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The ultraviolet photoelectron spectroscopy of Group IV 2–15 atom cluster anions

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Rice University, 1989
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THE ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

OF GROUP IV 2-15 ATOM

CLUSTER ANIONS

by

MARY JO CRAYCRAFT

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ABSTRACT

Ultraviolet Photoelectron Spectroscopy
of Group IV 2-15 Atom
Cluster Anions

Mary Jo Craycraft

The ability to map valence electronic structure is the result of a recent advance in photoelectron spectroscopy; its union with cluster molecular beam technology. The task of interpreting the spectra is hampered by a serious lack of understanding of cluster electronic structure in general. Recently progress has been made in finding models for single s valence electron systems. Alkali and noble metal clusters can be treated as free electron systems and simple interatomic potentials can be used with rare gas clusters. Neither a smeared jellium background nor a simple interatomic potential is adequate to describe covalent bonding, however. The isoelectronic Group IV members have a valence configuration of ns²np². All readily form clusters, and the elements differ in both their atomic and bulk properties; thus the series provides an ideal system for studying electronic structure.

The mass selected cluster ion beam is crossed with a UV beam (6.42 or 7.9eV) and the resulting photodetached electrons collected
with the aid of judiciously arranged magnetic fields. The spectra are found to be unique for each size cluster. Some spectra show a significant gap between the two lowest binding energy features, indicating that the neutral cluster is a closed shell species. The clusters with such gaps are minima in a plot of EA as a function of cluster size.

The UPS also vary with the cluster composition. Carbon is unique; an even-odd alternation in electron affinities switches from odd minima for clusters containing less than ten atoms to odd maxima for larger clusters. This corresponds with an alternation in singlet and triplet ground states and a switch from chain to ring structures previously predicted by theory (K.S. Pitzer E. Clementi, J. Amer. Chem. Soc. 81 4477 (1958) and R. Hoffmann, Tetrahedron 22 521 (1965)).

The spectra of the remaining group IV members are remarkably similar to each other for clusters of up to ten atoms, as is the trend in the electron affinities as a function of cluster size. This similarity in electronic structure may imply similarity in geometries. At ten, Si and Ge behavior diverges from that of Sn and Pb.
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Most of all I would like to express my love and appreciation for my family; I simply could not have achieved this without their love and support.
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CHAPTER I.

INTRODUCTION
1.1. INTRODUCTION TO CLUSTERS

Links between the microscopic and macroscopic world are the means by which scientists gain insight to the mechanisms and significance of natural phenomena. Clusters are such a link. Aggregates of atoms of homogeneous or heterogeneous composition, clusters afford the unique opportunity to study various parameters as a function of cluster size. The evolution of bulk properties can thus be observed step by step. Small clusters are within the realm of theoretical calculations, and so readily allow direct comparison of ab initio results with experimental data. Larger clusters provide a foundation for theoretical models.

Cluster generation is a subject unto itself, one which is extensively covered in the literature. Various methods of cluster production have been developed, and the field is still being extensively explored and advanced. Once a suitable cluster beam has been formed, a multitude of prospects exist for its study. The following brief overview of experiments from this lab alone illustrates what a vast field cluster research is.

Comparison of relative intensities in cluster time of arrival mass spectra can impart information as to the relative stabilities of different size clusters, which may imply geometrical and or general electronic structural information. All elements have "magic numbers" to some degree - that is, clusters of a certain number of atoms whose intensity is greater than that of other clusters in the same
size range. This increased occurrence is likely a manifestation of a particularly favorable electronic and/or nuclear geometry. The size of the dominant cluster(s) varies with the cluster composition. An extreme example of the type of information to be rendered from such observations is the discovery of the soccerball-structure for some 60 atom clusters of carbon.\(^2\) This structure was first postulated in an attempt to explain an extraordinarily stable cluster size.

Photodissociation experiments shed further light on structure, as well as revealing reaction dynamics. These experiments involve crossing a cluster ion beam with a laser beam and detecting any resulting charged photodissociation products. The photon energy may be varied and the fluence dependence of the daughter fragments examined in order to determine the dissociation, and therefore binding, energies. Clusters illustrate different mechanisms of dissociation. Metal clusters typically lose one atom at a time upon successive photon absorptions,\(^3\) while clusters of the semi-conductor elements, Si and Ge, break into chunks for \(n > 8.\)\(^4\) Large carbon clusters composed of an even number of atoms lose two atoms at a time (the odd lose 1 first) until the cluster contains 32 atoms. Instead of losing a pair of atoms, the \(\text{C}_{32}\) cluster "explodes" into a number of smaller (10 - 19 atoms) clusters. Those clusters initially less than 32 atoms in size photodissociate via successive losses of three C atoms.\(^5\)

Chemisorption studies on clusters also aid in the elucidation of reaction dynamics. Reactants may be injected into the flow
channels prior to expansion. Often a small reaction chamber will be added to allow more collisions between the clusters and the reactant. The recent reaction studies as a function of cluster size in an ICR, where the reactant is not added until the ICR cell (so the reactivity of the ions is exclusively observed) found reactivity patterns vary with both cluster size and composition, a phenomenon which could perhaps aid in surface characterization.

Adsorption on metal clusters is of particular interest, because of their applicability to the study of catalytic mechanisms. Dramatic dependencies of reactivity on cluster size have been seen. CO$_2$, for example, reacts with small Nb clusters in an interesting pattern. Detection of the cation products shows that clusters from the single atom up through seven atoms chemisorb CO on their surfaces, while clusters with more than eight atoms (at least up through the teens) chemisorb CO$_2$. Semi-conductor reactivity patterns are also very interesting and are currently being studied. Small silicon clusters do react with ammonia in a very size dependent manner.

Obviously, the main features which change with cluster growth are electronic structure and the geometrical orientations of the nuclei. Changes in secondary physical properties can give indirect structural information. Fluctuations of ionization potential with cluster size in some metals have already been correlated with size dependent reactivity; both of which likely parallel an electronic structural trend.
An understanding of how reactivity (which undoubtedly depends on structure) varies with cluster size may lead to a better understanding of catalysis and/or surface physics and chemistry. New periodic trends found in an investigation of the elements should increase our fundamental chemical knowledge. Study of the evolution of metallic and semi-conductor band structure clearly requires a means of probing electronic structure. An understanding of cluster electronic structure, therefore, should lead to an increased understanding of the world, the universe and everything.

Atomic valence electronic structure will determine the nuclear geometry for small clusters and this geometry will in turn have a fixed molecular electronic structure. It is this "fingerprint" which we attempt to take a picture of with photoelectron spectroscopy. The width of the view depends on the energy of the photons used to photodetach the electrons; the more energetic, the more deeply the electronic structure can be probed. More information has already been obtained with photons < 8eV than can be interpreted by the current level of theory. With the development of suitable UV lasers, the entire valence region could be explicitly mapped out. The effects of adsorbates on electronic structure and the development of band structure could be studied in intimate detail. Cluster electronic structural information from UPS has been awaited by the cluster theoretical community and should prove invaluable in evaluating calculations.\textsuperscript{84,76c}
1.2. INTRODUCTION TO PHOTOELECTRON SPECTROSCOPY

Photoelectron spectroscopy, PES, basically consists of exposing an atom or molecule to electromagnetic radiation and determining the energy of any ejected electrons, in order to calculate the energy with which they were bound. Conservation of energy requires that any input energy not used up in the actual ejection process be either in the ion or in the electron. Conservation of momentum requires that most of the excess translational energy end up in the electron. Measurement of the electron kinetic energy therefore reveals how much energy it took to eject that electron, its ionization energy, leaving the ion in a particular excited state. Because these transitions are usually not adiabatic, that is they are not generally between entities in their ground vibrational states, they are governed by the Franck Condon principle.

This principle is based on the assumption that an electronic transition occurs so rapidly that the nuclei remain in the same position while it happens, and then readjust to the new excited state equilibrium geometry. The transition takes place to the excited state vibrational level with the greatest probability density at the unexcited equilibrium bondlength. Because this type of transition can be represented as a vertical line on a potential energy diagram including both states, it is known as a vertical transition. Ionization of a neutral will occur most frequently as a vertical
transition, thus the vertical ionization energy is what is usually measured.

Another useful approximation in PES is known as Koopman's theorem. This involves using the ground state wavefunctions to describe the excited state orbitals for calculating ionization potentials. This implies that only a single electron interacts with the light, and that the other electrons are unaffected by its absence. This approximation neglects the relaxation energies, which are on the order of 1-3 eV for valence electrons, and 10-50 eV for core electrons. It is useful, however, especially for relative purposes, to approximate the binding energy of an electron as the energy it takes to remove it. The negative ion photodetachment energy is thus approximately equivalent to the electron affinity.

Obviously more energetic photons can eject more tightly bound electrons. Typical valence electron binding energies are such that ultra-violet light is necessary to remove them, in which case the PES is referred to as UPS, while the deeper core electrons require vacuum U.V. or X-rays (XPS). A photoelectron spectrum can show electrons ejected from all orbitals with binding energy less than that of the input photon energy (assuming collection of even the lowest kinetic energy electrons). Thus the ionization potentials for more than just the outermost electrons can be determined.

The nature of a bonding orbital can also be determined from photoelectron spectra. The more involved in bonding an electron, the
more disruption its removal will cause. This will show up as vibrational structure in the spectrum.

Other processes besides a simple one-electron ejection process can occur. If an inner electron is removed, a hole is created into which an outer electron can "fall in". The excess energy, that is the difference between the energy levels, is fluoresced, usually as an X-ray photon. Analysis of the X-ray fluorescence yields energy level information. This excess energy may also eject an electron with a lower binding energy. This is known as the Auger process, and the ejected electron called an Auger electron. Auger spectroscopy also yields electronic structure information.

ESCA, electron spectroscopy for chemical analysis, is a branch of PES. The innermost electron binding energies of an element are characteristic of it, thus the peaks in an X-ray photoelectron spectrum can be used to determine unknown atomic compositions. Moon rocks were analyzed in this manner (and found to contain Mg, Al, Si, C, K, Ca, Ti, Na and O). Bond formation causes a slight shift in energy, and so shifts the electron peak in the photoelectron spectra. Inequivalent but similar atoms can therefore be distinguished. \(^{13}\)

Photoemission is also related to PES. It involves the study of electron ejection from bulk surfaces. The amount of energy necessary to remove an electron from the bulk is termed the work function.

PES of negative ions is common. Ions are easily manipulated; their charge yields a handle with which to steer, focus, separate, and detect them, and it takes less energy to remove the "extra"
electron, so photon sources in the required energy range are more readily available than those necessary for ionizing neutrals. Detachment of the extra electron yields the electron affinity of the neutral, while ejection of more tightly bound electrons yield their ionization potentials. Photodetachment spectroscopy involves scanning the frequency of the incident photons to determine the energy necessary to detach the extra electron.

The PES technique has had many founding fathers. The photoelectric effect was one of the breakdowns in classical mechanics which prompted the emergence of quantum mechanics. The history of photoelectron spectroscopy is intimately entwined with that of both modern physics and chemistry. In 1900, M. Plank was able to explain blackbody radiation by requiring radiated energy to be quantized. P. Lenard, in 1902, observed that the number of electrons emitted from a metal surface by shining light on it was dependent on the color of the light, and that if a given color did not cause photo-ejection of electrons, it would not do so no matter how intense the light source was. Einstein accounted for this classically unexplainable effect in 1905, when he proposed that not only is light radiated with quantized energy, but it is also absorbed as such. He expressed the relationship between the photo-ejected electrons and the energy of the incident photons as

\[ \frac{1}{2}mv^2 = hn - W \]

where \( m \) = electron mass \( h \) = Planck's constant
\[ v = \text{electron velocity} \quad W = \text{work function of the metal} \quad n = \text{frequency of incident radiation} \]

which R. Millikan verified in 1916 by performing photo-emission experiments, measuring the kinetic energy of electrons ejected from different metals.\textsuperscript{14}

During the 1920's, H. Robinson used photographic film to record the photoelectron spectrum of gold, and established the correlation between the electron peaks and atomic structure.\textsuperscript{15}

PES was extended to ions in the 1950's, when it was realized that removal of the extra electron from the ion is roughly equivalent to the electron affinity of the neutral.

Detecting photodetached electrons via current measurements allowed experiments to be performed under vacuum. Mass selected ion beams were crossed with a filtered light beam from a C arc, a very intense source of light. Beam modulation and phase sensitive detection techniques were utilized to subtract the background. The electron affinities of \textsuperscript{1}H, \textsuperscript{1}O, \textsuperscript{12}C and \textsuperscript{34}S were determined by Branscomb and colleagues by this method, as well as those of \textsuperscript{1}OH and \textsuperscript{1}O\textsubscript{2}.\textsuperscript{16}

The molecular beams in these and similar experiments were typically formed from a discharge type source. The thermal motion of the parent in the molecular beam was the major resolution limiting factor of this period. Other significant linebroadeners were due to the light source, i.e. natural linwidth, pressure, Doppler and Stark broadening.\textsuperscript{17}
The laser was incorporated into PES experiments soon after its development. An Ar ion laser was used to obtain the photoelectron spectrum of NO\(^{-}\) in 1971.\(^{18}\)

The inclusion of supersonic expansion techniques in molecular beam generation in the 1970's led to the development of sources of cold unsupported clusters.\(^{19}\) PES has been done on clusters deposited on various substrates, but deposition is structured on metals, and deposition on amorphous carbon does not allow for mass selection.\(^{20}\) Dehmer and Dehmer coupled a supersonically expanded beam of Xe clusters to a PESpectrometer in 1978,\(^ {21}\) and observed the anticipated improvement in resolution, due to reduction of Doppler and rotational broadening from the parent.

