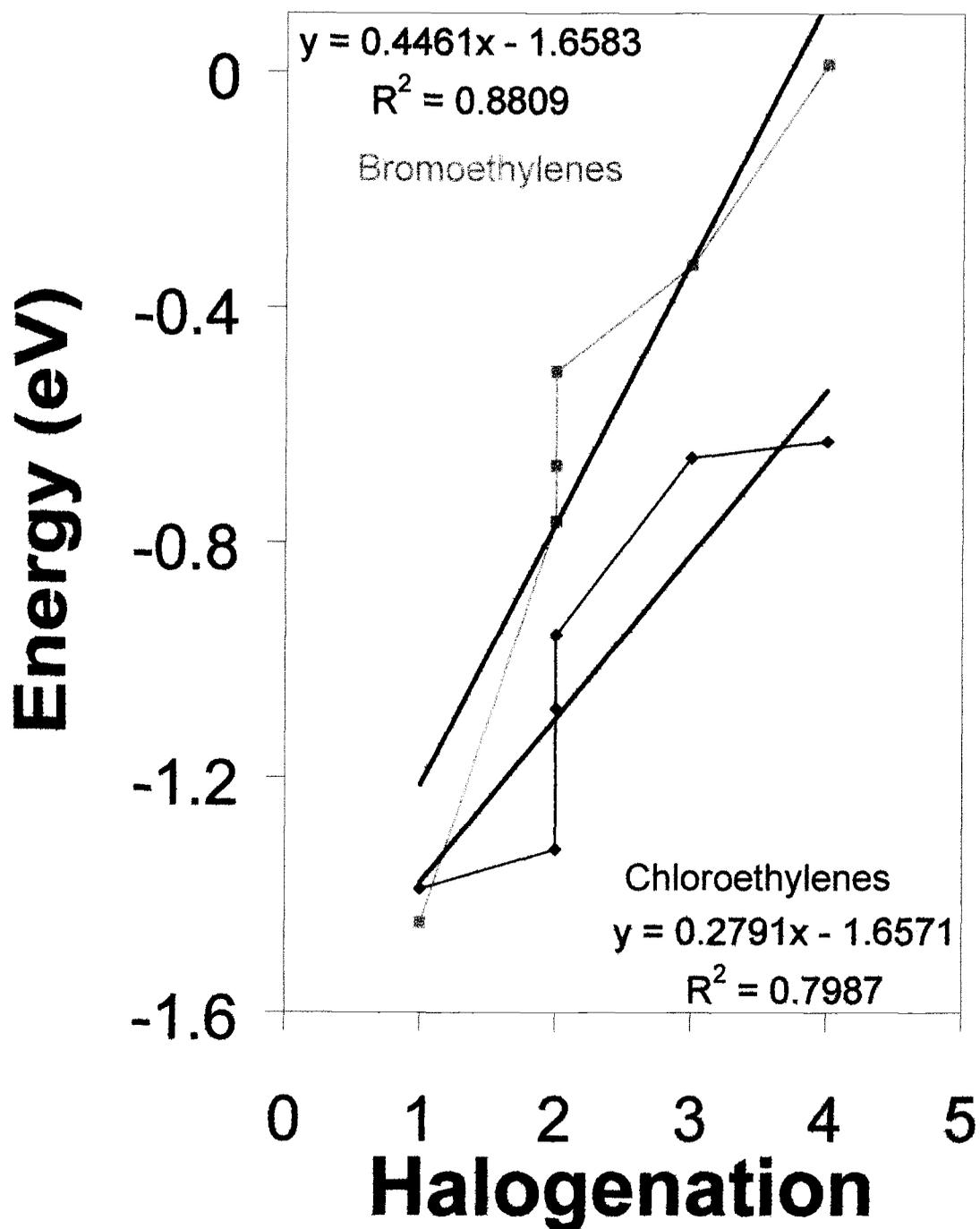


Figure 4.4 – Comparison of the VEAЕ for the chloroethylenes and bromoethylenes by halogenation (number of halogens on the compound) vs. energy.

is concluded that molecular ions should form for all species except vinyl chloride if these molecules have sufficiently long lifetimes ($\sim 10^{-6}$ s) to be detected by mass spectrometry. With the exception of vinyl bromide, the brominated compounds all have calculated VEAEs that are significantly less negative and calculated AEAs that are more positive than those for the corresponding chloroethylenes.

The AEAs show that the more highly substituted the compound, the more stable the molecular ion should be due to the increasing AEA with increasing halogenation. There are two exceptions to this trend; first, the AEAs for tetrachloroethylene and trichloroethylene, with 0.505 eV and 0.656 eV, respectively (Table 3.1) are in the reverse order expected. This is in contrast to the analogous bromoethylenes which show the correct order, i.e. tetrabromoethylene (1.551 eV) and tribromoethylene (1.174 eV) AEAs but between tribromoethylene and the *geminal* (1.267 eV) and *trans* (1.299 eV) dibromoethylene the AEAs are in the opposite order displayed by the chloroethylenes. The AEAs of the *cis* compounds (0.176 eV for dichloroethylene and 0.979 eV for dibromoethylene) are lower than the *trans* compounds (0.522 eV for dichloroethylene and 1.299 eV for dibromoethylene) for each halogen which is surprising given that the predicted global energy minimum would lead to the conclusion that they should have very similar energies (Fig 4.5). However the resulting AEAs suggest that the expected lowest energy structure may not be achieved due to the compound being trapped in a potential well for rotation about C-C bond caused by steric interactions resulting in the determination of a local energy minimum and not the total global energy minimum (Fig 4.6). Given the inability of theoretical calculations to decipher these situations the abnormalities in calculated AEAs may be due to similar problems that are at present