Pollard and coworkers improved Dehmer and Dehmer's apparatus design in 1981. They reduced the background signal by improving the vacuum, reducing the pressure in the electron detachment region to 3 x 10\(^{-9}\) torr, designing detection electronics incorporating multichannel detection (first used in valence PES by Siegbahn\(^ {22}\)), extensively sheathed their ionization and electron collection region with mu-metal, and designed an electron collector involving a hemispherical electron energy analyzer. A quadruple mass spectrometer characterized the beam. Supersonic molecular beams of N\(_2\) and of ethylene were probed with the HeI line. The system was tested with a pulsed excimer laser, operating on both ArF and KrF, but problems arose due to the narrow range of arrival times of the electrons (\(Vt < 1\) usec).\(^ {23}\)
In pursuit of increased collection efficiency, various electrostatic and magnetic field configurations have been used to guide photoejected electrons to a detector. K. Siegbahn and associates used a rotationally symmetric, inhomogeneous \((r^{-2})\) dependent) magnetic field to collect electrons. The electrons enter the central portion of the radial spectrometer, where the magnetic field is greatest, and develop helical trajectories about the radial magnetic field lines. The asymmetry of the field causes the electron helical trajectories to drift outward. This results in the electrons spiraling out from the center, thus extending the actual flightpath immensely. Their 0.3m overall diameter analyzer corresponds to a flight path of about 700m.\(^{24}\)

The magnetic field geometry used in the design of our spectrometer was initially conceived of by Beamson, Porter and Turner. In 1977, they utilized an axially symmetric homogeneous magnetic field to collect electrons. Their PES experiments were performed in an ICR cell, where electrons photoejected from neutrals could move only along the axis of the magnetic field, and therefore were readily collected and analyzed following retardation and deflection by perpendicular electric fields.\(^{25}\) These experiments lead them to propose a photoelectron spectrometer design incorporating an axially symmetric inhomogeneous magnetic field, one where the flux lines either converge or diverge along the field axis. The effect of the magnetic field on the electron will be discussed in greater depth in chapter II. Basically the electron develops a
helical trajectory which encloses the same amount of magnetic field flux at all times. Since the electrons spiral along their own trajectories along parallel field lines, their initial spatial arrangement is preserved, but magnified due to the spreading out in the region of lower magnetic field. This lead Beamson et.al. to the development of photoelectron spectromicroscopy in 1981.26

Another spectrometer based upon the same principles as that designed by Beamson et. al. was developed by Kruit and Read in 1982, for use in multiphoton ionization experiments with rare gases.27

The field of PES is now so broad that it is beyond the scope of this paper to follow the multitude of developments. Pertinent recent studies will be mentioned in the text where relevant.

This thesis presents the details of our photoelectron spectrometer which incorporates an axially symmetric, inhomogeneous magnetic field design, built onto a previously existing supersonically cooled cluster ion beam apparatus. Electrons from negative cluster ions of the desired mass are photodetached with ultraviolet light, and collected with the aid of judiciously arranged magnetic fields. Pulsed operation allows the use of time of flight techniques on both the parent ions and the photoelectrons. The use of UV grants access to the details of valence electronic structure. This apparatus has been used to collect the UV photoelectron spectra (UPS) of Group IV cluster anions containing 2 - 15 atoms. Various trends with cluster size and composition have been discovered and are discussed.
CHAPTER II.

APPARATUS
2.1. CLUSTER SOURCE

A one inch diameter disc (FIG.1 (2)) of the material to be studied is placed in the path of a focused Nd-YAG pulsed laser beam (1). The disc is both rotated and translated through the beam path such that fresh surface is continually exposed to the one mm. diameter 532 nm beam (10-15 mj). This disc source is of similar design to that of O'Brien et.al..30 Vaporization of the disc surface creates a dense plasma, which is swept down the channel by a pulse of He (200 psi backing pressure). Clustering and charge exchange collisions occur in transit, as well as cooling collisions with the He carrier gas. Mass analysis of window deposits indicate $10^{10}$ to $10^{12}$ clusters are produced per cycle. Current measurements (Cary 401 vibrating reed electrometer) show that ions of each charge are present in quantities of $10^3 - 10^5$.

Supersonic expansion from the 2mm channel into the main chamber cools the clusters even further. A 55 degree internal angle, lcm. aperature skimmer (Beam Dynamics) (3) then allows only the central portion of the forward expansion to pass through into the next, "A", chamber, thus forming a molecular beam, which is skimmed once again (4) while passing into the ion extraction, B, chamber. This cluster seeded beam is moving at the terminal velocity of He:
FIGURE 1. Schematic of overall apparatus.
1. vaporization laser beam  2. target  3,4. molecular beam skimmers  
5. extraction electrodes  6. cluster ionizing laser beam  7,12. horizontal  
deflectors  8,13. vertical deflectors  
9,10. einzel lenses  11. N₂(1) dewar  14. mass gate  15. decelerator  
16. solenoid mount  17. light skimmer  18. detachment laser  19. photo-electron  
flight tube
(3) \[ u_c = \left( \frac{2T_0C_p}{\text{MW}} \right)^{1/2} \]

where

- \( T_0 \): stagnation temperature (He prior to expansion)
- \( C_p \): heat capacity
- \( \text{MW} \): molecular weight

Room temperature He (298K) has a terminal velocity of 0.1759 cm usec\(^{-1}\), while 400K He achieves 0.2039 cm usec\(^{-1}\). An on-axis excimer beam (6) can ionize the He in order to detect its time of arrival. Monitoring the ionized carrier gas also allows overlapping of the vaporization laser firing time with the peak of the He pulse. Cluster formation in the peak of the He pulse provides the opportunity for more collisions with the carrier gas, in order to achieve maximum cooling of the clusters. The clusters arrive at about the same time as the He, an indication that they are efficiently cooled by this procedure.

2.2. CHARGE AND MASS SELECTION

The negatively charged cluster ions are separated from the positively charged and neutral clusters by extraction with a Wiley-McLaren two stage pulsed accelerator\(^3\) (Fig.1,(5)) into a perpendicular flight tube. A set of horizontal (7) and vertical (8) deflectors correct non-axial velocity components and two einzellenses (9,10) refocus the beam as it traverses the flight-tube. An
additional set of deflectors (12,13) just prior to the electron chamber enables maximization of the overlap of the UV laser beam with the ion beam. Time of flight separation enables pulsed mass gating techniques.

The mass gate (Fig.1 and 2,(14)) consists of three plates, the outer two grounded. The central plate maintains a repulsive potential, i.e. 1 KV for 1KV extracted ions, until the clusters of the desired mass approach, at which time it is pulsed to ground for just long enough to let them through, typically 1.5 usec. The decelerator (15) is a fourth plate on the mass gate stack, with a 1.5" long, 1" diameter tube attached. The deceleration voltage (typically 850 V for 900 - 1KeV ions ) is on while the ions pass through the decelerating field, and then pulsed to ground once all the ions have entered the tube, but before any leave it. Timing the pulse to ground in such a manner prevents reacceleration of the ions and eliminates the need to maintain high potentials in the electron chamber. The necessity of deceleration shall be discussed in the resolution section.

An inline detector (two microchannel plates in series) at the end of the cluster ion flight path generates time of flight mass spectra and aids in optimization of the various voltages and pulse timings. The pulse timings are triggered through a CAMAC crate timing generator (Kinetic Systems, 3655) and nanosecond delay generator (Lecroy, 4222) under computer (IBM-AT) control.
2.3 ELECTRON DETACHMENT

The beam of mass-selected negatively charged clusters is crossed with a pulsed UV laser beam (Fig.1 and 2 (18)), either the ArF, 193nm (6.42eV), or F₂, 157nm (7.9eV), line from an excimer (Lumonix TE-861 with EASM-1 electrodes) laser. This is the first anion cluster beam photoelectron spectrometer capable of handling such energetic photons. Since most valence electron binding energies are in the few eV range, the feasibility of thorough bonding electron studies and the study of band structure development with increasing cluster size will rely on the ability to detach electrons with photons in the ultraviolet range.

Extensive modifications were required to accommodate the use of UV light. The work functions of the construction materials of the chamber and most of its contents are lower than the energy of the photons used in the experiments, so reflections readily generate secondary electrons. Special precautions must therefore be taken to minimize scattered light. Sharp edged baffles along the laser beam path define the beam (17), skimming off the outer edges of the Gaussian beam profile. Successive baffles reduce admittance of light diffracted from the rim of the previous. Strategically placed shielding assures that the unavoidable diffuse scattered light could not reenter the detachment zone. UV grade fused silica light entrance and exit ports are angled (15 degrees) to reduce the reflections from their surfaces and carefully positioned light
deflectors re-direct the primary reflections from the window surfaces. Since the 157nm. line is absorbed by O₂, a N₂ purged tube is placed between the front optic of the excimer laser and the entrance port to the chamber.

The diffusion pump on the electron chamber was replaced with a cryopump (CTI CRYOTORR 8) to eliminate pump oil vapor and achieve as high vacuum as possible. Background pressure in the 10⁻¹⁰ torr range reduces the general background available for U.V. ionization. A turbomolecular pumped (Balzer’s, 170 l/s) pre-electron chamber with a liquid nitrogen cryotrap was incorporated into the flight tube, for cleaning the cryostat and to reduce the conductance from the preceding lower vacuum regions of the apparatus. Conductance limiters, cylinders with 2" long, 1.5" diameter aperatures, were placed in the flight tube to further aid in background reduction.

The entire stainless steel chamber, electron flight tube and almost all chamber components were electropolished and mechanically polished to a mirror surface. Everything was scrupulously cleaned with spectroscopic grade solvents prior to and after assembly. Ultrahigh vacuum compatible materials were used whenever possible in construction of the chamber components, and particular care was paid to keep the chamber contents to a minimum. A special protuberance into the E chamber (16) was designed to enable external mounting of the solenoid, to enable its removal when baking the chamber and to retain the spacious design and high vacuum compatibility of the
interior. A closeup of the extraction region is shown in the following Figure 2.
FIGURE 2. Schematic of extraction chamber.
14. mass gate 15. decelerator 16. solenoid mount 17. light skimmer
18. detachment laser 19. photo-electron flight tube
20. flight tube solenoid 21. inline detector
2.4. ELECTRON COLLECTION: THE MAGNETIC TIME OF FLIGHT PHOTOELECTRON SPECTROMETER (MTOPPES)

2.41. INTRODUCTION

Photodetachment of the electrons in the strong field end of an axially symmetric inhomogeneous magnetic field results in parallelization of the electron trajectories as they follow the diverging field lines to the detector in the weaker end of the field. The strongest part of the field is behind the detachment zone, in order to turn around electrons ejected away from the electron flight tube. This allows collection of all electrons ejected over almost 4π sr. The magnetic fields are arranged in such a manner as to steer most of the secondary electrons away from the collection area. The magnetic field geometry is generated by the superposition of the fields from two solenoids. A computer program has been written to plot the field lines and simulate their effects on the electron time of flight.
2.42. THE MAGNETIC FIELDS

2.421. THE MAGNETS

A large ratio of magnetic fields is necessary to parallelize the electron trajectories, so the flight tube solenoid magnetic field should be quite small, but it must be high enough that the radius of the electron helical trajectories is not too large. This will be discussed in more detail in the electron trajectories section. What is important for the discussion of the magnetic fields is that the initial magnetic field must be strong and fall off rapidly, while the magnetic field in the flight tube should be relatively weak.

The high magnetic field in the region of the detachment zone is generated by a pulsed solenoid external to the chamber. This solenoid slides into a flange-mounted nipple, which extends into the UPS chamber. The external mounting aids in keeping the chamber as empty as possible, to avoid light and electron scattering, and to maintain a high vacuum. The extension stops just before the center of the chamber, where the molecular and cluster ion beams cross. This enables placing the region of highest magnetic field density 15 mm behind the detachment zone. A 1 cm radius hole, the "dimple", in the mount (see fig. 2) decreases the surface exposed to the light near the critical region. In addition, the configuration of the magnetic field lines through the dimple is such that most electrons
ejected in the -z direction can be reflected by the field and collected, instead of being scattered.

This solenoid itself is composed of 18 layers, 18 turns each, of 24 gauge magnet wire. The coil is wrapped around a water cooled copper core, and embedded in Al epoxy for rapid heat dissipation. The pulsed mode of operation keeps the heat buildup to a minimum. The overall measured resistance is 2.5 ohms and the current through it from five 12V batteries is measured to be 24 amps.

The lower magnetic field solenoid is wrapped on a 15.24cm (6") inner diameter PVC pipe, which slides over the 10.16cm (4") diameter, 2.4m long, electron extraction flight tube. It has a density of 11 turns per cm. (28 turns per inch). The optimal magnetic field for electrons collection corresponds to a current of 125 mA, generated by a D.C. power supply. A 25.4cm (10") i.d. mu metal wrapped (inside and out) PVC pipe slides over the flight tube solenoid encasing the flight tube. Mu metal is a ferromagnetic material with a very high permeability, which draws the magnetic field lines into it. A long (length at least four times the radius) cylinder or sphere made of mu metal greatly attenuates the external field seen by the interior. Penetration of external fields through the cylinder ends is inversely proportional to the diameter of the opening, so the shielding is extended past the detector to insure that the field lines in the electron flight tube are determined solely by the solenoids. This concentric PVC pipe arrangement facilitates removal of the solenoid and direct wrapping of the flight tube with heating tapes for baking.
Care is taken to avoid placement of magnetic materials near the E chamber, to preserve the distribution of the applied magnetic field lines.

2.422. THE MAGNETIC FIELDS

The magnetic field can be calculated via the integrated Biot-Savart equation:

\[ B = \frac{u_0 I}{4\pi} \frac{dl \times \mathbf{r}}{r^2} \]

where \[ u_0 = 4\pi \times 10^{-7} \text{ N/A}^2 \]
\[ I = \text{applied current} \]

For a thin coil along the field axis this becomes:

\[ B_z = \frac{u_0 n I R^2}{2 (R^2 + z^2)^{3/2}} \]

where \[ n = \text{total number of coils} \]
\[ R = \text{magnet radius} \]
\[ z = \text{distance from magnet center} \]

The field in the dimple (\[ z \rightarrow 0 \]) is very large, 5000-6000 gauss, but falls off rapidly. At the detachment zone, \[ z = 15 \text{ mm} \], the field has decreased by about an order of magnitude, to a value of
approximately 600 gauss. This field is pulsed on 2.7ms prior to the arrival of the ion packet in the detachment zone, to assure that the field has achieved its maximum constant value by the time the electrons are photoejected. The long rise time of the pulse is due to the large inductance (about 2mH) of the coil. The pulse remains on for a total of 3ms, in order that all detached electrons have passed into the flight tube before the magnetic field is turned off.

The presence of the magnetic field is felt by the ions entering the chamber, imparting a radial component to their trajectories (the behavior of charged particles in magnetic fields will be discussed at length in the following section). The radius of this motion is on the order of tens of centimeters, and can be compensated for by redirecting the ion beam slightly via adjustment of the voltages on the second set of deflectors in the ion flight tube.