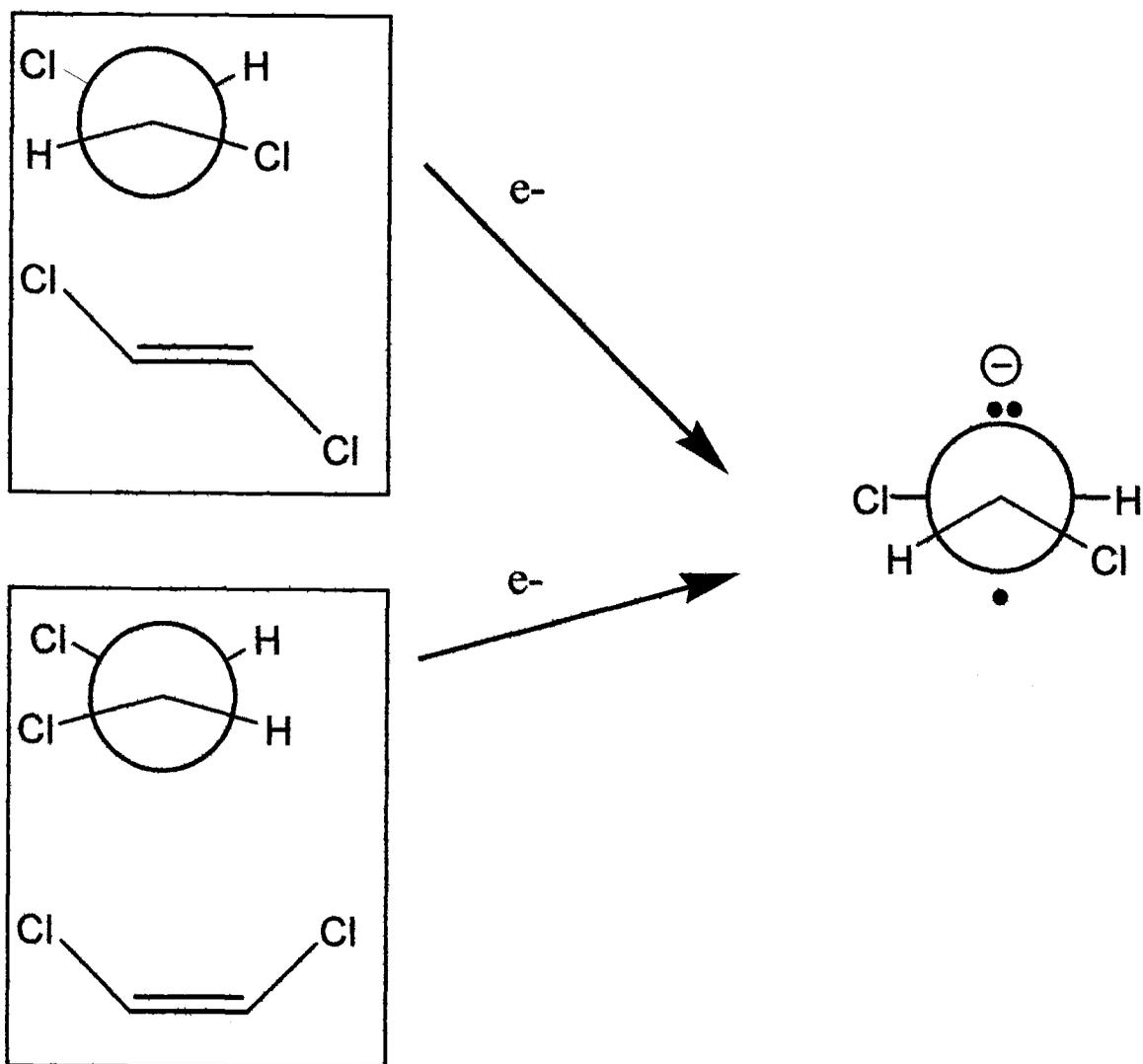


Figure 4.5 – Predicted geometric result of addition of an electron to either *cis* or *trans* dichloroethylene.

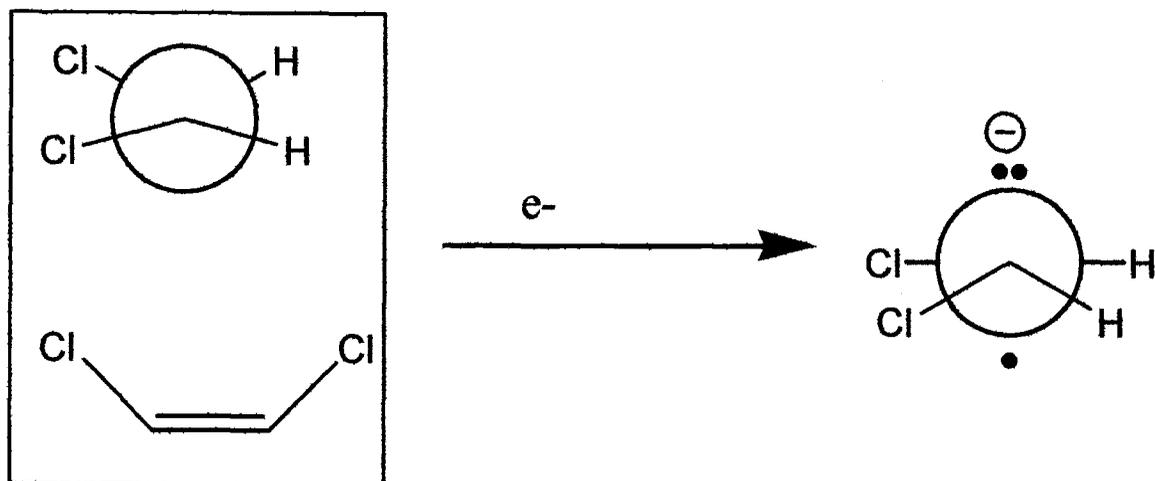


Figure 4.6 – Possible geometry resulting from energy minimization that does not result in a global energy minimum for AEA of the *cis* dichloroethylene.

undetected but would not a significant problem for the VEAEs since there is no change in molecular geometry.

The differences in VEAEs between *geminal*, *cis*, and *trans* substitutions (Table 3.1) are intriguing since the *geminal* (-0.957 eV for dichloroethylene and -0.509 eV for dibromoethylene) is lower in energy for both halogens than either *cis* (-1.322 eV for dichloroethylene and -0.669 eV for dibromoethylene) or *trans* (-1.083 eV for dichloroethylene and -0.764 eV for dibromoethylene). This suggests that there is a more favorable formation of a negative ion on one carbon of the ethylene bond in *geminal* dichloroethylene (Fig 4.7). The *cis* and *trans* compounds do not have unique carbons given their symmetric (Fig 4.8) and, therefore, the difference in VEAE can be attributed to the effects of the relative orientations of the halogens. However, since the relative order of the compounds are inverted between chloroethylenes (*cis* > *trans*) and the bromoethylenes (*trans* > *cis*), no general trend is readily apparent.

In light of the regio-specific effects on VEAEs, it is interesting to note that the *geminal* structures require only slightly lower energy electrons than the *trans* geometry for both chloroethylenes (~0.06 eV) and bromoethylenes (~0.03 eV) given the aforementioned possible problem with the *cis* AEAs (Table 3.1). This suggests that there is limited effect for the relative position of stabilizing groups in overall AEA and that stabilization is primarily a numerical effect in contrast to VEAE which is both number and position specific.

The overall less negative VEAEs and the more positive AEAs of the bromoethylenes compared to the chloroethylenes result in larger changes in energy

(Table 3.1). This is likely due to the charge capacity of the different halogens as described by Olthoff et al.¹⁶

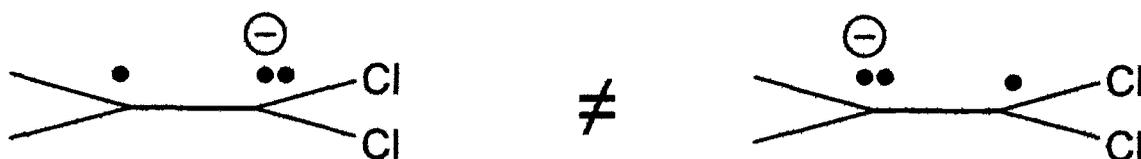


Figure 4.7 – The non-equivalent carbons are shown as the carbanions for both possible negative ions for the π^* orbital of *geminal* dichloroethylene.

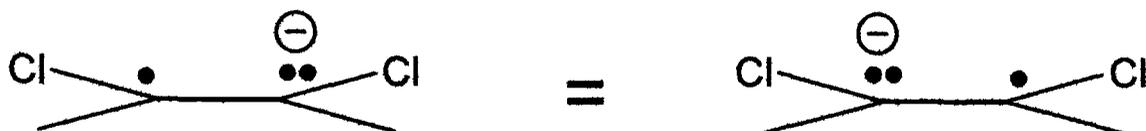
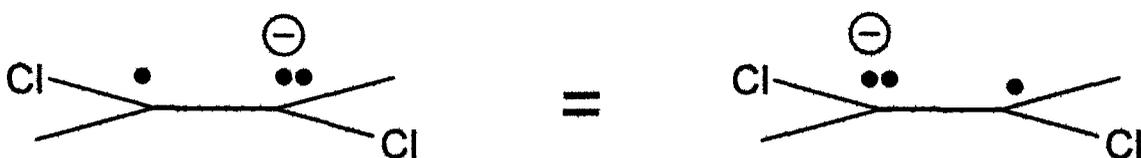


Figure 4.8 – Equivalent radical negative ion structures from either *cis* or *trans* dichloroethylene.

The calculated FIFEs (Tables 3.2 and 3.3) show that formation of the halide negative ion via fragmentation is limited by the energy required for the vertical transition. With the exception of the vinyl compounds and tetrachloroethylene, all calculated FIFEs for halide ion formation are either positive or within 200 meV of zero. The vinyl compounds have only slightly higher FIFEs, at 0.256 eV for vinyl chloride (Table 3.2) and 0.269 for vinyl bromide (Table 3.3) while the calculated energy for tetrachloroethylene is -0.430 eV (Table 3.2). The corresponding negative ions for chloride ion production from the chloroethylenes, $(M-Cl)^{\cdot-}$, are generally of the same

magnitude as the VEAE (Table 3.5). The two exceptions are tetrachloroethylene at 3.868 eV and vinyl chloride at 3.314 (Table 3.2).

The FIFEs for halide negative ion formation from the bromoethylenes (Table 3.3) is approximately the same magnitude as it is for chloroethylenes (Table 3.2), while the formation of $(M-Br)^-$'s have a lower energy requirement than the chlorinated analogous by ~ 1 eV. Tetrabromoethylene's $(M-Br)^-$ FIFE is an exception with a ~ 4 eV lower energy requirement than the analogous ion from tetrachloroethylene. Calculations for *cis*- and *trans*-dibromoethylenes show a positive FIFE for the $(M-Br)^-$ and a negative FIFE for the Br^- (Table 3.3). The reversal is due to the calculations converging on an unreasonable structure involving bromine bridging of the carbon-carbon bond.

The halide and $(M-X)^-$ formed at near to zero eV (Table 3.5) are unexpected in view of the calculated VEAEs (Table 3.1) showing negative values for all compounds except for tetrabromoethylene. However, given the calculated FIFEs for formation of halide negative ions, production of these ions would be favored at these energies due to the generally positive electron resonance energies. Presently there is no clear explanation of these near to zero ions and given that this is the first known study of bromoethylenes by REC-MS previous explanations of near to zero ions have been based upon chloroethylenes. The two explanations put forth to explain near to zero ions from tetrachloroethylene are first, that the inverse proportionality of the attachment cross section to electron energy allows fragmentation to effectively compete with autodetachment (Table 3.5). Secondly, out-of-plane distortion may provide orbital mixing and allows for the formation of negative ions from near to zero energy electrons.

In order to attempt to resolve this unanswered question, an out-of-plane constrained model of tetrachloroethylene was constructed and the calculations showed that in *syn* out-of-plane bending, the VEAE becomes favorable (Table 3.4). While the exact angle of out-of-plane distortion at which the vertical transition becomes a horizontal transition or favorable with a 0 eV electron was not calculated, it apparently lies between 10 and 20 degrees. When the energy difference of the neutral molecule's planar geometry and the structure with a fixed distortion angle at 20 degrees are compared, the difference in energy between the two structures is only 0.2077 eV (Table 3.4). This means that the vertical transition is now favorable but not by raising the energy of the neutral molecule and, thereby the vibrational level of the initial geometrical starting state. It is also clear from these results that the *anti* conformation results in a dramatic increase in the energy required for the vertical transition. (Table 3.4) This is surprising since the optimal (adiabatic) geometry for the negative ion of tetrachloroethylene is more similar to the *anti* structure.

Further examination of the calculated VEAEs (Table 3.1) for the chloroethylenes and the formation of specific fragmentation channels (Table 3.6) and the associated resonance energy allows one to conclude that the formation of the Cl^- is energetically limited by the energy of the resonance. Tetrachloroethylene remains an anomaly in this trend with formation of Cl^- being reported at near to zero energy. It is important to note that this result is in conjunction with the detection of a molecular ion, M^- at near to zero energy as well. This suggests that the Cl^- is a result of the adiabatic geometry of the M^- with a non-planar structure and that it is possible because of the relatively long lifetime, 14 μs ,³ of the tetrachloroethylene negative ion. The important feature of the non-planar

geometry is the possibility of $\pi^* \sigma^*$ orbital mixing that has been observed in more, complex aromatic π systems, involving both out-of-plane bending in chlorodioxins as well as functional group interactions in alkyl phthalates.⁴⁶⁻⁴⁸

The possibility $\pi^* \sigma^*$ orbital mixing via out-of-plane bending represents a new theory for the formation of near to zero fragment ions in which predissociation from the out-of-plane distortion is the mechanism for rationalizing the production of these ions.⁴⁹ The possibility of dissociative electron attachment with haloethylenes cannot be correct because the calculated VEAES for the $M^{\cdot-}$ are in good agreement with the energy of the fragment ions. Therefore the experimental data and calculated values are in better agreement with predissociation as the source of fragment ions.

4.3 Data Analysis Software

The program extractor works as intended with a dramatic savings in time for data processing. However, there is the possibility for improvement in data parsing by using a binary data reading format and optimizing the reading of data lines. The exact means by which this would result in an improvement is that less time would be spent starting at the beginning of the file being processed, each time a new peak is to be parsed. Put another way, if there are two peaks to be processed, one starting at line 5000 and one at line 5050, the program reads all the lines up to the first peak, extracts it as described above, and then goes back to the beginning to read all the lines until reaching the second peak. This reading of lines would reduce efficiency dramatically in files with large mass ranges with

many peaks at the high end of the mass range. However, at present the majority of mass peaks are at lower masses and, therefore, file processing is not as severely affected.

5. Conclusions

In the analysis of haloethylenes using a REC-MS it has been found that there are several channels for negative ion formation and several new effective yield curves for the chloroethylenes that have not previously been reported. The most important "new" ion reported here is the long-lived molecular negative ion for trichloroethylene with a yield maximum near zero eV. In addition the first REC-MS results are presented for bromoethylenes. Furthermore, the results shown previously by ETS that bromination produces lower resonance energies, are experimentally verified by comparison of analogous chlorinated and brominated compounds and specifically trichloroethylene and tribromoethylene. The high energy resonances ($\sim 6 - 10$ eV) are most likely Feshbach resonances due to correlations with $N \rightarrow S$ transitions determined by EELS and the Rydberg state of the ionization potential determined by photoelectron spectroscopy as potential parent states.

The previously reported effects of regio-specificity for halogen substitution are not experimentally validated for bromoethylenes even though these trends are apparent in the theoretical data. The reason for this is that the brominated compounds studied, except for vinyl bromide, have resonance maxima for halide ion formation within experimental error of zero and were, therefore, effectively equivalent in value. As a means of explaining this Olthoff et al ¹⁶ proposed that the electron capacity of the halogen is the important characteristic in stabilizing the negative charge and thereby lowering the energy necessary for the vertical transition. While the electron affinity of fluorine (3.399 eV), chlorine (3.628 eV), bromine (3.378 eV), and iodine (3.063 eV) are close in

magnitude, the bond strengths between carbon and the different halogens differ dramatically. This provides the thermochemical rationale for why fluorine with an average bond strength of ~104 kCal/mol forms halide ions at higher electron energy than chlorine at ~69 kCal/mol or bromine at ~54 kCal/mol. The thermochemical rationale is further supported by correlation with the computational results showing that the production of most Cl^- and Br^- are limited by the vertical electron attachment energies. In addition theoretical results show that the VEA is dependent on both the number of substituents and the location of the substituents while the AEA is dominated by the number of substituents with little effect from their position.