For the field on the axis of an infinitely long coil (i.e. a solenoid where the length is much greater than the radius), the magnetic field is independent of the solenoid radius and the previous equation reduces to:

\[
B_z = u_0nI
\]

where the previous definitions apply. The magnetic field of the flight tube solenoid calculated in this manner is 1.7 gauss.

The off axis field is much more complicated to calculate, since the radial magnetic field components must be taken into
consideration. A computer program\textsuperscript{85} has been written to calculate the magnetic field at any region in our MTOFPES. The field is initially calculated for a unit coil, via explicit calculation of the Biot-Savart law, equ.\((4)\), for a grid of points. This time consuming step need only be performed once and then stored. The magnetic fields due to various solenoid configurations can then be calculated by scaling the field from the unit coil appropriately. The program also follows the electron trajectories and simulates the time of arrival spectra.

A computer simulation of the magnetic field in the extraction region due to the superposition of the fields from both solenoids, under the previously mentioned parameter values, is shown in Figure 3.
FIGURE 3. Magnetic field geometry in the electron detachment (E) chamber used to collect the photodetached electrons. The cross-hatched rectangle represents the location of the external pulsed solenoid. The detachment zone is indicated by an arrow on the x axis.
2.43. ELECTRON TRAJECTORIES

An electron, or any charged particle, in an electric or magnetic field experiences a force given by the Lorentz force equation:

\[ F = q \left( E + (v \times B) \right) \]

where
- \( F \) = force
- \( E \) = electric field
- \( B \) = magnetic field
- \( q \) = charge
- \( v \) = velocity

Assuming that the efforts to avoid patch potentials and stray fields were successful, \( E \) is zero, or is at least negligible. Thus, the electron is subject only to a force from the magnetic field:

\[ E/q = v \times B \]

If we choose the axial symmetry axis of the electron flight tube to be the \( z \) axis, and \( x \) and \( y \) to be the other two axes of a Cartesian coordinate system, the force on the electron can be broken up into its component forces:
(9) \[ \mathbf{F} = F_x + F_y + F_z \]

\[ \mathbf{F} = (v_y B_z - v_z B_y) \mathbf{x} + (v_z B_x - v_x B_z) \mathbf{y} + (v_x B_y - v_y B_x) \mathbf{z} \]

In the case of a uniform magnetic field this reduces to:

\[ \mathbf{F} = v_y B_z \mathbf{x} + v_x B_x \mathbf{y} \]

These forces in the x and y directions alone result in a radial force, which will cause the electron to move in a circular orbit perpendicular to the magnetic field. From Newton's second law and the following definitions of acceleration and mass, the radius of the orbit can be found:

(10) \[ |r| = \frac{(mv)}{(qB)} \]

\[ v = (v_x^2 + v_y^2)^{1/2} \]

\( m \) - particle mass

acceleration; \( a = \frac{v^2}{r} \)

The angular frequency of this orbital motion is called the cyclotron frequency, and is given by:

(11) \[ \omega_c = \frac{v}{r} = \frac{qB}{m} \]

The net force in the z direction in a homogeneous field is zero, the velocity in the z direction determined solely by the
velocity with which it entered the field. An electron trajectory in an homogeneous field, therefore, is a helix of constant radius. An inhomogeneous magnetic field, such as that in our detachment zone, shown in Figure 4, contributes an acceleration in the z direction. Superimposed upon the radial motion is the resulting translational motion in the z direction due to the additional force from the radial component of the magnetic field:

\[
|B_r| = \left( B_x^2 + B_y^2 \right)^{1/2}
\]

This force pushes the electron along the magnetic field axis, toward the lower field, resulting in a helical trajectory with a gradually increasing radius.
FIGURE 4. Components of the magnetic field in the detachment region.
A useful concept in discussions of slowly varying fields is that of adiabatic invariance. The assumption of adiabaticity allows many simple calculations which would otherwise be very complex. As explained in Jackson, an action integral, $J_1$, may be defined as

$$J_1 = \oint p_1 \, dq_1$$

where the integration is over a complete cycle of a general coordinate of periodic motion, $q_1$, and $p_1$ is the momentum along that coordinate. The basic idea is that if a property of a system in a particular state of periodic motion is changed adiabatically, the state of motion of the new system will be such that the action integrals retain their initial values. An adiabatic change requires that the property be changed slowly with respect to the relevant change in motion, and the changing property not be related to the period of that motion. Properties represented by the action integral therefore are constants of the motion, and are referred to as adiabatic invariants.

The orbital motion of an electron in a homogeneous magnetic field is periodic. If the change in field strength in a varying magnetic field is gradual enough that it appears constant to the electron during any given revolution of its helical orbit, the field may be considered to be changing adiabatically. The action integral over the particle's orbit for an adiabatically changing magnetic field results in:
\[(14) \quad J = q(Br^2)\]

The quantity in parenthesis is the magnetic flux through the particle's orbit. Due to the inverse proportionality between the cyclotron radius and the magnetic field shown in equation (10), a decline in the energy of the cyclotron motion increases the radius of gyration. A consequence of the adiabatic invariance of the flux is that if the field strength changes adiabatically, the cyclotron radius will adjust to always encompass the same number of field lines, i.e. to retain a constant magnetic flux through the orbit. Thus, in an adiabatically changing magnetic field the electron trajectories are parallelized as the electrons enter the lower field. As the field decreases, conservation of angular momentum, \(L\),

\[(15) \quad L = \left( \frac{2mE_{\text{cyclotron}}}{qB} \right)\]

requires the energy in the cyclotron motion to decrease with the magnetic field. Conservation of energy,

\[(16) \quad E_{\text{total}} = E_{\text{cyclotron}} + E_z\]

then requires that the decrease in cyclotron energy be accompanied by a corresponding increase in the energy of the motion along the magnetic field axis. Photo-ejected electrons initially going the
"wrong way" will move into regions of increasingly higher magnetic field. The magnetic force will decrease the energy of axial translation, thus increasing the energy of cyclotron motion. This will continue until all of the electron kinetic energy is in the cyclotron motion, at which point the electron is reflected. This is known as the magnetic mirror effect and is the principle upon which magnetic bottles for plasma containment are based; charged particles are trapped in magnetic fields which are strong at the ends and weak in the middle so that they oscillate back and forth, reflecting off alternate ends.

If adiabaticity is assumed, the condition for reflection is that the tangent of the angle from the $z$ axis that the electron is ejected along be less than the square root of the ratio of the high field to the lower field, minus 1. The ratio of the perpendicular velocity to the parallel is the tangent of that angle, therefore reflection will occur when:

$$
\left| \frac{v_{0//}}{v_{0+}} \right| < \left( \frac{B_{\text{max}}}{B_0} - 1 \right)^{1/2}
$$

(17)

where $B_0$ = initial magnetic field

$B_{\text{max}}$ = maximum magnetic field

$v_{0//}$ = initial velocity parallel to $B$

$v_{0+}$ = initial velocity perpendicular to $B$
Some electrons emitted directly in the backwards ($z < 0$) direction will have such a large parallel velocity component that they will not be reflected by the magnetic field. Equation (17) gives a 35 degree cone of loss. This is only 2.2% of the 4 pi sr the electrons could possibly be emitted over, thus the calculated collection efficiency of this MTOFFES, for isotropically ejected electrons under the currently employed parameters, is 97.8%.

As mentioned in the magnetic field discussion, a computer program has been written to simulate the electron time of flight. The routine which calculates the trajectories begins with the magnetic field results and the three coordinates of position of the electron and the associated momenta in the lab frame. The Lorentz forces are calculated and used to obtain the acceleration in each direction. In order to decrease the step size necessary to follow the trajectories, a reference frame with more slowly varying coordinates has been created. The reference frame is centered on the axis of the cyclotron orbit. The axial direction will be the same at any point as that of the total magnetic field at that point. The cyclotron radius specifies another direction, and the third can be represented by the cross product of the other two. The reference frame can thus be defined by $B$, $E_C$, and $B \times E_C$, where the cyclotron radius is given by:

\[
E_C = \frac{1}{|I|} \frac{v \times B}{|v \times B|}
\]
The position coordinates, velocities and accelerations are transformed into this reference frame. The velocity and position are incremented by a very tiny time step, the new values transformed back to the lab frame for storage, and the loop repeated. The time of flight spectra is generated by weighting the time of arrival of an electron by the relative number of electrons ejected at the same angle to the magnetic field axis.

The program includes an optional subroutine which treats the motion adiabatically. Time of flight simulations calculated with and without assuming adiabaticity compare favorably with each other.

Figure 5 shows a computer simulated electron time of arrival plot of electrons ejected from Cu⁺ with 2.33eV photons (Nd-YAG 2nd harmonic). The electron affinity of the copper atom is 1.227 eV.

2.5. ELECTRON DETECTION

The detector at the end of the electron flight tube consists of three microchannel plates (Galileo Electro-Optics). Microchannel plates are made from millions of glass fibers which have been coated internally with a photo-sensitive material. The parallel fibers are drawn out to where the fiber i.d. is 10 - 100 microns and .5 mm plates are sliced off at a slight (8 degree) angle. The front and back surfaces are metal coated to provide electrical contact. These surfaces then act as electrodes for $10^4$ - $10^7$ electron multipliers.
FIGURE 5. Comparison of computer simulated and experimentally obtained electron time of flight.
a) Undecelerated parent ion (900eV) b) Parent decelerated to 250 eV c) Parent 20eV.
Each plate has a gain of $10^3 - 10^4$. Microchannel plates are often used in imaging techniques, since the numerous parallel channels preserve the position of the initial electrons. The use of three such plates in series grants us detector sensitivity of less than one electron per average event.

2.6 SIGNAL PROCESSING AND BACKGROUND SIGNAL

The signal from the detector is put through two Comlinear 10x preamplifiers for a 100x amplification and is then digitized (Transiac 2001). Each of 1024 bins stores 10 ns of information. The discriminator level is set such that an electron count is above the baseline, but most noise is not.

A complete electron time of arrival spectrum is recorded ten times per second (the entire experiment is performed at 10 Hz). The ion extraction stack is pulsed during every other experimental cycle, to provide a constant monitor of the background signal. The no-ion background can be subtracted from the ion present data, assuring that the spectrum is entirely due to the cluster under study. This background is minimal. Careful detachment laser alignment reduces the background contribution to the electron signal to about two electrons per ten electron collection event.

The background level is considerably higher in the absence of the high magnetic field. The rapid divergence of the magnetic field lines shown in Fig. 3 traps the ejected electrons on the interior
field lines and most stray electrons on the outer ones. This carries the appropriate electrons to the detector, and leads the undesirable electrons away from the electron flight tube. With only the flight tube solenoid on, the branching out of the field lines does not occur and most of the electrons generated near the detachment zone make it to the detector.

Accumulation and averaging of the data is usually done for 10,000 cycles (in ion-present mode; 20,000 total experimental cycles). The computer program can transform this intensity as a function of time, I(t), data to intensity as a function of energy, I(E), via:

\[ E = \frac{1}{2} m v^2 \quad v = \frac{1}{t} \]

\[ \frac{dE}{dt} = m v \frac{dv}{dt} \quad \frac{dE}{dt} = -l^2 m/v^3 \quad dt = -dE t^3 / l^2 m \]

\[ \int I(t) \, dt = \int I(E) \, dE \]

(19) \[ I(t) \, dt = I(t)(-t^{-3}/ml^2) \, dE \]

\[ I(E) = (-t^3/ml^2)I(t) \]

where \( t = \) time

l = flight tube length

others as previously defined
Since \( l \) and \( m \) are constant for any one spectrum, the time information in each bin is therefore simply multiplied by \( t^3 \) and stored in the \( E \) array. Actually several adjacent bins (the number of bins is a function of the resolution) are averaged prior to transformation to smooth the conversion. The signal can thus be plotted as either a time of arrival or a photoelectron energy spectrum, as shown in Figure 6.

2.7. Resolution

The major factor limiting the resolution results from the use of a moving anion source and the extremely high collection efficiency. Intensity and resolution are generally inversely proportional. Parameter adjustment to benefit one is usually detrimental to the other. It is not surprising therefore, that the ability to collect electrons over almost \( 4\pi \) sr. will contribute to an energy spread.

The generally most severe effect is due to the parent ion contribution to the electron velocity. This effect is heightened by the perpendicular electron extraction. Electrons ejected on the axis of the molecular beam in the direction of the parent ion velocity will have that velocity in addition to what they would have had if ejected perpendicularly. Electrons emitted 180 degrees to those will have the "normal" velocity minus that of the parent. The velocity spread is thus two times the parent velocity. For this reason the
FIGURE 6. The UPS spectrum can be plotted as either a function of time or of energy, as shown here for the UPS (ArF, 193nm.) of Ge7⁻.
ions are decelerated, as mentioned in the apparatus discussion. This spread in velocity corresponds to an electron energy spread of:

\[ dE = m_e \cdot v_e \cdot dv_e. \]

\[ dv_e = 2v_{\text{ion}} \]

\[ dE = m_e \cdot (2E_e/m_e)^{1/2} \cdot 2(E_{\text{ion}}/m_{\text{ion}})^{1/2} \]

\[ dE = 4 \cdot (E_eE_{\text{ion}})^{1/2} \cdot (m_e/m_{\text{ion}})^{1/2} \]

Figure 7 illustrates the effect of deceleration on the resolution. A 2 eV electron from a 50 eV Cu\(^{+}\) parent ion has an energy spread of about 30 meV, a 4 eV electron 167 meV. Without deceleration the atom would have 500 or 750 meV spread from 2 and 4 eV electrons, respectively. Note that deceleration is not as critical for clusters of higher mass. Figure 8 shows the mass dependence of this energy spread.