The formation of halide and molecular negative ions at near to zero energies given the ETS data showing that fragmentation proceeds from the π^* orbital and that the vertical transition energies, for all compounds tested, are negative by several hundred meV. The calculations for tetrachloroethylene suggest that deformations from a planar structure results in a lowering of the necessary energy for the vertical transition but it does not definitively resolve this issue. The most viable answer to the origin of the near to zero energy fragment ions is a predissociation model where the non-planar structure of the tetrachloroethylene negative ion allows for π^* σ^* mixing that leads to formation of Cl^- .

Presently, the Visual Basic program "Extractor" works as designed and provides a considerable improvement over manual data manipulation. However even with this clear advantage there are some additional refinements that could be added. First the manual mass selection should allow more delimiters for separating masses. This requires slightly more intelligence in the data input routines. Secondly and perhaps more important is the

addition of a batch option input files. This would allow for processing of more spectra by potentially acquiring data on one day, setting up a batch file to run overnight and analyzing data the next day. Further use of this program will lead to additional modifications and refinements as research dictates.

References

1. Christophorou, L. G.; *Electron-Molecule Interactions and Their Applications* (1984) Academic Press, Inc., Orlando, Fla. Vol. 1.
2. Christophorou, L. G.; *Electron-Molecule Interactions and Their Applications* (1984) Academic Press, Inc., Orlando, Fla. Vol. 2.
3. Johnson, J. P.; Christophorou, L. G.; Carter, J. G.; *J Chem Phys.* (1977) 67, 2196-2215.
4. Voinov, V. G.; Vasil'ev, Y. V.; Morr , J.; Barofsky, D. F.; Deinzer, M. L.; Gonin, M.; Egan, T. F.; Fuehrer, K.; *Anal Chem* (2003) 75 (13), 3001-3009.
5. Voinov, V. G.; Vasil'ev, Y. V.; Ji, H.; Figard, B. J.; Morr , J.; Egan, T. F.; Barofsky, D. F.; Deinzer, M. L.; *Anal Chem* (2004) 76(10), 2951-2957.
6. Sandhu, J. S.; *Indian J. Chem.* (1972) 10, 667-668.
7. Moore, J. H. *J. Phys. Chem.* (1972) 76(8), 1130-1133.
8. Koerting, C. F.; Walzl, K. N.; Kuppermann, A.; *Chem Phys Lett* (1984) 109(2), 140-144.
9. Kaufel, R.; Illenberger, E.; Baumgartel, H.; *Chem Phys Lett* (1984) 106(4), 342-346.
10. Illenberger, E.; Baumgartel, H.; Suzer, S.; *J Electron Spectroscopy Related Phenomena* (1984) 33 (2) 123-139.
11. Drexel, H.; Sailer, S.; Grill, V.; Scheier, P.; Illenberger, E.; Mark, T. D.; *J Chem Phys* (2003) 118 (16), 7394-7400.
12. Chen, E. C. M.; Wiley, J. R.; Batten, C. F.; Wentworth, W. E.; *J Phys Chem* (1994) 98, 88.
13. Nakagawa, S.; Shimokawa, T.; *Bull. Chem. Soc. Jpn.* (2000) 73, 1491.
14. Wiley, J. R.; Chen, E. C. M.; Wentworth, W. E.; *J Phys Chem* (1993) 97, 1256.
15. Chen, E. C. M.; Albyn, K.; Dussack, L.; Wentworth, W. E.; *J Phys Chem* (1989) 93, 6827.
16. Olthoff, J.; Tossell, J. A.; Moore, J. H.; *J Chem Phys* (1985) 83 (11), 5627-34.
17. O'Malley, T. F.; *Phys Rev* (1966) 150, 14-29

18. Benitez, A.; Moore, J. H.; Tossell, J. A.; *J Phys Chem* (1988) 88 (11) 6691-98.
19. Oster, T.; Kühn, A.; Illenberger, E.; *Int J Mass Spec* (1989) 89, 1-72.
20. Underwood-Lemons, T.; Gotthard, S.; Tossell, J. A.; Moore, J. H.; *J Chem Phys* (1996) 105 (18), 7896-903.
21. Buchanan, W. *PC Interfacing, Communications and Windows Programming* (1999) Addison Wesley Limited, Harlow, England.
22. Dorman, F. H.; *Chem Phys* (1966) 44 (10), 3856.
23. Ajello, J. M.; Chutjian, A.; *J Chem Phys* (1979) 71, 1079.
24. Chutjian, A.; Alajajian, H.; *Phys Rev A* (1985) 31, 2885.
25. Massey, H. S. W. *Negative Ions* (1950) Cambridge University Press, Cambridge, England.
26. Smirnov, B. M. *Negative Ions* (1982) McGraw-Hill, USA.
27. Schulz, G. J.; *Rev Modern Physics* (1973) 45(3), 423.
28. O'Malley, T. F.; *Phys Rev* (1966) 150, 14-29 _____ Double
29. Jordan, K. D.; Burrow, P. D.; *Acc Chem Res* (1978) 11,341
30. Christophorou, L. G.; Carter, J. G.; Collins, P. M.; Christodoulides, A. A.; *Chem Phys* (1971) 54 (11), 4691.
31. Christodoulides, A. A.; Christophorou, L. G.; *Chem Phys* (1971) 54 (11), 4706.
32. Jaguar Manual, v4.1, Schrödinger, Inc. (2001).
33. Maestro Manual, v4.1, Schrödinger, Inc. (2001).
34. Personal Communication w/ Dr. Gable.
35. Visual Basic Manual, v6.0 Professional Edition, Microsoft Co. (1985- 1998).
36. Matejcik, S.; Ipolyi, I.; Illenberger, E.; *Chem Phys Lett* (2003) 5-6, 375.
37. Bahrim, C.; Thumm, U.; Fabrikant, I. I.; *Phys. Rev. A* (2001) 63, 042710.
38. Bardsley, J. N.; Mandl, F.; *Reports on Progress in Physics* (1968) 31(2) 471-531.

39. Huheey, J. E., *Inorganic Chemistry*, 3rd ed. Harper and Row, New York 1983, pp 155.
40. Chiu, N. S.; Burrow, P. N.; Jordan, K. D.; *Chem Phys Lett* (1979) 68 (1) 121.
41. Heni, M.; Illenberger, E.; Baumgärtel, H.; Süzer, S.; *Chem Phys Lett* (1982) 87 (3) 244.
42. Heni, M.; Kwiatkowski, G.; Illenberger, E.; *Ber. Bunsenges. Phys. Chem.* (1984) 88, 670.
43. Burrow, P. D.; Modelli, A.; Chiu, N. S.; Jordan, K. D.; *Chem Phys Lett* (1981) 82 (2) 270.
44. Mazurkiewicz, P. H.; Deinzer, M. L.; *JACS* (1999) 121, 3421.
45. Laramée, J. A.; Mazurkiewicz, P. H.; Berkout, V.; Deinzer, M. L.; *Mass Spec Rev* (1996) 15, 15.
46. Berkout, V. D.; Mazurkiewicz, P. H.; Deinzer, M. L.; *JACS* (1999) 121, 2561-2570.
47. Pearl, D. M.; Burrow, P. D.; Nash, J. J.; Morrison, H.; Jordan, K. D.; *JACS* (1993) 115, 9876 -9877.
48. Pearl, D. M.; Burrow, P. D.; Nash, J. J.; Morrison, H.; Nachtigallova, D.; Jordan, K. D.; *J Phys. Chem.* (1995) 99, 12379- 12381.
49. Freeman, P. K.; Srinivasa, R.; Campbell, J.-A.; Deinzer, M. L.; *JACS* (1986) 108, 5531-5536.
50. Ingolfsson, O.; Weik, F.; Illenberger, E.; *In. J Mass Spec* (1996) 155, 1-68.

Appendix

Appendix – Source Code for VB program Extractor

Option Explicit

Dim LengthOfMass%, Mass%, LinesInFile%, MassOfInterest%(1000), Threshold As Integer

Dim ScanWidth%, NumberOfScans%, NumberOfMasses%, Lines%, Counter As Integer

Dim FinalValues!(1000, 2), EFCdata!(1000, 4), Level%, MassValues(35000, 2) As Single

Dim TotalBytesInFile As Long

Dim Spotter As Integer, MostIntensePeak As Single, EnergyPeakMax(2000, 5) As Single

Private Sub AutoPeakCHK_Click()

'Setting the control for peak selection for the autopeak selection

If AutoPeakCHK.Value = 1 Then

 MassTXT.Enabled = False

 MassTXT.BackColor = &H80000003

 MassTXT.Text = "AutoPeak Finder Selected"

 ThresholdTXT.Visible = True

Else: MassTXT.Enabled = True

 MassTXT.Text = ""

 MassTXT.BackColor = &H80000005

 ThresholdTXT.Visible = False

End If

End Sub

Private Sub CancelBTN_Click()

 End

End Sub

Private Sub ClearBTN_Click()

 'clearing inputs to start conditions

 InCD.FileName = ""

 InTXT.Text = ""

 'clearing outputs to start conditions

 If OutputCHK.Value = 0 Then

 OutCD.FileName = ""

 OutTXT.Text = ""

 End If

 'clearing peak extraction settings to start conditions

 If AutoPeakCHK.Value = 1 Then

 Exit Sub

 Else

```

    MassTXT.Text = ""
End If

```

```
End Sub
```

```
Private Sub InBTN_Click()
```

```

    'clear file name
    InCD.FileName = ""

```

```

    'if a directory location is already present then go there else start in F:

```

```

    If InCD.InitDir = "" Then

```

```

        InCD.InitDir = "F:\"

```

```

    End If

```

```

    'set paremeters to file type selection

```

```

    InCD.Filter = "Text Files (*.txt) | *.txt|All Files (*.*)|*.*"

```

```

    InCD.FilterIndex = 1

```

```

    InCD.Flags = cdIOFNFileMustExist Or cdIOFNPathMustExist

```

```

    InCD.Action = 1

```

```

    'force file selection and let user know they haven't selected a file

```

```

    If InCD.FileName = "" Then

```

```

        MsgBox "No file selected"

```

```

        Exit Sub

```

```

    End If

```

```

    InTXT.Text = InCD.FileName

```

```
End Sub
```

```
Private Sub mnuExit_Click()
```

```

    End

```

```
End Sub
```

```
Private Sub mnuIn_Click()
```

```

    'clear file name

```

```

    InCD.FileName = ""

```

```

    'if a directory location is already present then go there else start in F:

```

```

    If InCD.InitDir = "" Then

```

```

        InCD.InitDir = "F:\"

```

```

    End If

```

```

    'set paremeters to file type selection

```

```

    InCD.Filter = "Text Files (*.txt) | *.txt|All Files (*.*)|*.*"

```

```

    InCD.FilterIndex = 1

```

```

    InCD.Flags = cdIOFNFileMustExist Or cdIOFNPathMustExist

```

```
InCD.Action = 1

'force file selection and let user know they haven't selected a file
If InCD.FileName = "" Then
    MsgBox "No file selected"
    Exit Sub
End If
InTXT.Text = InCD.FileName

End Sub

Private Sub mnuOut_Click()
    'informs user if output is locked by oterh selection
    If OutputCHK.Value = 1 Then
        MsgBox "Output File Locked"
        Exit Sub
    End If

    'clear name to allow new selection
    OutCD.FileName = ""

    'if a directory location is already present then go there else start in F:
    If OutCD.InitDir = "" Then
        OutCD.InitDir = "F:\"
    End If

    'setting output limitations
    OutCD.Filter = "Text Files (*.txt) | *.txt|All Files (*.*)|*.*"
    OutCD.FilterIndex = 1
    OutCD.Flags = cdlOFNFileMustExist Or cdlOFNPathMustExist
    OutCD.Action = 2

    'force output file name selection
    If OutCD.FileName = "" Then
        MsgBox "No file selected"
        Exit Sub
    End If

    'match output file displayed to actual location selected
    OutTXT.Text = OutCD.FileName

End Sub

Private Sub OutBTN_Click()
    'informs user if output is locked by oterh selection
    If OutputCHK.Value = 1 Then
```

```

    MsgBox "Output File Locked"
    Exit Sub
End If

'clear name to allow new selection
OutCD.FileName = ""

'if a directory location is already present then go there else start in F:
If OutCD.InitDir = "" Then
    OutCD.InitDir = "F:\"
End If

'setting output limitations
OutCD.Filter = "Text Files (*.txt) | *.txt|All Files (*.*)|*.*"
OutCD.FilterIndex = 1
OutCD.Flags = cdlOFNFileMustExist Or cdlOFNPathMustExist
OutCD.Action = 2

'force output file name selection
If OutCD.FileName = "" Then
    MsgBox "No file selected"
    Exit Sub
End If

'match output file displayed to actual location selected
OutTXT.Text = OutCD.FileName

End Sub

Private Sub OutputCHK_Click()
    If OutputCHK.Value = 1 Then
        OutTXT.Enabled = False
        OutTXT.Text = "Output locked to Input File _XXX"
    Else: OutTXT.Enabled = True
        OutTXT.Text = ""
    End If
End Sub

End Sub

Private Sub StartBTN_Click()
    Dim n%, x%, i%, MinE As Single, MaxE As Single, WidthE As Single
    Dim Scans$, NewDir$, ScansNo$, Emin$, Emax$, EWidth As String
    Dim EStep As Single

    'Check for fatal input error: no input file
    If InCD.FileName = "" Then

```

```
    MsgBox "No Input file selected"  
    Exit Sub  
End If
```

```
'sets output file name to input file name for sequential file creation  
If OutputCHK.Value = 1 Then  
    OutCD.FileName = InCD.FileName  
End If
```

```
'Check for fatal input error: no output file  
If OutCD.FileName = "" Then  
    MsgBox "No Output file selected"  
    Exit Sub  
End If
```

```
'Check for input error: threshold to low - all mass values then a peak  
If ThresholdTXT.Text < 1 Then  
    MsgBox "Invalid Threshold selected: Must be greater than 1."  
    Exit Sub  
End If
```

```
'Check for input error: Unreasonable threshold - almost no peak qualify  
If ThresholdTXT.Text > 1000 Then  
    MsgBox "Invalid Threshold selected: Must be smaller than 1000."  
    Exit Sub  
End If
```

```
'Check for fatal input error: no valid no. of lines to read to generate peaks/spectra  
If SurroundTXT.Text < 1 Then  
    MsgBox "Invalid Line No selected: Must be greater than 1."  
    Exit Sub  
End If
```

```
'Check for fatal input error: to many peaks selected to read and will read more than one  
mass  
If SurroundTXT.Text > 100 Then  
    MsgBox "Invalid Line No selected: Must be smaller than 100 to prevent adjacent  
peak extraction."  
    Exit Sub  
End If
```

```
'Begin file processing  
Open InTXT.Text For Input As #1
```

```
'skip first 4 lines but count them in total lines (LinesInFile)  
For n = 1 To 4
```

```

    Line Input #1, Scans
    LinesInFile = LinesInFile + 1
Next

'find energy scan width
ScansNo = Mid$(Scans, 20, 3)

'Convert from string to int
ScanWidth = CInt(ScansNo)

'skip next 9 lines but count them in total lines (LinesInFile)
For n = 1 To 9
    Line Input #1, EWidth
    LinesInFile = LinesInFile + 1
Next

'find start energy value
Emin = Left$(EWidth, 6)
'convert to single variable type
MinE = CSng(Emin)

'find ending energy value
Emax = Right$(EWidth, 5)
'convert to single variable type
MaxE = CSng(Emax)

'calculate energy step
WidthE = MaxE - MinE
EStep = WidthE / (ScanWidth)

'set width of peak to read in lines from user input value
Lines = CInt(SurroundTXT.Text)

'Fill Energy scale in Final Data
'Use the calibration from the OregonToF output
If FileCalCHK.Value = 1 Then
    For n = 1 To ScanWidth
        FinalValues(n, 1) = EStep * (n - 1) + MinE
        'fill EYC data for Energy scale
        EFCdata(n, 0) = FinalValues(n, 1)
    Next
'Default scale without calibration
Else
    For n = 1 To ScanWidth
        FinalValues(n, 1) = EStep * n
        'fill EYC data for Energy scale