An additional dE encountered in collecting electrons so efficiently is due to the time some electrons have spent travelling in the -z direction, prior to their reflection from the magnetic field. This time can be calculated by integrating:

\[ z \int_{15 \text{mm}}^{1} \frac{dz}{v_z} \]
FIGURE 7. The effect of deceleration on resolution for two different electron energies ejected from Cu' (63.54 amu) and Cu10'.
FIGURE 8. Dependence of resolution on parent ion mass.
If we treat the problem adiabatically, the ratio of the perpendicular velocity to the magnetic field is constant and the parallel velocity \( v_z \) is given by:

\[
(22) \quad v_z^2 - v_0^2 = v_0^2 - v_+^2 \frac{B_f}{B_0}
\]

The upper limit of integration for equ (21), the \( z \) at which the electron is reflected, is found by solving the above for the \( B_z \) at which \( v_0^2 = 0 \), and then equ.(4) is solved for \( z \) at that field. For a 111 cm us\(^{-1}\) electron (about .5eV) this distance is 1.584 mm. A short program (HP 15C) calculates \( B_z \) and integrates the following:

\[
(23) \quad \int_{15\text{mm}}^{B_0} \left( v_0^2 - v_+^2 \frac{B_z}{B_0} \right)^{-1/2} \, dz
\]

after substituting in equ.(4):

\[
B_z = \frac{\mu_0 I}{2} \frac{R^2}{(R^2 + z^2)^{3/2}}
\]

An angle of 18 degrees, slightly greater than that defining the loss cone (equ.(17)) was used to calculate the corresponding perpendicular velocity, to ascertain the time for an electron which had so much \( v_z \) that it almost couldn’t reflect. This results in 21.35ns for the 111cm/us electron under consideration to reach the point at which it is reflected. Thus the extra time an electron
ejected along the -z axis has to travel, compared to an electron ejected along the +z is 42.7 ns, which gives a dE of about 140 meV.

An energy spread also results from electrons detached in the magnetic field with the same speed, but different velocities parallel and perpendicular to the magnetic field. The greater the angle to the magnetic field axis the electron is ejected, the greater the magnitude of the perpendicular velocity component. As shown in equ.(22), the parallel velocity can be easily calculated if we assume adiabaticity. It has also been shown previously that the energy of the cyclotron motion is transferred to the axial motion as the magnetic field decreases. Conservation of energy requires the total velocity to remain constant, since the magnetic field does not do any work on the electron, but merely changes its direction. Electrons emitted with the same speed will ultimately achieve approximately the same parallel velocity. The velocity spread can be calculated in the following manner. If all the initial velocity is perpendicular to the magnetic field, equ.(22) becomes:

\begin{align}
\nu_{//} &= \nu_0 \left( 1 - \frac{B_2}{B_0} \right)^{1/2} \\
\text{If all the initial velocity is parallel to the magnetic field, } \nu_0 &= \nu_{//}, \text{ so:} \\
\Delta \nu &= 1 - \left( 1 - \frac{B_2}{B_0} \right)^{1/2} \\
&= \frac{\nu_0}{B_0} \left( 1 - \frac{B_2}{B_0} \right)^{1/2}
\end{align}
This expression has a value of about .00175 for magnetic field strengths of 2G and 600G. An electron with \( v_0 = 100 \text{ cm us}^{-1} \) (about .4eV) has a velocity spread of .167 cm us\(^{-1}\), corresponding to a spread in energy of approximately 9.5 meV. Note that as the ratio of the perpendicular velocity to the magnetic field is a constant, a large magnetic field ratio improves the resolution. The minimum field strength is limited, however, as a weaker field results in a larger cyclotron radius for the electrons. This radius must be kept small enough that most of the parallel electron trajectories end on the 30mm active area of the detector.

The \( dE \) from these three major effects is plotted in figure 9 as a function of electron kinetic energy. The lines designated "A" in the figure represent equ.20, the \( dE \) from the parent velocity spread:

\[
dE = 4(E_{\text{ion}}m_e/m_{\text{ion}})^{1/2}E_e^{1/2}.
\]

The "B" line is the result of the transformation via equ.19:

\[
dE = 2E_e \frac{dt}{t},
\]
FIGURE 9. Relative effects on resolution.

"A" lines represent $dE = 4(E_{ion}m_e/m_{ion})^{1/2}E_e^{1/2}$, the energy spread resulting from the parent ion velocity.

The energy spread from the turning around time of 2 ejected electrons, $dE = 0.04E_e$, is plotted as line "B".

Line "C" represents the energy spread due to the different original velocity components of the electron, $3.336E_e$.

See text for derivations and discussion.
where \( dt \) is the turn around time for \(-z\) ejected electrons, given by equ.23. The value of the integral is a constant for a given ratio of magnetic fields, so that \( dt \) is proportional to \( 1/v_0 \). Substitution into equation (25), along with \( t = 1/v \) and use of .0195 for the constant integral (the value from an electron ejected 18 degrees from \(-z\), about the minimum angle an electron could be ejected and still be reflected) leads to \( dE = .04E_{e-} \). This is what is plotted as line "B". Note that \( dE/E \) is a constant for a set magnetic field geometry. Line "C" is also intrinsic to a specific magnetic field ratio. It represents the energy spread due to the different original velocity components of the electron. Equ.25 gives \( dv \). Substitution into the expression \( dE = mv dv \) (equ.19), \( dE \) in meV can be equated to \( 3.336E_{e-} \).

Note that although the parent ion velocity is always a concern, at high electron kinetic energies the resolution may actually be limited by the turn around time, particularly for heavier parent ions.
SECTION II.

EXPERIMENTAL RESULTS AND DISCUSSION
CHAPTER III.

CARBON
3.1 INTRODUCTION

Carbon, 12amu, is the lightest of the group IV elements. Its four valence electrons usually form four bonds per atom. The s and p orbital energies are close enough that sp hybridization is extensive in carbon bonding. Because of the extensive overlap between π orbitals, this element concatenates more readily than any other. Not only is the C - C bond quite stable at 356kJ/mol, but the bond energy of C - O is less, 336kJ/mol.\textsuperscript{35} Carbon is also unique in the tremendous number of compounds it forms, including carbides, halides, oxides, cyanides, sulfides, carbonates, plus a truly vast array of organic compounds.

Carbon is found almost everywhere. Underground it is found as oil, natural gas, precious and nonprecious minerals. All the organic matter in the soil and some of the inorganic include C. Above the surface all life is C-based, as well as most of the natural and synthetic materials we eat, drink, wear, play with or take for medicinal purposes. C is found in the atmosphere as CO\textsubscript{2} and above it in some stars, planets, meteors and interstellar dust.

Carbon is most frequently found in one of its three natural allotropic forms; graphite, diamond or amorphous. Diamond is normally a type of cubic packed carbon, although a rare hexagonal form has been found in meteorite fragments. Graphite has two different crystalline arrangements. The α type is hexagonal and can be converted mechanically to the rhombohedral β phase.
Heating of the $\beta$ phase to over 1000°C restores the $\alpha$ phase.\textsuperscript{36}

The graphite packing of carbon atoms produces one of the softest materials known, whereas the denser diamond packing of the same carbon atoms produces one of the hardest! This illustrates the importance of bonding in determining the physical properties of materials. Homogenous bonding, that is bonding to other atoms of the same element, and heterogenous bonding, to atoms of a different element, are the interactions among the valence electrons of different atoms. Thus it is obvious that a thorough understanding of these interactions is mandatory for a thorough understanding of physical and chemical properties.

3.2 The UPS

In the following figure are the UPS of small carbon cluster anions. These clusters were vaporized with 2.33eV (532nm), ionized with 6.42eV (193nm) and the electrons photodetached with 7.9eV (157nm). Since the electrons are photodetached from an anion, the least bound electron will either have occupied the LUMO of the neutral cluster, or shared the HOMO. A separation between the least bound and the next most weakly bound electron is therefore a rough measurement of the neutral cluster's HOMO-LUMO gap. For a gap to be present of course requires that the neutral have been a closed shell (full HOMO) species. A simple inspection of the spectra for the
C CLUSTER ANION UPS

FIGURE 11. C_{2-20} UPS WITH 7.9 eV PHOTODETACHMENT.
presence of these HOMO-LUMO gaps thus yields electronic structural information. It is evident from Figure 11 that HOMO-LUMO gaps occur in the odd-\(n\) \(C_n^-\) UPS, and are absent in the even-\(n\), for \(2 < n < 10\). This even-odd alternation is also found in the electron affinity values.

3.3 SELECTING ELECTRON AFFINITIES

These approximate "electron affinities" could be more aptly termed "the energy it takes to remove the least bound electron", but that is rather cumbersome. There are several reasons that the number is only an estimate of the electron affinity. As discussed in Chapter I, there are two types of electron affinity, adiabatic and vertical. Adiabatic means the actual energy difference between the ground vibrational states of the neutral and the anion. Because the potentials for the anion and neutral are generally offset slightly, and because there is plenty of energy available for vibrational excitation, transitions are more likely to occur to between non ground vibrational state levels. These are referred to as vertical transitions, and the binding energy of the least bound electron the vertical electron affinity. Since we do not know the geometries of the clusters, nor if there is a geometry change upon electron removal, the Frank Condon overlap is hard to estimate, and the EA is thus difficult to measure precisely.
In order to compensate for these and other effects, the EA's are selected by taking an intercept of a linear extrapolation of the lowest energy feature of the UPS and adding a constant. This constant is 0.2eV for UPS taken with 7.9eV photodetachment and 0.25eV for those obtained with 6.42eV photons. These constants were determined by measuring the half-width-half-max of the lowest energy features on all the UPS where this feature is relatively narrow. These constants are consistent among different elements, remain constant over a wide mass range and have been verified by comparison of Cu cluster EA's determined by UPS with those measured via another photodetachment technique.10

Figure (12) is a plot of the electron affinities listed in Table I., determined in this manner, as a function of cluster size. Note the even-odd alternation in the electron affinity values. The odd-n clusters have the lower EA's for n < 11. Recall it is these same clusters which have the HOMO-LUMO gaps. This trend is due to the alternation of singlet and triplet ground states in the short linear chain structures. The reversal of the trend at n = 10, above which the odd-n clusters then have the higher EA's, can be explained by a switch from chains to ringed structures.

Carbon particles were studied in flames and carbon arcs prior to the development of molecular beam techniques.37 Early carbon studies predicted this very behavior.

Pitzer and Clementi predicted an EA oscillation in smaller clusters in 1958,38 when they used a semi-empirical molecular orbital
Figure 12. C\textsubscript{n} - Electron Affinity as a Function of Cluster Size.
<table>
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(MO) approach to characterize carbon vapor. Their calculations predicted that linear chains of doubly bonded carbons would dominate, both in vapor and in liquid carbon. A basic MO picture is sufficient to conceptualize their theory. The 2s electrons interact to form a σ band made up of \( \sigma_g \) and \( \sigma_u \) MO's. There are 4n valence electrons per C atom. Four of these remain unpaired on the terminal carbons, leaving 4n-4 to be placed via the Aufbau principle. Half of these, 2n-2, go into the σ band. The other half enter the π band formed from the π MO's from the 2p atomic orbitals (the σ lie higher in energy). The π orbitals composing the band are doubly degenerate and therefore hold 4 electrons.

For odd-n clusters 2n-2 yields a multiple of 4, so that the electrons fill the π orbitals evenly and thus produce singlet ground states. An extra electron, to form an anion, must then enter a higher orbital. This accounts for the HOMO-LUMO gap seen in the UPS. Even-n clusters, on the contrary, have two extra electrons after filling the lowest π orbital, and must be placed in a higher energy orbital, resulting in triplet ground states. These electrons are bound less tightly, which explains the lower electron affinities of the even-n clusters.

Single determinant Hartree-Fock calculations using both double-zeta and double-zeta plus polarization basis sets performed recently on \( C_{2-6} \) found singlet ground states for both \( C_2 \) and \( C_3 \) and an oscillation in the following 4, 5 and 6 atom clusters, in the same manner as Pitzer and Clementi.\(^{39}\)
The switching of the even-odd pattern which occurs after \( n = 10 \) has also been previously predicted. R. Hoffmann performed extended Huckel calculations on \( C_n \) in 1965.\(^{40} \) He found chains to be the most stable structures for small \( C_n \), but that at \( n = 10 \) ring structures became competitive. Note that the UPS of \( C_{11}^- \) shown in Figure 11 seems to have a split feature. This is actually the superposition of two separate features, as can be seen from Figure 13. If the \( C \) cluster ions are from the source, that is residual ions from the plasma, the lower energy portion of the peak is enhanced and the higher energy side goes away. The electron affinity is that shown in the lower portion of the figure, and the value fits in with those of the larger clusters thought to have ring structures. When an ionization laser is used to ionize the clusters, the UPS of \( C_{11}^- \) has a much smaller HOMO-LUMO gap and higher EA, shown in the upper panel of Figure 13 and as the unconnected dot in Fig.12. This EA value fits in with those of the smaller linear clusters. Other clusters were tested to see if they behaved similarly, but \( C_{11}^- \) seems to be unique in this respect.

Further evidence of a switch in preferred geometries at \( n = 10 \) comes from photofragmentation data, where the photodissociation cross section decreases dramatically from \( C_9^+ \) to \( C_{10}^{10+} \).\(^{41} \)
**Figure 13.** $C_{12}^-$ UPS under different conditions. See text for discussion.
Rolfing, Kaldor and Cox\textsuperscript{42} have treated a graphite sample with KOH before vaporizing it. They claim that the presence of $K_2C_{6\cdot24}^+$ is evidence of linear chains existing up to at least $C_{24}^+$. Since their mass spectrum also contained unreacted $C_n^+$, and they used UV light to ionize, perhaps they were photofragmenting rings formed in the plasma, and the ones which reacted with K's on their termini then could not close back up. Of course the possibility also exists that some fundamental difference in our sources gives us rings and them chains.
CHAPTER IV

SILICON
4.1 INTRODUCTION

Si, 28amu, is the third row member of Group IV. Si concatenates much less readily than C, and the π orbitals do not form multiple bonds. The Si dimer bond strength, 226kJ/mol, is considerably less than that of C₂, 356kJ/mol, and the Si-O bond strength much greater, 368kJ/mol (vs.336).³⁵ This explains why Si does not occur naturally as a pure element, but bound to oxygen, with a coordination number of four. Divalent compounds of Si are normally thermodynamically unstable, but have been observed in high temperature chemistry. Si and O₂ are the two most abundant elements in the earth's crust. Si comprises 28 wt%, primarily as its oxide and as silicates.

Si as sand and clay has been very important in the development of civilization; especially as major components of building materials, such as bricks, glass and steel. Si is also an important building component for many marine animals. Its transmittance of over 95% of the IR (from 1.3-6.7um) makes it important in optics.³⁶ Another very important use of Si in modern technology is as a semiconductor.

Semiconductors differ from insulators and metals in their electronic structure. When the gap between electronic states is so small that room temperature kT can thermally excite electrons, the material is a metal. A slightly larger gap, where somewhat more energy is required for a transition, yields a semiconductor material,
and when the gap is so large that considerably more energy is required, the material is an insulator. The material properties are thus dictated by the electronic structure. Si, Ge and Sn undergo phase transitions at high pressure to become metallic as their crystalline structure packs more densely. The packing also influences other physical characteristics. As discussed in the previous chapter, different packing of C atoms results in materials as different as graphite and diamond. Similarly different packings result in different materials for Si. Three dimensional structures of SiO$_2$ with Al replacing some Si atoms (aluminasilicates) form negatively charged frameworks which become feldspars, zeolites, lapus lazuli, etc., depending on which cation they incorporate. Chains of SiO$_4$ tetrahedral units build up into sheets and form micas, again illustrating the importance of a thorough understanding of electronic structure.

4.2 MASS SPECTRA AND MAGIC NUMBERS

Until recently, the only experimental data available with which to test a cluster electronic/geometry structure theory were a few mass spectra and photofragmentation results. Such studies have shown that 4, 6 and 10 seem to be "magic numbers" for small positively charged clusters of Si. Magic number is a term used to indicate a cluster which has a greater intensity than those surrounding it, usually at least 20%. These magic numbers often correspond to
Mass Spectrum of Six-
r910; e400; Ne12%

FIGURE 14. Siₙ MASS SPECTRUM.
particularly favorable geometries. Noble gas clusters, for instance, typically have a much greater relative abundance of 13, 19 and 55 atom clusters, corresponding to icosahedral forms.

In the fragmentation studies of Si$_n^+$ clusters with more than ten atoms, the parent clusters were found to fragment preferentially into 6 - 11 atom fragments, particularly 6 and 10. These studies of Heath et al. and Bloomfield et al. involved photo-ionizing the neutral clusters and some of the mass spectral features thus attributed to fragmentation. Liu et al. and Zhang et al. used positive ions formed in the original vaporized plasma.

Positive Si cluster ions with n < 9 do not exhibit the same tendency to fragment into pieces that the larger clusters do. The Bloomfield study$^{43}$ and Smalley lab unpublished results$^{44}$ show that the small clusters lose single atoms successively, as seen previously for metal cluster fragmentation. Recent collision-induced dissociation (5eV Ar) of positively charged Si cluster ions found similar results; the 6, 7 and 10 atom clusters are favored products as both the neutral and charged daughter fragments$^{45}$ from clusters with n > 9, while the smaller clusters preferentially lose single atoms.

Bloomfield et al. discussed the fragmentation data in terms of a microcrystalline model for cluster structures. Two of the most stable structures that this predicts are a six membered chair ring and a ten atom adamantane cage. This is consistent with the special stability of the 6 and 10 atom clusters. Electronic structure
calculations disagree upon whether or not cluster structures are indeed such pieces of the bulk diamond lattice.

4.3 ELECTRONIC STRUCTURE CALCULATIONS

Calculation of the electronic structure and properties of clusters with ab initio methods is a formidable task. Until recently, only the dimer and trimer were treated at this level. Clusters with more atoms had approximations be made in their theoretical treatment. Koutecky has performed pseudopotential MO-LCAO + CI calculations on Si and Ge clusters composed of up to 7 atoms, neglecting d orbitals. Ge₄ was calculated with and without the d functions to determine the effects of their neglect, and found that for that particular cluster the inclusion of the d's changed the values of the energy levels, but not their ordering. JT splitting was also ommitted. This method was used to compare diamond lattice segments, closepacked structures, linear chains and pentagonal geometries. Their conclusions were that Si and Ge clusters are electronically very similar and that closepacked or pentagonal structures are preferred.⁴⁶

Local density functional methods have also been used to calculate small Si cluster electronic structure. The local density formalism requires considerable computational effort and must be resolved for every new geometry to be considered.⁴⁷ The extensive
calculations preclude its application to large systems or to using it to examine all possible geometries for minimal energy. For this reason it is it has been applied to cluster calculations in combination with molecular dynamics techniques and with tight binding methods.

One of the molecular dynamics techniques used in studies of Si cluster geometries is simulated annealing. This technique replaces the Monte Carlo method where one particle position must be updated and the energy recalculated for each step. The simulated annealing technique updates all particle positions with each step. This method predicts non-crystalline fragment geometries.

Another molecular dynamic technique involves the use of the Stillinger - Weber three body interaction potential. A planar pentagon is found to be the most stable geometry for Si\textsubscript{5} and two such structures stacked for Si\textsubscript{10}. Philips proposes that stacked ring structures are very important in Si clusters - and that 15, 18 and 21 are trilayered cylinders. The non-crystalline geometry predictions of the Feuston et al. calculations are shown in Figure 15, along with those from the two following techniques.

The tight binding method requires estimating the nearest neighbors for the Hamiltonian used to minimize the cluster total energy. Different energies for the same geometry result from different selections of nearest neighbors. Tomanek and Schluter minimized the effect by maintaining a particular nearest neighbor map throughout the optimization of the geometries. The more time
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</table>

**Figure 15. Comparison of Predicted S1 Cluster Geometries.**
consuming local density functional treatment is then used on the more likely geometries suggested from the tight binding calculations. Their preferred cluster geometries are also close packed structures, not bulk crystal fragments. The following table presents the HOMO-LUMO energy gaps calculated by these two methods, along with our experimental measurements.

Raghavachari and coworkers\textsuperscript{52} have recently extended the realm of all electron ab initio molecular orbital calculations to 2 - 10 atom Si clusters. The cluster geometries were determined by the Hartree-Fock method with double-zeta sp plus a set of d-type polarization functions on each Si, the 6-31G* basis set. Electron correlation effects were included via complete fourth-order Moller-Plesset perturbation theory. This theory predicts close packed structures for small Si clusters. The relatively higher stability of 6 and 10 atom clusters is again predicted for their octahedral based geometries. They have found all proposed structures to be less stable than a tetracapped octahedron, TCO, except for a tetracapped triangular prism, TTP, proposed by Ballone and Andreoni, which he found competitive. Both the TCO and the prismatic structure are predicted to have a HOMO-LUMO gap of approximately 2eV.\textsuperscript{48a} The experimental value is about 1.7eV.
Table II. CALCULATED vs EXPERIMENTAL HOMO-LUMO GAPS (eV)

(After Tomanek and Schluter)

<table>
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<tr>
<th>n</th>
<th>Egap(LDA)</th>
<th>Egap(TB)</th>
<th>HOMO</th>
<th>LUMO</th>
<th>EXPERIMENT (APPROXIMATE)</th>
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<td>A</td>
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</table>

B = bonding, A = antibonding, N = nonbonding
4.4 THE UPS

The fragmentation experiments have give valuable clues to geometrical structure, but have been recently superceded by advances in photoelectron spectroscopy\textsuperscript{53} which now permit its application to clusters. Details of the valence electronic structure can now be compared directly with theory. Raghavachari is currently attempting to assign lines in the C and Si UPS. The need for such data is evident in the cluster geometry calculations, where the results vary with the level of the technique used to calculate them.\textsuperscript{54} The ordering of close lying levels varies with the inclusion of electron correlation and the value of the differences between states depends on the choice of basis.\textsuperscript{55}

The UPS for the different size clusters are distinct. The spectra in Figure 16 have HOMO-LUMO gaps in the UPS of the 4, 6, 7 and 10 atom clusters. These spectra were obtained with 7.9eV photodetachment. Figure 17 shows our previously published UPS of 3-12 atom Si cluster anions taken with 6.42eV electron detachment. The spectra are better resolved in the lower energy data due to use of the same 10ns time bin transient digitizer in both sets of experiments. The overall characteristics of each cluster UPS are the same under both conditions. Since the electron binding energies remain constant, the electron kinetic energies, and therefore their arrival times, are different for the different energy detachments.
Si CLUSTER ANION UPS

FIGURE 16. Si$_3$-20$^{+}$ UPS WITH 7.9 eV PHOTODETACHMENT.
Figure 17. $Si_{3-12}^-$ UPS with 6.42 eV photodetachment.
All peaks were observed to shift slightly, signifying the absence of Auger events.

4.5 THE ELECTRON AFFINITIES

Electron affinities and the presence or absence of HOMO-LUMO gaps are the most readily obtained information from the UPS. The EA(n) is shown in Figure 18, following the list of calculated and experimental EA values in Table III. The individual variation of the UPS is reflected in the E.A. values; the clusters with the lowest electron affinities are those with large HOMO-LUMO gaps. This indicates that the neutral cluster has a closed shell, so that the additional electron must have occupied the neutral LUMO. This electron is then not bound as tightly, and the EA is lower. Information of this type should aid in the elucidation of cluster geometries. Comparison of spectra and EA(n) patterns among different periodic groups should establish trends which will establish the basis for physical and chemical variation.
Si

EA vs Cluster Size

![Graph showing EA vs Cluster Size for Si]  

**Figure 18.** $\text{Si}_n^-$ electron affinity as a function of cluster size.
<table>
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CHAPTER V.

GERMANIUM
5.1 INTRODUCTION

Ge (72.6amu) is the fourth row member of Group IV. Ge chemistry is intermediate between that of Si and Sn. Like Si, Ge is a very important room temperature semiconductor. They are both transparent to most of the infra-red and therefore have a variety of applications in optics. The trend of decreasing catenation down the periodic column continues with Ge; it only forms catenated hydrides, up to Ge$_9$H$_{20}$. Unlike Si, Ge dihydrides are stable. Ge more readily accepts higher coordination numbers than Si. Ge and Sn form β-diketonato complexes, as well as various other organo-complexes with Pb analogues.\textsuperscript{35}

5.2 MASS SPECTRA AND MAGIC NUMBERS

Prior to development of cluster UPS, Ge clusters were studied by examination of mass spectra and fragmentation products. Martin and Schaber\textsuperscript{56} produced small Ge clusters by thermal evaporation, condensation in He and ionized them with 70eV electrons. The positive ions were detected with a quadrupole mass spectrometer. Maximal intensity was observed for the 6, 10, 14, 15 and 18 atom cluster anions, with the 13, 17 and 20 atom clusters the weakest. The mass spectra of Heath et.al.\textsuperscript{43a} contained significantly less signal for the 1 - 5 atom clusters than did Martin & Schaber. They
Mass spectrum of Ge\(_n\) on inline detector

10-21-1987

Time (microseconds)

FIGURE 19. Ge\(_n\) MASS SPECTRUM.
concluded that the dramatically increased intensity in the 6 - 11 atom range was the result of photofragmentation during 6.42eV photoionization. \( Si_n^+ \) and \( Ge_n^+ \) mass spectra obtained under these conditions were found to be virtually identical, with the 6, 7 and 10 atom clusters having maximal intensity. When the clusters were ionized with 7.9eV photons, however, the Ge mass spectrum practically terminated at 12, while the Si mass spectrum continued to include larger clusters. The intensity of \( Ge_{10}^+ \) also increased substantially. Since the mass spectra were so similar when 6.42eV photon ionization was used, the neutral distribution from the source is quite likely the same for both types of clusters. This then implies that the cross section for the more energetic photons is larger for the Ge clusters than the Si.

Si and Ge small cluster cation mass spectra are quite similar to each other.\(^{43}\) Liu et.al. compared Si and Ge positive and negative mass spectra and photoionized vs residual ions and found that although the relative intensity of the "magic numbers" did fluctuate somewhat, the definite dominance of 6 - 11 atom clusters was constant. Conditions which allowed fragmentation enhanced the magic numbers, especially the 10 atom cluster.

6 and 10 dominated \( Ge_n^+ \) mass spectra have also been reported by Schulze et. al., obtained by similar techniques to Martin & Schaber, except that the ionizing e- energy was 100eV.\(^{57}\) The electron high impact ionization method doubtlessly results in significant fragmentation. The latter group found that the relative intensities
were sensitive to the flow rate of the carrier gas, and manipulated the mass distribution by adjusting this parameter. Although the intensities fluctuated, the 6,10,14,15,16,18 & 23 atom clusters remained maxima.

5.3 The UPS

Figure 20 contains the UPS of Ge\textsuperscript{n}\textsuperscript{−} 2 < n <16 obtained with 7.9eV photodetachment and Figure 21 with 6.42eV. Most of these spectra bear a marked resemblance to the corresponding Si\textsuperscript{n}\textsuperscript{−} UPS shown in the previous chapter. This will be readily seen in Chapter VIII, where all the group IV UPS spectra are compared.

Ge has not been the subject of theoretical calculations to the same extent that the lighter group IV members have, due to the increased complexity. Pacchioni et.al. have performed ab initio calculation on Ge clusters 3 - 6, neglecting the d functions. They found that the inclusion of d orbitals did result in higher energies and shorter bond lengths, but that it did not effect the ordering of the ground and first excited states.\textsuperscript{58}

Using pseudopotential multi-reference configuration interaction (MRD-CI) methods, they found that geometries representing small pieces of a diamond lattice were less stable than more compact structures. For Ge\textsubscript{4}, a rhombus was preferred over a tetrahedron, square, T, or chain. The five atom cluster trigonal bipyramid is
Ge CLUSTER ANION UPS

FIGURE 20. Ge\textsubscript{2-15} UPS WITH 7.9eV PHOTODETACHMENT.
**Figure 21.** Ge$_3$-Ge$_{12}$ UPS with 6.42 eV photodetachment.
predicted to be more stable than a tetrahedral arrangement. Similarly for Ge₆, the stablest form is a capped trigonal bipyramid. The ground states of Ge₃-Ge₆ were all found to be singlets, the dimer a triplet.

5.4 The Electron Affinities

Figure 22 is a plot of the Ge E.A. values from Table IV. as a function of cluster size. These values were determined in the same manner as explained for C. Again a dramatic size dependence is seen, with minima corresponding to the UPS with HOMO-LUMO gaps present. The same pattern is seen as for Si. This will be shown in Figure*, Chapter VIII, where the two are compared directly.

Lowe has calculated the dimer electron affinity, using basic MO theory, to be 1.8+/-.5eV, which agrees with the experimentally observed value of 2eV. He predicted that the Si dimer EA would be higher by .4eV, and the Sn₂ value would be the same as that of Ge. The latter is confirmed by our spectra.⁵⁹
Ge

EA vs Cluster Size

![Graph showing EA vs Cluster Size for Ge with ArF and F2 lines.]