```

```

    EFCdata(n, 0) = FinalValues(n, 1)
  Next
End If

'Create a chromatogram to allow peak finding
FillMassArray

'If selected make a ms chromatogram
If OutputTICCHK.Value = 1 Then
  WriteTIC
End If

'not sure why here
n = 1
For n = 1 To 30000
  TotalBytesInFile = TotalBytesInFile + MassValues(n, 0)
Next

'Decide which way to choose which masses to find
'first case is auto extraction
If AutoPeakCHK.Value = 1 Then
  Threshold = CInt(ThresholdTXT.Text)
  FindMasses
'second case is manually typed in masses
Else
  ReadMasses
End If

'Set up output file structure if necessary
If SubDirCHK.Value = 1 Then
  'extract the path from this filename
  For i = Len(InCD.FileName) To 1 Step -1
    If Mid$(InCD.FileName, i, 1) = "\" Then Exit For
  Next
  ' when we get here, i% points to the rightmost "\"
  NewDir$ = Left$(InCD.FileName, i%) + Mid$(InCD.FileName, i + 1,
Len(InCD.FileName) - (i + 4))
  ' create a new folder under the input file's folder
  If Dir(NewDir, vbDirectory) = "" Then Mkdir NewDir$
  OutCD.FileName = NewDir$ + "\" + Mid$(InCD.FileName, i + 1,
Len(InCD.FileName) - (i))
End If

'initialize variable to do selection of mass of interest
Counter = 1

```

```
'initialize variable to count number of peaks in table
Spotter = 1
```

```
'Process each mass in turn
For x = 1 To NumberOfMasses
  Mass = MassOfInterest(Counter)
  Selectline
  FillArray
  ClearArray
  Counter = Counter + 1
Next
```

```
'Output EYC files
WritePeakOutput
```

```
'output peak table
PeakTable
```

```
'inform user that files done processing
MsgBox "Finshed Processing File"
```

```
'Clear up arrays to prevent any data overlap problems when running files back to back
FinalClear
```

```
End Sub
```

```
Public Sub FinalClear()
```

```
  Dim x%, z%
```

```
  x = 1
```

```
  z = 1
```

```
  For z = 1 To 30000
```

```
    MassValues(z, 0) = 0
```

```
    MassValues(z, 1) = 0
```

```
    MassValues(z, 2) = 0
```

```
  Next
```

```
  TotalBytesInFile = 0
```

```
  Counter = 1
```

```
  LengthOfMass = 1
```

```
  Mass = 0
```

```
  LinesInFile = 0
```

```
  For x = 1 To 1000
```

```
    MassOfInterest(x) = 0
```

```
    FinalValues(x, 0) = 0
```

```
    FinalValues(x, 1) = 0
```

```
    FinalValues(x, 2) = 0
```

Next

Threshold = 0
NumberOfScans = 0
NumberOfMasses = 0
Counter = 0
Lines = 0
Level = 0
ScanWidth = 0

End Sub

Public Sub FindMasses()

Dim a As Long, b%, Sum As Integer

a = 1

Level = 0

Sum = 0

NumberOfMasses = 1

For a = 1 To 49

Sum = Sum + MassValues(a, 2)

Next

Level = Int(Sum / 50)

If Level < 1 Then Level = 1

a = 1

b = 1

For a = 1 To 35000

If (MassValues(a, 2)) > (Threshold * Level) Then

Tag = 0

For b = 1 To 999

If MassOfInterest(b) = CInt(MassValues(a, 1)) Then

Tag = 1

Exit For

End If

Next

b = 1

If Tag = 0 Then

'Sent Mass of interest to rounded value, let user select peaks to look at

MassOfInterest(NumberOfMasses) = CInt(MassValues(a, 1))

NumberOfMasses = NumberOfMasses + 1

End If

End If

Next

```
'subtract 1 for the starting position of 1 to correct
NumberOfMasses = NumberOfMasses - 1
```

```
End Sub
```

```
Public Sub ReadMasses()
```

```
Dim x%, a%, b%, c%, f%, k%, TextLength%, Commas As Integer
Dim TextHolder$, Holder1$, Holder2$, CharHolder$, RightHolder As String
```

```
x = 1
```

```
a = 1
```

```
'Fill Array with null characters
```

```
For x = 1 To 999
```

```
    MassOfInterest(x) = 0
```

```
Next
```

```
'Get Masses entered and count length of string
```

```
TextHolder = MassTXT.Text
```

```
TextLength = Len(TextHolder)
```

```
'Find number of elements in string
```

```
Commas = 0
```

```
For a = 1 To TextLength
```

```
    CharHolder = Mid$(TextHolder, a, 1)
```

```
    If CharHolder = "," Then Commas = Commas + 1
```

```
Next
```

```
c = -1
```

```
'Fill MassData into Array except last value
```

```
If Commas >= 1 Then
```

```
    For a = 1 To Commas
```

```
        Holder1 = InStr(c + 2, TextHolder, ",")
```

```
        b = CInt(Holder1)
```

```
        Holder2 = Mid$(TextHolder, c + 2, b - (c + 2))
```

```
        MassOfInterest(a) = CInt(Holder2)
```

```
        c = b
```

```
Next
```

```
'Fill last value
```

```
'Find length of last group
```

```
f = 1
```

```

For k = 1 To (TextLength - 1)

    CharHolder = Mid$(TextHolder, TextLength - k, 1)
    If CharHolder = "," Then
        f = k
        k = TextLength - 1
    End If
Next

```

```

'Get last value and add to Mass value array
Holder2 = Mid$(TextHolder, TextLength + 1 - f, f)
MassOfInterest(Commas + 1) = CInt(Holder2)

```

```

Else
    'if only one value then set it to first location in array
    Mass = CInt(TextHolder)
    MassOfInterest(1) = Mass

```

```

End If

```

```

'Find the number of masses entered
NumberOfMasses = Commas + 1

```

```

End Sub

```

```

Public Sub Selectline()

```

```

    Dim Linenumber%, Max As Long, Min As Long, StartLine%, MaxLine%,
    LinesAvailable%, n%, z%, b%, c%, d%, e%, a As Integer
    Dim ByteSpacer As Long
    Dim Spacer$, WorkingLine$, Holder1$, Holder2 As String
    Dim q%, Background%(1000), g As Integer
    Dim Ave3 As Single, Ave5 As Single, MaxAve3 As Single, MaxAve5 As Single

```

```

    z = 1
    a = 1
    b = 1
    n = 1
    d = 1
    e = 1
    q = 1
    Linenumber = 1
    StartLine = 0
    Max = 0
    Min = 0
    LinesAvailable = 0