**FIGURE 22.** $\text{Ge}_n^-$ ELECTRON AFFINITY AS A FUNCTION OF CLUSTER SIZE.
**TABLE IV. Ge$_n$ ELECTRON AFFINITY VALUES (eV)**

<table>
<thead>
<tr>
<th>$n$</th>
<th>EA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Photodetachment</td>
</tr>
<tr>
<td></td>
<td>6.42eV</td>
</tr>
<tr>
<td>2</td>
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<td>1.9</td>
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<td>2.6</td>
</tr>
<tr>
<td>13</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER VI

TIN
6.1 INTRODUCTION

Sn, 118.7amu, the fifth row member of the group, undergoes a phase transition near room temperature and therefore is found in two different crystal structures. The α phase, known as gray tin, has a diamond type lattice. The bonding and antibonding states overlap in this phase, and therefore gray tin is semimetallic. At 13.2°C a transition occurs to the more densely packed tetragonal/bcc crystalline lattice. This metallic phase is known as β, or white, tin. A similar phase change from a semiconductive to a more closely packed metallic phase also occurs in both Si and Ge, but at greater pressures. Sn is commonly coated over other types of metals to prevent corrosion and other chemical reactions, as in tin food cans. Many tin alloys are industrially important. One Sn and Nb alloy is a low temperature superconductor.

6.2 MASS SPECTRA AND MAGIC NUMBERS

The following figure (23) is a time of flight mass spectrum of Sn cluster anions. It looks quite similar to that seen by Martin & Schaber and to that obtained by Duncan with a short cluster condensation channel; longer channels bias the mass distribution toward larger clusters. The drop off in intensity at larger cluster sizes may be caused by several effects. The sensitivity of the detector decreases with increasing mass, so undetected heavier
Snx mass spectrum w/ Brep = -1110V
dec21gm.dat

12-21-1987
Time (microseconds)

FIGURE 23. Sn MASS SPECTRUM.
clusters are present. This is evidenced by the large amount of
electron signal collected from what appears in the mass spectrum as
negligible parent, and from the appearance of electron signal when
the photodetachment laser is fired at the time corresponding to when
higher mass cluster anions would be at the detachment zone, even
though they cannot be seen in the mass spectrum. The latter was
relied on for obtaining the larger, 14 & 15 atom, cluster UPS of both
Sn- and Pb-.

The Duncan mass spectra of the larger clusters show that Sn$_{13}^+$
and Sn$_{14}^+$ are minima in intensity vs size. This is similar to mass
spectra of Pb clusters, where there is a major minima in the
intensity of Pb$_{14}$.

6.3 THE UPS

The UPS of Sn$_n^-$, for n < 16, are shown in Figure 24. These
cluster anions are residual ions from the source plasma, without
additional ionization techniques. The electrons were photodetached
with 6.42eV photons, the ArF line of an excimer laser. A group of
German scientists recently constructed an apparatus similar to ours,
except that they use colinear parent cluster detection, as opposed to
our perpendicular extraction. Unfortunately they use 3.68eV photons
for detachment, and so only observe the photodetachment threshold
region. It can be seen from Figure 25 that their data also displays
large HOMO-LUMO gaps for Sn$_4^-$ and Sn$_6^-$, and a long onset for Sn$_{10}^-$. 
FIGURE 24. Sn$_{2.15}$ UPS with 6.42 eV photodetachment.
FIGURE 25. Sn$_{3-12}$-UPS
WITH 3.68eV PHOTODETACHMENT.
From Gantefor et al.
Faraday Discussions of RSC

Intensity (arb. units)

Electron binding energy [eV]

Sn$_3^-$
Sn$_4^-$
Sn$_5^-$
Sn$_6^-$
Sn$_7^-$
Sn$_8^-$
Sn$_9^-$
Sn$_{10}^-$
Sn$_{11}^-$
Sn$_{12}^-$
Sn$_{13}^-$
Sn$_{14}^-$
Sn$_{15}^-$
Sn$_{16}^-$
Sn$_{17}^-$
Sn$_{18}^-$
Sn$_{19}^-$
Sn$_{20}^-$
Sn$_{21}^-$
Sn$_{22}^-$
6.4 THE ELECTRON AFFINITIES

Figure 26 is a plot of the estimated Sn EA values from Table V. as a function of the cluster size. A dramatic size dependence is evident. The minima in EA again correspond to the clusters whose UPS exhibit significant HOMO-LUMO gaps.

Electronic structure calculations for singly charged Sn clusters are currently limited to the dimer and trimer. Equilateral and isosceles triangle structures are predicted to be nearly degenerate geometries for the trimer, which is predicted to be more stable than Sn$_2$. Lowe, with basic MO theory, has estimated the Sn dimer EA to be about 1.8eV and to be the same as that of the Ge dimer, predictions which are corroborated by this data.\textsuperscript{59}
Sn

EA vs Cluster Size

**Figure 26.** $\text{Sn}_n^-$ electron affinity as a function of cluster size.
<table>
<thead>
<tr>
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<tr>
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</tr>
</tbody>
</table>
CHAPTER VII

LEAD
7.1 INTRODUCTION

Pb, 207.2 amu, is the sixth row member of Group IV. It is a very soft metal, a poor conductor which is quite resistant to corrosion. The three major naturally occurring isotopes are each an end product from one of the three series of naturally occurring radioactive isotopes; U, Ac and Th. Pb oxides are brightly colored and vary in their crystal structure. Yellow massicot has a complicated chain structure of PbO₆ octahedra linked by PbO₃ units, while litharge (Pb₃O₄) is layered and is red in color. Pb does not catenate readily. Although it does form some catenated organo-compounds such as Pb₂(CH₃)₆, they are not as stable as catenated compounds of the other group IV elements.

Pb has been involved in molecular beam studies for a long time because it has such a low melting point (327.5°C, BP = 1740°C) that it can be readily vaporized in an oven source. In the seventies Yokozeki and Stein investigated the deviations from bulk properties as cluster size was decreased. Pb microclusters were generated in an oven and adiabatically expanded in Ar carrier gas. This molecular beam was then crossed with a 40KV electron beam and the resulting electron diffraction patterns studied. Diffraction patterns of thin films showed that the lattice parameters of the microclusters were smaller than those of the bulk and that they decreased with decreasing cluster size. Deviations from bulk behavior were found
to occur once the cluster size fell to approximately 50-60 Angstroms (2000-3000 atoms/cluster).\textsuperscript{65}

7.2 MASS SPECTRA AND MAGIC NUMBERS

Figure 27 is a time of flight mass spectrum of Pb\textsuperscript{−} clusters. Just as for the Sn cluster anions in the previous chapter, this mass spectra is of ions generated in the original plasma in the source; no additional ionization methods were used. This a major advantage in studying the relative intensities, as the roles of ionization cross sections and fragmentation are minimized. Note that Pb\textsuperscript{7−} is a maxima. Again the mass resolution of the detector limits the size range of clusters which can be examined. This situation is currently being remedied by the addition of a double reflectron to the apparatus.

The seven atom cluster has been observed to be a maxima in Pb cluster mass spectra taken under a broad range of circumstances. Mass spectra observed in Japanese studies of oven generated, electron ionized, Pb clusters have a similar size range and distribution. The nozzle shape, length and orifice diameters were varied to determine their effects,\textsuperscript{66} as was the ionization electron energy (from 0 to 150eV).\textsuperscript{67} The mass spectral features were relatively independent of these parameters, although the absolute intensities were not.

Other studies at the Konstanz University in Germany have given similar results. Oven produced Pb clusters were supersonically
Mass Spectrum @ 1110 volts

Pb7-

Time (microseconds)

5-3-1988

FIGURE 27. Pb^- MASS SPECTRUM.
expanded in He carrier gas and electron ionized. The Konstanz group detected Pb$^+$ up to 400 atoms and has resolved them up to 100. The spectra show a lot of intensity fluctuations below $n = 20$. Pb$_7$ and Pb$_{10}$ are maxima, as are 13, 17 and 19, and show a very deep minima at 14. This differs from the other metals in the study; Sb clusters showed a sequence of fours, the In cluster intensity increased with $n$, and Bi has its own pattern. A spherical model predicts magic numbers at 7, 13 and 19, corresponding with pentagonal bipyramid, icosahedral and icosahedral plus a pentagonal cap geometries. Again, the various condensation parameters were varied to determine their effects on the mass distribution. These included the oven temperature, type, pressure and temperature of the carrier gas and length of the condensation region. The relative intensities of the clusters were independent of all these factors. The ionization electron energy was varied from 10 - 300 eV, and even though anything over 20eV resulted in fragmentation, the relative distribution remained unchanged.

Duncan et al. have found the same Pb cluster mass distribution for both neutral and positively charged clusters. Laser vaporized clusters supersonically expanded in He were laser ionized. The conditions for examining the neutral distribution are set by lowering the photon flux to the point where one photon events must dominate. Higher fluences allow multi-photon events and the mass spectra may reflect the dominant photofragmentation "daughter" products, rather than the more stable "parents". The mass spectra under both of these
conditions at two different ionization energies exhibit a relative maximum at seven. The ten atom cluster is only predominant when ionized with the more energetic, 157nm (vs 193), photons, a reminder that the ionization cross sections must also been considered when additional ionization techniques are used.

Begemann et.al. also found a mass distribution similar to ours, but attributed the lack of clusters with more than 15 atoms to total decomposition of the larger clusters from residual energy from their formation by a 20keV Xe⁺ sputtering technique.⁷¹

7.3 The UPS

The first UPS of Pb clusters are shown in Figure 28 & 29. The UPS in the first figure were obtained with ArF excimer laser photodetachment, and the second figure with F₂ photodetachment. The loss of resolution in the higher energy detachment spectra is due to the 10ns time bins in our transient digitizer - when the electrons are arriving more rapidly, more arrive within a given time frame. The higher energy allows us to probe more deeply into the valence band, however, so we trade off resolution for a bigger view.

The dimer UPS could only be obtained with the ArF line - electron signal could not be seen with F₂ photodetachment. The dimer binding energy is only .88eV.⁷². Both UV lines typically have more than enough energy to fragment a given cluster, but the photodetachment process is so much faster than a vibration that it
Figure 28. Pb\textsuperscript{-2-15} UPS with 6.42 eV photodetachment.
Pb CLUSTER ANION UPS

FIGURE 29. Pb\textsubscript{3-15} UPS WITH 7.9 eV PHOTODETACHMENT.
usually occurs first, and then the electron carries off most of the excess energy courtesy of conservation of momentum. If the dimer fragmented just prior to photodetachment, one would expect to see a UPS characteristic of the atom. If it were fragmenting immediately following photodetachment, we would still see electron signal. Since no electrons were observed, either the overlap between the cluster anion beam and the UV beam was extremely poor every time we tried; an unlikely situation, but possible, or the absorption cross section for the 157nm photon is negligible, again very unlikely, or, what seems most likely, is that the dimer is fragmenting rather than photodetaching. For the latter to occur, the F$_2$ photon must couple directly into a vibrational mode and the molecule fall apart extremely rapidly.

What makes the dimer even more interesting is the recent observation by M. Duncan that photofragmentation of singly charged small Pb cluster cations lose two Pb atoms in a one photon process. This contrasts with our previous observations that in this size range metal cluster cations tend to photofragment by successive loss of single metal atoms. Nb$_4^+$ was an exception to this trend. Due to the very strong dimer bond, fragmentation into two dimers was the dominant dissociation pathway, but even with an extremely stable dimer the larger Nb cluster cations fragmented via loss of atoms and not dimer units. This seems to indicate that Pb clusters are not behaving as "typical" metals; that the electrons are involved in specific bonds
between atoms in a set geometry, rather than delocalized over the entire cluster.

Note that the Pb cluster anion UPS from both wavelengths seems to have better resolution than the UPS of the preceding chapters. Another interesting aspect of these spectra is the increased frequency of gaps. These phenomena are best considered in comparison with the other group IV members, and so I leave their discussion to the next chapter.

7.4 THE ELECTRON AFFINITIES

Figure 30 is a plot of EA(n) from Table VI, for both the ArF and F₂ data. Once again the EA is found to vary considerably with the cluster size, indicating variation in cluster electronic structure. The reproducibility with different wavelengths is gratifying, as is the obvious absence of Auger peaks. Since Auger electron energies are independent of the excitation energy, the electrons would arrive in the same place in spectra taken with different wavelengths. The absence of such gives credence to our assumption that we are dealing primarily with one electron processes.

The decrease in EA at n = 13 may be an indication that the cluster is a packing in a typical fcc manner, as a cubo-octahedron. Each internal bulk atom in an fcc lattice has 12 nearest neighbors, thus the 13 atom cluster is the first cluster large enough to fulfill this condition. Special stability for 13 is also seen in inert gas
Pb

EA vs Cluster Size

FIGURE 30. Pb\textsuperscript{+} MASS SPECTRUM.
### Table VI. \( \text{Pb}_n \) Electron Affinity Values (eV)

(7.9eV Photodetachment)

<table>
<thead>
<tr>
<th>( n )</th>
<th>EA</th>
<th>Photodetachment</th>
<th>Laser Energy</th>
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<tbody>
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<td>15</td>
<td>2.31</td>
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<td>2.25</td>
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</tbody>
</table>
clusters, which also form closepacked crystals, but have shown
evidence in their mass spectra of forming Mackay icosahedra, which
explain observed magic numbers for up to \( n = 1000 \). Magic numbers
at 13, and 55 (\( 1 + \sum (10p^2 + 2) \)) correspond to spheroidal closed
shells, and capped icosahedral structures such as 19 yield secondary
magic numbers. The 13 atom icosahedral is slightly denser than the
fcc fragment. Whichever geometry \( \text{Pb}_{13} \) clusters actually assume, it
can be seen that the structure would be especially stable and thus
"magic", and the lower EA accounted for. This may also explain the
severe minima in intensity for \( n = 14 \) in the Pb mass spectra, the
reactivity of such a species would conceivably be very low.
CHAPTER VIII.

GROUP IV COMPARISON
8.1 INTRODUCTION

The Group IV elements differ in both their bulk and atomic properties. Since the members are isoelectronic, they all have a valence electronic structure of $ns^2np^2$ ($n$ indicating the row of the periodic table), and since all the members readily form clusters, the series provides an ideal system for studying periodic changes in electronic structure. This is not a simple undertaking, as the ability to map out valence electronic structure is a the result of some very recent advances in photoelectron spectroscopy, specifically its union with cluster molecular beam technology. The task of recognizing trends is hampered by a serious lack of understanding of cluster electronic structure in general. Some progress has been made very recently, in finding models for single $s$ valence electron systems. Alkali and noble metal clusters can be treated as free electron systems and simple interatomic potentials can be used with rare gas clusters. Neither a smeared jellium background nor a simple interatomic potential is adequate to describe covalent bonding. This makes the Group IV clusters particularly interesting to theoreticians. Here, for the first time, the UPS of all the Group IV elements are compared. The remainder of this chapter discusses the trends found in the data presented in the previous chapters.

8.2 EXPECTATIONS
The atomic electron affinities and bulk work functions are shown in Table VII. The cluster electron affinities must evolve from one to the other, but the big question is how rapidly and at what size clusters do bulk-like properties begin to be exhibited? Since the atomic work functions are dissimilar, but the bulk work functions are similar, at what point do they begin to converge? There is an abrupt change between Ge and Sn in the atomic electron affinities, but the resemblances among the I.P.'s seem to indicate a natural break between C and the remaining elements. Which trend is reflected in the UPS?

Chemical reactions are interactions between reactant valence electron configurations in an attempt to completely fill electronic subshells. Consequently, the chemical behavior reflects the electronic structure and vice versa. The chemistry of C and Pb differ from that of the other group members. C readily forms π-π bonds and is unique in its ability to concatenate. All the group IV members tend to form tetravalent compounds, but Pb also often forms divalent compounds. This implies that the UPS of C and Pb should differ from the others.

The bulk elements differ in their properties. C is unique, Si and Ge are semiconductors and Sn and Pb are metals. These differences arise mainly from the various types of crystalline packings. Carbon occurs naturally with diamond and graphite lattices. Si, Ge and Sn also have diamond phases, in which each atom is tetrahedrally
coordinated to four others. This arrangement requires sp³ hybridization, and is considered loosely packed. In this phase Si and Ge are semiconductors and Sn is a 0 gap semiconductor, or semimetal. Sn in the diamond, or α, phase is known as gray tin and the more common, more tightly packed metallic bcc β tin structure is called white tin. The transition between the two occurs near room temperature and pressure for Sn. Si and Ge require higher P to undergo a similar phase change from a diamond to a metallic lattice. Pb is only known to close pack in an fcc lattice. If the small cluster geometries are diamond lattice segments, the spectra should be similar for all but Pb, which would have different structures. Or, since the phase transition occurs at such low pressures for Sn, perhaps Pb at very low pressures, such as found in molecular beams, may have a previously unseen low pressure diamond phase and all the spectra could look alike. Enough speculation.

8.3 UPS COMPARISON

The Group IV cluster anion UPS are plotted together for ease in comparison in figs.31-35. There is a remarkable resemblance among the spectra of a given size for all the elements except C. The Pb UPS also differ in that there seems to be a distinct HOMO-LUMO gap in every for every cluster, although the overall features are quite similar to the corresponding Si, Ge and Sn spectra. In most of the UPS this appears to be partially due to a dramatic increase in
GROUP IV CLUSTER ANION UPS

C

Si

Ge

Sn

Pb

BINDING ENERGY
GROUP IV CLUSTER ANION UPS

BINDING ENERGY (eV)
GROUP IV CLUSTER ANION UPS

C
Si
Ge
Sn
Pb

BINDING ENERGY (eV)
GROUP IV CLUSTER ANION UPS

BINDING ENERGY (eV)
GROUP IV CLUSTER ANION UPS

BINDING ENERGY (eV)
### Table VIII. Group IV Spin Orbit Splitting (eV).

<table>
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<th>X</th>
<th>Ionization Potential</th>
<th>$x_2$ Bond</th>
<th>Spin Orbit $^3p_2 - ^3p_0$</th>
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<td>11.26</td>
<td>6.1</td>
<td>0.005</td>
</tr>
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<td>Si</td>
<td>8.15</td>
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<tr>
<td>Pb</td>
<td>7.42</td>
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From K. Pitzer, Accounts of Chemical Research 52(8), 271 (1978).
resolution, which will be discussed in a subsequent section. The width of the entire band of features also seems to narrow down the column, although this may be due to the same effect.

There is one particular case in which even the C UPS looks like thee others; for \( n = 7 \) all the UPS exhibit a large HOMO-LUMO gap. The non-C group IV elements all also have HOMO-LUMO gaps in the UPS of the 4 and 6 atom clusters, and long shoulders on the \( n = 10 \). A careful inspection of the UPS of the different elements reveals many more similarities among the spectral features of a given size cluster. The resemblance between the same size clusters is decidedly remarkable in light of the differences between the spectra of a given element. For one atom to change the appearance of the spectra to such an extent, while changing the material barely alters it, surely indicates that the clusters have very similar electronic structures, which may well require similar geometries. The pattern of EA\((n)\) of the different Group IV members parallels the correlation among all the members but C.

8.4 EA COMPARISON

The EA as a function of cluster size for all the members except C are shown together in fig.36. The EA\((n)\) for C was shown in Figure 12, and is obviously quite different from the others. The even-odd alternation in EA\((n)\) corresponds to an alternation of singlet and triplet ground states, switching from odd minima to even at \( n = 11 \).
GROUP IV

EA vs Cluster Size

\[ \text{EA (eV)} \]

\[ \text{Number of Atoms in Cluster} \]

- Si
- Sn
- Ge
- Pb
PLEASE NOTE:

Page(s) not included with original material and unavailable from author or university. Filmed as received.
This flip marks the structural change from short chains to monocyclic ring structures, as discussed in Chapter III.

The figure shows a truly impressive correlation among the patterns of EA(n) for all the other clusters up to n = 10. An even-odd alternation in electron affinity is also exhibited in this plot, with the exception of n = 7, up to at least n = 11. In contrast to the C clusters, however, the odd-n clusters are the maxima and the even the minima. n = 7 has such an anomalously low electron affinity that it is even lower than the even-n clusters, 6 and 8, on either side of it.

The clusters which are minima in the EA(n), n = 4, 6, and 7, are also those clusters with HOMO-LUMO gaps. Because these clusters are closed shell as neutrals, it is reasonable that they would have the lowest affinity for an additional electron. One would thus expect the clusters immediately preceding these in size to have large electron affinities, as the extra electron would be completing a shell filling, and their UPS to lack HOMO-LUMO gaps. This is indeed the case.

The similarity of the n < 10 UPS for all the Group IV elements except C implies that these very small clusters have similar electronic structure, which in turn implies that they may also have similar nuclear geometries. This is not too surprising for the very small clusters. Obviously all elements have the same geometry for the dimer, which doesn't have any choice but to be linear. A trimer can be either bent or linear, but it seems intuitive that it will
require extra energy or special bonding to maintain linearity, and therefore in this situation the geometry is again fairly predetermined. As the number of atoms in the cluster is increased, more geometrical options become available. It is reasonable that isoelectronic elements have similar geometries in a regime where nuclear geometry is dictated by valence electronic structure. Since the bulk elements have different crystalline lattices, somewhere in between the atom and the bulk these elements will start packing differently, but at what size? At what point will different options be favored by the different elements? What causes the different elements to begin to behave differently? The size of the atoms could prevent some elements from packing as closely as others at a given pressure, but it is the group IV member with the largest atoms, Pb, which packs the most densely. A stronger bond energy between atoms might cause the atoms to pack more densely, but again this conflicts with what happens; Pb is the most weakly bound. The unique characteristic of Pb is its divalency, which may result in the closer packing - or result from it. How and at what size cluster does this happen? The number of atoms necessary for a cluster to begin to show bulk characteristics is expected to vary depending upon the property under consideration. Most of the atoms in small clusters are surface atoms, and therefore their properties are not expected to be the same as those typical of the bulk, where most of the atoms are not on the surface. It is therefore quite interesting to see that the EA(n)'s of Si, Ge, Sn and Pb diverge at n = 10.
8.5 DIVERSION AT n = 10

At n = 10, the Group IV elements diverge in their behavior. The EA of Si and Ge seem to proceed toward their bulk work functions in a size dependent manner. Sn continues an even-odd alternation after ten, switching minima, just as C does, but still in the opposite manner; after n = 10 it is the odd-n clusters which are the minima in EA. The EA values remain similar to those of Si and Ge, however. Pb changes pattern the most. The EA follows the trend of increasing to n = 12, but then falls off for 13 and gets even lower for 14.

This divergence in behavior between the semiconductive and metallic elements may indicate the beginning of a transition to bulk behavior. For the spectra to begin to differ, the electronic structure must begin to differ. This could be caused by differences in geometry, by d orbitals becoming involved to different degrees, or by varying amounts of sp hybridization.

The geometry might begin to differ for semiconductors as they "freeze out". Are cluster properties aptly described by bulk-type adjectives, in terms of bulk-like properties? Is it relevant to discuss whether or not a five atom cluster is a semiconductor or metallic? Perhaps the lack of bulk crystal structure indicates that the element is a "liquid". The loss of sequential single atoms for
fragmentation of clusters with $n < 10$ may imply lack of molecular structure; that the clusters are cohesive agglomerations and are not composed of discrete units. If this were the case, however, one would expect a spherical drop model would adequately describe the cluster potential, and this is not the case.\footnote{71}

Geometries might also begin to vary at ten merely because it is the first opportunity. As mentioned previously, a dimer or trimer have few variations possible. Isoelectronic elements could be expected to arrange themselves similarly for four and five atom clusters, and evidently higher than that. If all form an octahedron for $n = 6$, the next few clusters merely involve capping that structure. After tetracapping the octahedron for $n = 10$, however, various possibilities finally exist. Additional caps can be added, although this is obviously going to start crowding things, and the framework is likely to shift around. It may be something as simple as atomic radii which dictate the divergence at this point.

Another possibility is that decreasing $sp$ hybridization down the group causes the major differences among the elements, but that the hybridization is not extensive enough to allow crystal type geometries (or a gradual phase to such) until $n = 10$. The C atom core consists merely of two $1s$ electrons, which are very close to the nucleus. This allows C atoms to get close enough to each other for the $2p\pi$ orbitals to overlap and allow $\pi-\pi$ bond formation. The other members of group IV are too large for such an occurrence, and thus have different chemistry. The molecular orbitals formed from $s$ and $p$
atomic orbitals are energetically too far apart in Pb, even in the bulk, for sp hybridization, which precludes the tetragonal bonding required in a diamond crystalline lattice. The orbitals are too far apart for extensive hybridization in the small semiconductor clusters as well; the s and p AO's are least 7 - 8 eV apart.\textsuperscript{77} Pacchioni et.al. have calculated that the MO's formed from the s and p AO's are still separated by at least 5.5eV in the Ge tetramer.\textsuperscript{58} Sn and Pb dimer outer valence MO's are also calculated to be almost purely p in character.\textsuperscript{63} Koutecky et.al. have found that varying degrees of sp hybridization due to the different radii of s and p orbitals in different rows plays a dominant role in differences in stability for different isoelectronic clusters.\textsuperscript{78} Phillips also attributes the similarities and differences among the group members' mass spectra to reduced sp hybridization down the row.\textsuperscript{50} Perhaps the divergence at n = 10 is a result of an onset in sp hybridization in Si and Ge, which affords different geometric opportunities for them than the metals.

Yet another indication that Si and Ge are closepacked like the metals Sn and Pb, up until n = 10, is that the small semiconductors (n < 9) photofragment via loss of successive single atoms, a metallic trait. The larger semiconductor clusters preferentially dissociate into 6 - 11 atom chunks, especially n = 6 and 10. Evidently it takes ten atoms for the group IV elements (besides C) to develop different electronic structures. Perhaps ten atoms is sufficient for Si s and p derived MO's to hybridize. Si and Ge differ slightly at n = 10.\textsuperscript{79} The extent of shoulder on the Ge\textsubscript{10}\textsuperscript{-} UPS varied from day to day. None
of the other spectra, even others with long shoulders, varied in the same manner. The NO's are a little farther apart in Ge than Si, so perhaps the ten atom clusters have different degrees of hybridization, resulting in different geometries, or at least different stabilities. This is supported by photofragmentation studies of medium size Si and Ge clusters, where \( n = 10 \) is a preferred daughter fragment for both, but \( \text{Ge}_9^+ \) and \( \text{Ge}_{10}^+ \) fragment readily and \( \text{Si}_9^+ \) and \( \text{Si}_{10}^+ \) do not.\(^4\)

8.6 Resolution improves with row

8.61 Possible causes

The spectral features in the UPS narrow from Si to Pb. The spectrometer resolution is limited by the broadening of the electron time-of-arrival due to the parent ion velocity perpendicular to the electron collection flight-tube at the time of photodetachment and the turn around time of electrons initially ejected away from the detector (Section 2.6). Neither of these effects can account for this effect. Compare the spectra of two clusters of similar mass, for instance \( \text{Si}_{13}^- \) (about 364amu) and \( \text{Sn}_3^- \) (356amu) in Fig.31 and 34. It is quite obvious that Si has intrinsically broader peaks, and that the overall structure has a broader bandwidth.

Another factor which affects the width of the peaks is the nature of the photoejected electron. The peakwidth depends on how much the detached electron was participating in a bond. A
delocalized nonbonding electron will have a narrower energy spread than an electron ejected from a bonding orbital. If the geometry of the neutral and the ionic ground states differ, which they are more likely to do if the photoejected electron is removed from a bond, the potential energy surfaces for the two will be offset and the Franck-Condon overlap for an adiabatic transition will be low. Vertical, rather than adiabatic, transitions will dominate the spectra. Since this additional vibrational structure is unresolved in this type of photoelectron spectrometer, we see it as a broadening of the electronic feature. Transitions to excited electronic states of the neutral may also be a source of broadening. Because we do not know the FC overlap, nor the vibrational temperatures involved, we can only estimate the vertical electron affinities from these spectra.

It is tempting to ascribe the increased resolution down the column to decreasing localization of the electron, which would correlate with the increasing metallicity of the elements. This same phenomenon is seen in the noble metals, however, which precludes the possibility that this is an intrinsic difference between semiconductors and metals. Cu anion small cluster UPS have broader features than Ag, which has broader ones than Au.\(^80\) Al also has broad peaks in its UPS. Contrary to Group IV, however, where the electron binding energies decrease down the column, Au has more tightly bound electrons than Ag. Thus a comparison of these sixth row elements shows that Pb has both the least tightly bound electrons and the narrowest featured UPS for its column, while Au has both the
narrowest peaks and the most tightly bound electrons in its family. 
The dependence of the narrowing upon only the position of the element 
in the periodic table leads to the conclusion that the narrowing is 
due to relativistic effects.

8.62 RELATIVISTIC EFFECTS

There are two major competing effects on the radial 
wavefunctions. Relativistic contraction occurs in the heavier 
elements due to the increased amount of time the electrons in them 
spend near the increasingly positive nucleus. The decreased radius 
results from the relativistic mass increase corresponding to the 
relativistic velocity. At the same time, the contracted inner shells 
screen the outer orbitals from the large nuclear charge.