```

```

'Find first mass of interest in mass list
Do Until MassOfInterest(Counter) = Int(MassValues(z, 1))
  z = z + 1
  Linenumber = Linenumber + 1
Loop

```

```

'if mass too small to be reasonable, then skip
If MassOfInterest(Counter) <= 14 Then Exit Sub

```

```

'First local max of mass values
Max = MassValues(Linenumber - 20, 2)

```

```

MaxLine = Linenumber - 20
StartLine = MaxLine
For e = 1 To 29
  If Max < MassValues(Linenumber - 20 + e, 2) Then
    Max = MassValues(Linenumber - 20 + e, 2)
    MaxLine = Linenumber - 20 + e
  End If
Next

```

```

'Find start of peak
Min = MassValues(MaxLine, 2)
e = 1
For e = 1 To 20
  If Min <= (Threshold * Level) Then Exit For

  If Min > MassValues(MaxLine - e, 2) Then
    Min = MassValues(MaxLine - e, 2)
    StartLine = MaxLine - e
  End If
Next

```

```

'Skip to starting point of interest to check length of file
Open InTXT.Text For Input As #1
For n = 1 To (StartLine + 12)
  Line Input #1, Spacer
Next

```

```

'check that there are the expected number of lines
Do Until EOF(1)
  Line Input #1, WorkingLine
  LinesAvailable = LinesAvailable + 1
  If LinesAvailable >= Lines Then LinesAvailable = Lines
Loop

```

```

Close #1

n = 1

'Skip to starting point of interest to get data
Open InTXT.Text For Input As #1 'Random As #1 Len = 3000 TotalBytesInFile
For n = 1 To (StartLine + 12 - Lines)
    'ByteSpacer = ByteSpacer + MassValues(n, 0)
    Line Input #1, Spacer
Next

'decide whether to use background subtraction
If BackgroundSubCHK.Value = 1 Then
    'get background array
    For d = 1 To (Lines - 1)
        'Get #1, , WorkingLine
        Line Input #1, WorkingLine
        c = 8
        For a = 1 To (ScanWidth - 1)
            Holder1 = InStr(c + 1, WorkingLine, " ")
            b = CInt(Holder1)
            Holder2 = Mid$(WorkingLine, c, b - c)
            Background(a) = Background(a) + CInt(Holder2)
            c = b
        Next
    Next

Next

'average over 30 scans, i.e. divide by lines read
'a = 1
'For a = 1 To (ScanWidth - 1)
'    Background(a) = Int(Background(a) / Lines)
'Next
Else
    n = 1
    For n = 1 To (Lines - 1)
        'ByteSpacer = ByteSpacer + MassValues(n, 0)
        Line Input #1, Spacer
    Next
End If

d = 1
a = 1
b = 1
'make local data for summing of electron energy

```

```

'Get #1, ByteSpacer, WorkingLine
For d = 1 To LinesAvailable - 1
  'Get #1, , WorkingLine
  Line Input #1, WorkingLine
  c = 8
  For a = 1 To (ScanWidth - 1)
    Holder1 = InStr(c + 1, WorkingLine, " ")
    b = CInt(Holder1)
    Holder2 = Mid$(WorkingLine, c, b - c)
    FinalValues(a, 2) = FinalValues(a, 2) + CInt(Holder2)
    c = b

'Make peak based EYC
'Total peak EYC- without 34-38
If MassOfInterest(Counter) <> 34 Or 35 Or 37 Or 38 Then
  EFCdata(a, 1) = EFCdata(a, 1) + CInt(Holder2)
End If

'high mass EYC - i.e. without 35 and 16
If MassOfInterest(Counter) >= CInt(EYCTXT.Text) Then
  EFCdata(a, 2) = EFCdata(a, 2) + CInt(Holder2)
End If

Next

Next

Close #1

'Subtract Background
If BackgroundSubCHK.Value = 1 Then
  a = 1
  For a = 1 To (ScanWidth - 1)
    FinalValues(a, 2) = FinalValues(a, 2) - Background(a)
    If FinalValues(a, 2) < 0 Then FinalValues(a, 2) = 0
  Next
End If

'Find peak Max
g = 1
For g = 1 To (ScanWidth - 1)

  'rethink here
  EnergyPeakMax(Spotter, 0) = MassOfInterest(Counter)

```

```

If EnergyPeakMax(Spotter, 1) < FinalValues(g, 2) Then
  'Intensity of Max
  EnergyPeakMax(Spotter, 1) = FinalValues(g, 2)
  'Energy associated with this max
  EnergyPeakMax(Spotter, 3) = FinalValues(g, 1)
  'Set max for relative intensity calculation
  If MostIntensePeak < FinalValues(g, 2) Then
    'not setting max intensity to Cl- ions
    If MassOfInterest(Counter) <> 34 And MassOfInterest(Counter) <> 35 And
MassOfInterest(Counter) <> 36 And MassOfInterest(Counter) <> 37 And
MassOfInterest(Counter) <> 38 Then
      MostIntensePeak = FinalValues(g, 2)
    End If
  End If

  'move to next E peak if lower than 10% and not background
  ElseIf EnergyPeakMax(Spotter, 1) <= (FinalValues(g, 2) * 0.1) And
EnergyPeakMax(Spotter, 1) >= 3 Then
    Spotter = Spotter + 1

  'However if a small intensity then erase
  ElseIf EnergyPeakMax(Spotter, 1) <= 3 Then
    EnergyPeakMax(Spotter, 1) = 0
  End If

  'calculate max by 3 average
  If g >= 10 And g < (ScanWidth - 10) Then
    'if near end of e spectra don't calculate
    Ave3 = (FinalValues(g - 1, 2) + FinalValues(g, 2) + FinalValues(g + 1, 2)) / 3
    If MaxAve3 < Ave3 Then
      MaxAve3 = Ave3
      EnergyPeakMax(Spotter, 4) = FinalValues(g, 1)
    End If
  End If

  'calculate max by 5 average
  If g >= 10 And g < (ScanWidth - 10) Then
    'if near end of e spectra don't calculate
    Ave5 = (FinalValues(g - 2, 2) + FinalValues(g - 1, 2) + FinalValues(g, 2) +
FinalValues(g + 1, 2) + FinalValues(g + 2, 2)) / 5
    If MaxAve5 < Ave5 Then
      MaxAve5 = Ave5
      EnergyPeakMax(Spotter, 5) = FinalValues(g, 1)
    End If
  End If
Next

```

```

'Move to next loaction in array
'Final check of energy peak to decide if real energy peak
If EnergyPeakMax(Spotter, 3) <= 11 And EnergyPeakMax(Spotter, 3) >= 0 Then
    Spotter = Spotter + 1
End If