The d and f electrons have higher angular momentum, so they do 
not approach the nucleus as closely as those in s and p orbitals, and 
therefore are not affected directly to the same extent. An indirect 
effect occurs from the contraction of the s and p’s inside the d and 
f orbitals. The screening of the latter from the nuclear charge is 
increased, resulting in their outward expansion. Since the s and p 
orbitals outside the d’s and f’s are also contracting, the order of 
the valence electron energy levels can’t be readily predicted a 
priori.

The other major relativistic effect is the spin orbit splitting 
of orbitals into subshells. L-S coupling breaks down for heavy
elements. In group IV 1-s coupling is a good approximation for the first four elements, but j-j coupling is required for Pb. This effect splits an 1 shell into subshells with j = 1 +/- s. The group IV valence p orbital, l = 1, is therefore split into two, p_{3/2} and \( p_{1/2} \). The p_{1/2} is usually lower in energy and accommodates two \((2j + 1)\) electrons. This leads to the ground state atomic electron configuration for Pb of [Xe]4f^{14}5d^{10}6s^{2}6p_{1/2}^{2}. The spin orbit effect will be larger for the anion, as the occupation of the 6p_{3/2} by a single electron will increase the anisotropy. The LUMO is thus the 6p_{3/2}, which will accommodate four electrons. Since the anionic electron enters this orbital, when the spin orbit splitting is large enough to resolve it is seen in the UPS as a HOMO-LUMO gap. Table VIII lists the spin orbit energy for all the group IV members. The UPS become increasingly better resolved down the column as the spin orbit coupling increases. The Pb spin orbit splitting is great enough to resolve the least bound electron in the p3/2. This is about .6 to .8 eV, as can be seen from the Pb UPS, for clusters with n = 3-15, with a few exceptions. n = 4, a magic number and one of those for which Si, Ge, and Sn also have a HOMO-LUMO gap, has a greater splitting, about 1 eV. n = 11 and 12 have even more unusual behavior. The splitting decreases at n = 11, to about .2eV, and seems to vanish for n = 12.

This same effect narrows the spectral features in the noble metal spectra through the course of the column. In this case, however, the anion's electron enters the 6s shell, which is radially
TABLE VIII. GROUP IV SPIN ORBIT SPLITTINGS (eV).

<table>
<thead>
<tr>
<th>X</th>
<th>IONIZATION POTENTIAL</th>
<th>X₂ BOND</th>
<th>SPIN ORBIT $^3P_2 - ^3P_0$</th>
</tr>
</thead>
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<td>C</td>
<td>11.26</td>
<td>6.1</td>
<td>0.005</td>
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<tr>
<td>Si</td>
<td>8.15</td>
<td>3.2</td>
<td>0.03</td>
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<tr>
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<td>7.88</td>
<td>2.8</td>
<td>0.17</td>
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<tr>
<td>Sn</td>
<td>7.34</td>
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<tr>
<td>Pb</td>
<td>7.42</td>
<td>1.0</td>
<td>1.32</td>
</tr>
</tbody>
</table>

contracted, thus increasing the energy with which it is bound. This relativistic contraction is so great for the 6s orbital that it gives Au higher IP's and EA's than Ag.
The UPS of Group IV cluster ions have been presented for the first time. The spectra are unique for each size cluster, and show remarkable similarities for clusters of the different elements of a given size. Carbon differs from its fellow members due to its ability to form π-π bonds. The EA(n) values exhibit an even-odd alternation, which reflects an alternation in singlet and triplet ground states. The odd minima for n < 10 become maxima for n > 10. This flip marks a change from linear chains to ring structures.

The spectra of the other Group IV elements show many similarities, except that Pb UPS seems to have an "extra" lowest energy feature, compared to the others. This may be the result of p orbital splitting. The EA(n) for these elements is parallel up to n = 10. This implies similar geometries for the very small clusters. The divergence at ten is the first evidence of the onset of the evolution of bulk type behavior.

The apparatus is currently being redesigned for the next generation of experiments. A double reflectron will allow extension of studies to larger clusters and a new source is being designed to increase the cluster intensities. The list of future experiments for this apparatus is extensive. Noble metals and the Group IV elements have been examined so far. A group of transition metals needs to be studied for identification of metallic trends. Studies of elements whose reactivities have been measured may result in a correlation
between electronic structure and reactivity. The UPS can be monitored before and after reactions to see how adsorbates alter electronic structure. Mixed element clusters may also aid in establishing electron number trends. Experiments further in the UV may allow probing the evolution of d band involvement in bonding.
APPENDIX A

TABLE OF DATA FILES DISPLAYED IN FIGURES
GROUP IV DATA FILE RECORD
GROUP IV FILES (.DAT) & ELECTRON AFFINITIES (eV)

electron affinities = xintercept + .20 eV ArF
electron affinities = xintercept + .25 eV F₂

<table>
<thead>
<tr>
<th>Num</th>
<th>C+F²</th>
<th>Si+F²</th>
<th>Ge+F²</th>
<th>Sn+ArF</th>
<th>Pb+ArF</th>
<th>Pb+F²</th>
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<td>2</td>
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<td>oct23cs</td>
<td>2.27</td>
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<td>3.55</td>
<td>edec9as</td>
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<td>oct20es</td>
<td>2.03</td>
</tr>
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<td>oct20ds</td>
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<td>dec4ds</td>
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<td>dec5bs</td>
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<td>oct21cs</td>
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<td>edec9es</td>
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<td>edec9fs</td>
<td>3.45</td>
<td>051988es</td>
<td>3.35</td>
</tr>
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<td>edec9gs</td>
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<td>3.65</td>
<td></td>
<td></td>
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<td>edec9gs</td>
<td>3.45</td>
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<td></td>
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<td>edec10bs</td>
<td>3.95</td>
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<td></td>
</tr>
<tr>
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<td>oct17bbm</td>
<td>2.65</td>
<td>edec10cs</td>
<td>3.85</td>
<td></td>
<td></td>
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</tbody>
</table>
APPENDIX B

CALIBRATION
Calibration of the UPS involves three factors: energy, distance and time. A general form for finding these factors follows:

\[ E_{KEe} = E_0 + \frac{1}{2} m \left( x - x_0 \right) / (t - t_0) \]

where

- \( E_{KEe} \) = electron kinetic energy
- \( E \) = energy
- \( x \) = distance electron travels
- \( t \) = electron flight time
- \( t_0 \) = offset

Au- is used to calibrate the apparatus for two main reasons. Atoms are not always readily made in our cluster source when the flows and channel diameters and lengths are optimized for clustering. Gold atom is readily made without altering the source conditions, which makes it a good candidate for a calibration standard. It is very expensive, though, so it would be preferable to use something less expensive. The main feature which makes gold worth the expense is that it has three separate transitions spanning our energy range; corresponding to electron binding energies of 2.309, 3.445 and 4.967eV. Calibration constants which fit the Au UPS peaks to the actual values are then used to calibrate the other UPS. The current calibration routine optimizes the factors with a least squares fit.
The program was written by Shi-He Yang and revised by Kelly Taylor. The code is included in this appendix, following a table of the calibration constants used to optimize the data presented in this thesis.
### Calibration Factors

\[ E = A + \frac{B}{(t-C)^2} \]

<table>
<thead>
<tr>
<th>Clusters Detachment</th>
<th>Au data file</th>
<th>Calibration factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si\textsubscript{ALL} \textsuperscript{-}</td>
<td>7.9eV</td>
<td>dec1bm.dat</td>
</tr>
<tr>
<td>Ge\textsubscript{2.9} \textsuperscript{-}</td>
<td>7.9</td>
<td>nov7as.dat</td>
</tr>
<tr>
<td>Ge\textsubscript{10-15} \textsuperscript{-}</td>
<td>7.9</td>
<td>051988i.dat</td>
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<tr>
<td>Sn\textsubscript{2-12} \textsuperscript{-}</td>
<td>6.42</td>
<td>dec18ams.dat</td>
</tr>
<tr>
<td>Sn\textsubscript{13-15} \textsuperscript{-}</td>
<td>6.42</td>
<td>050488.dat</td>
</tr>
<tr>
<td>Pb\textsubscript{2-15} \textsuperscript{-}</td>
<td>6.42</td>
<td>050488.dat</td>
</tr>
<tr>
<td>Pb\textsubscript{3-15} \textsuperscript{-}</td>
<td>7.9</td>
<td>052488q.dat</td>
</tr>
</tbody>
</table>
#include <stdio.h>
#include <math.h>
#include <dos.h>
#include <nr.h>
#include <nrutil.h>
#include <ctype.h>

float Ft[3]; /* flight time in usecs for three Au peaks */
float En[3]; /* kinetic energy of Au peaks */
float a[64];

struct equation
{
    float dev; /* mean square deviation */
    float A; /* kinetic energy = A + B/(t[i] - C)^2 */
    float B;
    float C;
};
float Amin, Amax, Ainc, Bmin, Bmax, Binc, Cmin, Cmax, Cinc;

struct equation sbase[3000]; /* see initsbase also for array size dec */

/**********************************FUNCTIONS**********************************/

main()
{

    float w, x, y, z;
    int l=0, m=0, i;

    En[0]=4.111; En[1]=2.975; En[2]=1.453;  /*ArF kinetic energies */
    /*En[0]=5.588; En[1]=4.452; En[2]=2.93;*/  /*F2 kinetic energies */

    Ft[0]=2.43; Ft[1]=2.725; Ft[2]=3.31;
    Amax=0.20; Bmax=35.0; Cmax=.03;
    Ainc=.04; Binc=.1; Cinc=.01;
    Amin=-.200; Bmin=31.0; Cmin=-Cmax;

    x=Amin;
initsbase();
requestenergy();
while (x<\text{Amax})
{
    x+=\text{Ainc};
    y=\text{Bmin};
    while (y<\text{Bmax})
    {
        y+=\text{Binc};
        z=\text{Cmin};
        while (z<\text{Cmax})
        {
            z+=\text{Cinc};
            w=0.0;
            for (l=0; l<3; l++)
            {
                w+-(\text{En}[l]-(x+y/((\text{Ft}[l]-z)\times(\text{Ft}[l]-z))))\times(\text{En}[l]-(x+y/((\text{Ft}[l]-z)\times(\text{Ft}[l]-z))));
            }
            \text{sbase}[m].A = x;
            \text{sbase}[m].B = y;
            \text{sbase}[m].C = z;
            \text{sbase}[m].dev = w;
            m++;
        }
    }
}
printf("\n\r Amax = %f  Bmax = %f  Cmax = %f , %d", Amax, Bmax, Cmax, m);
getch();
/*for (i=0;i<m;i++)
{
    printf("\n\r %d, %f, %f, %f, %f
", i, sbase[i].A, sbase[i].B, sbase[i].C, sbase[i].dev);
}
getch();*/
sort(m, sbase-1);
display10(m);
}

/*******************************************************************************/
void sort(n, ra) /* Heapsort of struct equation */
int n;
struct equation ra[];
{
    int l, j, ir, i;
    struct equation rra;

    l=(n >> 1)+1;
    ir=n;
    for (; ;) {
        if (l > 1)
            rra=ra[--l];
else {
    rra=ra[ir];
    ra[ir]=ra[l];
    if (--ir == l) {
        ra[l]=rra;
        return;
    }
}
i=l;
j=l << 1;
while (j <= ir) {
    if (j < ir && ra[j].dev < ra[j+1].dev) ++j;
    if (rra.dev < ra[j].dev) {
        ra[i]=ra[j];
        j += (i=j);
    }
    else j=ir+1;
}
ra[i]=rra;
}

="/*****************************************************************/
requestenergy

y( void );
requestenergy( )
"


{
    int i;
    char response;
    cls();
    printf("\n\r\t\t\t\tAP3 FLIGHTTIMES");
    loop5down:
    locate(4,4,0);
    for (i=0;i<3;i++)
        printf("\nFt[%d] = %f usec\tfor \tEn[%d] = %f \n",i,Ft[i],i,En[i]);
    locate(10,4,0);
    printf("\nDo you want to enter new time coordinates [y/n]? ");
    scanf("%s",&response);
    switch (response)
    {
    case 'n': return; break;
    case 'y':
        locate(5,0,0);
        for (i=0;i<3;i++)
            {
            printf("Ft[%d] = %f",i);
            locate(5+i,8,0);
            scanf("%f",&Ft[i]);
            }
    }
return; break;

default: requestenergy();
}

 display10(n) /* displays 10 lines at a time of sbase w/ m element */

int n;
{
    char response;
    int i,j;
    cls();
    printf("\n\r\t\t\t\tAP3 FLIGHTTIME CALIBRATIONS\n\n");
    printf("\t\tMinimum Square Deviations (DEV) for Equation:\n");
    printf("\t\tEn = A + B/((Ft-C)*(Ft-C)\n\n");
    printf("%6.3f < A < %6.3f, step %6.3f  Ft[0] = %4.3f usec,\n",Amin,Amax,Ainc,Ft[0],En[0]);
    printf("%6.3f < B < %6.3f, step %6.3f  Ft[1] = %4.3f usec,\n",Bmin,Bmax,Binc,Ft[1],En[1]);
    printf("%6.3f < C < %6.3f, step %6.3f  Ft[2] = %4.3f usec,\n",Cmin,Cmax,Cinc,Ft[2],En[2]);
    printf("\tDEV (eV*eV)\t\t\tA (eV)\t\t\t\t\t\tB (us*us*eV)\t\t\t\t\t\tC (us)\n\n");
    for (i=0;i<10;i++)
    {

printf
("\t%5.2e\t%6.3f\t%5.2f\t%5.4f\n",sbase[i].dev,sbase[i].A,sbase[i].B,sbase[i].C);

next10lines:
printf("Display the next 10 deviations? [y/n] ");
scanf("%s",&response);
switch (response)
{
    case 'n': return; break;
    case 'y':
        j++;
        locate(12,0,0);
        for (i=j*10;i<(j+1)*10;i++)
            printf
("\t%5.2e\t%6.3f\t%5.2f\t%5.4f\n",sbase[i].dev,sbase[i].A,sbase[i].B,sbase[i].C);
        goto next10lines; break;
}
}

/***********************************************************/

initbase()
{
    int i;
}
for (i=0;i<3000;i++)
{
    sbase[i].dev=sbase[i].A-sbase[i].B=sbase[i].C=0.0;
}
}
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