```

```
End Sub
```

```
Public Sub FillArray()
```

```
    Dim LocalName As String
```

```
    Dim a%, c As Integer
```

```
    c = 1
```

```
    a = 1
```

```
'don't write any files with mass/z lower than 14 b/c they aren't useful
```

```
If Mass <= 14 Then Exit Sub
```

```
If Right$(OutCD.FileName, 4) = ".txt" Then
```

```
    a = Len(OutCD.FileName)
```

```
    OutCD.FileName = Left(OutCD.FileName, a - 4)
```

```
End If
```

```
LocalName = OutCD.FileName + "_" + CStr(Mass) + ".txt"
```

```
If Dir(LocalName, vbDirectory) <> "" Then
```

```
    a = Len(LocalName)
```

```
    LocalName = Left(LocalName, a - 4)
```

```
    LocalName = LocalName + "_2" + ".txt"
```

```
End If
```

```
Open LocalName For Output As #2
```

```
For c = 1 To (ScanWidth - 1)
```

```
    Print #2, FinalValues(c, 1); " "; FinalValues(c, 2)
```

```
Next
```

```
Close #2
```

```
End Sub
```

```
Public Sub FillMassArray()
```

```
    Dim WorkingLine$, Holder1$, Holder2 As String
```

```
    Dim n%, a%, b%, c%, d%, FirstBreak%, Sum As Long
```

```
n = 1
a = 1
b = 1
c = 1
d = 1
```

```
'initialize array at 0
For d = 1 To 30000
  MassValues(d, 0) = 0
  MassValues(d, 1) = 0
  MassValues(d, 2) = 0
Next
```

```
Do Until EOF(1)
```

```
  Line Input #1, WorkingLine
  Holder1 = InStr(2, WorkingLine, " ")
  FirstBreak = CInt(Holder1)
  MassValues(n, 1) = CSng(Left$(WorkingLine, FirstBreak)) 'Convert first value to
mass value
  MassValues(n, 0) = Len(WorkingLine)
```

```
  'Fill Data into Array of Mass and total ions
  c = FirstBreak
  For a = 1 To (ScanWidth - 1)
    Holder1 = InStr(c + 1, WorkingLine, " ")
    b = CInt(Holder1)
    Holder2 = Mid$(WorkingLine, c, b - c)
    Sum = Sum + CInt(Holder2)
    c = b
```

```
  'Make total data EYC
  'Total EYC- without 34-38
  If MassOfInterest(Counter) <> 34 And MassOfInterest(Counter) <> 35 And
MassOfInterest(Counter) <> 36 And MassOfInterest(Counter) <> 37 And
MassOfInterest(Counter) <> 38 Then
    EFCdata(a, 3) = EFCdata(a, 1) + CInt(Holder2)
  End If
```

```
  'high mass EYC - i.e. without 35 and 16
  If MassOfInterest(Counter) >= CInt(EYCTXT.Text) Then
    EFCdata(a, 4) = EFCdata(a, 2) + CInt(Holder2)
  End If
```

```
Next
```

```

    MassValues(n, 2) = Sum
    Sum = 0
    LinesInFile = LinesInFile + 1
    n = n + 1
    a = 1

```

```

Loop

```

```

Close #1

```

```

End Sub

```

```

Public Sub WriteTIC()

```

```

    Dim LocalName$, ThresHolder As String
    Dim a%, c As Integer
    c = 1
    a = 1

```

```

    ThresHolder = ThresholdTXT.Text

```

```

    If Right$(OutCD.FileName, 4) = ".txt" Then
        a = Len(OutCD.FileName)
        OutCD.FileName = Left(OutCD.FileName, a - 4)
    End If

```

```

    LocalName = OutCD.FileName + "_MS_" + ThresHolder + ".txt"

```

```

    If Dir(LocalName, vbDirectory) <> "" Then
        a = Len(LocalName)
        LocalName = Left(LocalName, a - 4)
        LocalName = LocalName + "_2" + ".txt"
    End If

```

```

    Open LocalName For Output As #2

```

```

    For c = 1 To (LinesInFile - 13)
        Print #2, MassValues(c, 1); " "; MassValues(c, 2)
    Next

```

```

    Close #2

```

```

End Sub

```

```

Public Sub WritePeakOutput()

```

```

Dim LocalName$, ThresHolder As String
Dim a%, c As Integer
c = 1
a = 1

'tells something about for output files
ThresHolder = ThresholdTXT.Text

'Get just filename to append to clarify output files
If Right$(OutCD.FileName, 4) = ".txt" Then
    a = Len(OutCD.FileName)
    OutCD.FileName = Left(OutCD.FileName, a - 4)
End If

'Output peak EYC
LocalName = OutCD.FileName + "_p_EYC_" + ThresHolder + ".txt"

If Dir(LocalName, vbDirectory) <> "" Then
    a = Len(LocalName)
    LocalName = Left(LocalName, a - 4)
    LocalName = LocalName + "_2" + ".txt"
End If

Open LocalName For Output As #2

For c = 1 To (ScanWidth - 1)
    Print #2, EFCdata(c, 0); " "; EFCdata(c, 1)
Next

Close #2
c = 1

'Output peak high mass EYC
LocalName = OutCD.FileName + "_p_highEYC_" + ThresHolder + ".txt"

If Dir(LocalName, vbDirectory) <> "" Then
    a = Len(LocalName)
    LocalName = Left(LocalName, a - 4)
    LocalName = LocalName + "_2" + ".txt"
End If

Open LocalName For Output As #2

For c = 1 To (ScanWidth - 1)
    Print #2, EFCdata(c, 0); " "; EFCdata(c, 2)
Next

```

```
Close #2
```

```
c = 1
```

```
'Output Total EYC
```

```
LocalName = OutCD.FileName + "_t_EYC.txt"
```

```
If Dir(LocalName, vbDirectory) <> "" Then
```

```
    a = Len(LocalName)
```

```
    LocalName = Left(LocalName, a - 4)
```

```
    LocalName = LocalName + "_2" + ".txt"
```

```
End If
```

```
Open LocalName For Output As #2
```

```
For c = 1 To (ScanWidth - 1)
```

```
    Print #2, EFCdata(c, 0); " "; EFCdata(c, 3)
```

```
Next
```

```
Close #2
```

```
c = 1
```

```
'Output Total High EYC
```

```
LocalName = OutCD.FileName + "_t_highEYC.txt"
```

```
If Dir(LocalName, vbDirectory) <> "" Then
```

```
    a = Len(LocalName)
```

```
    LocalName = Left(LocalName, a - 4)
```

```
    LocalName = LocalName + "_2" + ".txt"
```

```
End If
```

```
Open LocalName For Output As #2
```

```
For c = 1 To (ScanWidth - 1)
```

```
    Print #2, EFCdata(c, 0); " "; EFCdata(c, 4)
```

```
Next
```

```
Close #2
```

```
End Sub
```

```
Public Sub PeakTable()
```

```
Dim LocalName$, ThresHolder As String
```

```
Dim a%, b As Integer, c As Integer
```

```
c = 1
```

```

a = 1
b = 1

'tells something about for output files
ThresHolder = ThresholdTXT.Text

'Get just filename to append to clarify output files
If Right$(OutCD.FileName, 4) = ".txt" Then
    a = Len(OutCD.FileName)
    OutCD.FileName = Left(OutCD.FileName, a - 4)
End If

'Output peak table
LocalName = OutCD.FileName + "_peaktable_" + ThresHolder + ".txt"

If Dir(LocalName, vbDirectory) <> "" Then
    a = Len(LocalName)
    LocalName = Left(LocalName, a - 4)
    LocalName = LocalName + "_2" + ".txt"
End If

'Correct relative intensity values
For b = 1 To Spotter
    EnergyPeakMax(b, 2) = (EnergyPeakMax(b, 1) / MostIntensePeak) * 100
Next

'open output file
Open LocalName For Output As #2

'Print header line for data labels
Print #2, "m/z Intensity(I) %RI Emax EaveMax3 EaveMax5"

For c = 1 To Spotter
    Print #2, EnergyPeakMax(c, 0); " "; EnergyPeakMax(c, 1); " "; EnergyPeakMax(c,
2); " "; EnergyPeakMax(c, 3); " "; EnergyPeakMax(c, 4); " "; EnergyPeakMax(c, 5)
Next

Close #2
End Sub

Public Sub ClearArray()
    Dim c As Integer
    For c = 1 To (ScanWidth - 1)
        FinalValues(c, 2) = 0
    Next
End Sub

```