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RICE UNIVERSITY

LOW ENERGY ELECTRON ATTACHMENT TO \( C_{60} \) IN RYDBERG ATOM-\( C_{60} \) COLLISIONS

by

CARLA D. FINCH

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF ARTS

APPROVED, THESIS COMMITTEE

\( \text{[Signature]} \)
F. B. Runnig, Director
Professor of Physics

\( \text{[Signature]} \)
K. A. Smith
Distinguished Faculty Fellow

\( \text{[Signature]} \)
M. D. Corcoran
Professor of Physics
Department Chair

Houston, TX
May, 1996
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Abstract

$C_{60}^-$ ion formation has been observed in collisions between K(np) Rydberg atoms with principal quantum numbers $35 \leq n \leq 125$, which corresponds to electrons with mean energies in the range $\sim 2 \text{ meV}$ to $\sim 170 \mu\text{eV}$, and $C_{60}$ molecules. This results from Rydberg electron transfer and has permitted study of the low energy electron attachment properties of Buckminsterfullerene, which is known to capture free electrons with energies up to $\sim 12 \text{ eV}$. Present data agree with a previous Rydberg atom study but disagree with theoretical predictions and also with previous free electron-$C_{60}$ studies. Results from both theory and the free electron experiments suggest that a potential barrier of $\sim 240 \text{ meV}$ exists for electron capture by $C_{60}$, preventing electron capture at very low energies. The present data are compared with previous experiments and with theory, and possible explanations for the observed discrepancy, including evidence for an image-charge-bound state of $C_{60}$, are discussed.
ACKNOWLEDGMENTS

I would like to take this opportunity to thank several people for their contributions to this work. First, I extend my sincerest appreciation to my advisor, Dr. Barry Dunning, for his guidance and for providing the different perspective often needed to solve experimental setbacks.

Dr. Bruce Johnson spent countless hours, away from his own work, explaining the various theoretical and chemical aspects of $C_{60}$ to me - generally more than once. I am very grateful for his time and patience. Dr. Peter Nordlander also deserves my recognition not only for his image-charge-binding calculations, but also for providing answers to any questions I posed about those calculations.

Next, I need to thank my colleague, Rich Popple, without whom this work could not have been accomplished. Through all the weeks and months of utter frustration and hand-to-hand combat with gremlins, his patience and help have been greatly appreciated. Also, I must thank the other graduate students and postdocs in this lab for numerous discussions through which I have learned an enormous amount.

Finally, no structure can be built without a foundation. Each of my achievements in life has been a direct result of gifts given to me by my family. Their endless love and encouragement have instilled in me the confidence and the motivation to strive for excellence. For this I cannot thank them enough. Also, I cannot overlook the inspiring discussions with Shelby Jones whom I thank for his presence and interest. Lastly, I give my undying love and gratitude to my fiancé, Steve Fordham, for his continual support and uplifting attitude throughout even the most discouraging circumstances.
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CHAPTER 1:
Introduction

Over the last several years substantial interest has grown concerning the properties of Buckminsterfullerene. The soccer ball-shaped molecule consisting of sixty carbon atoms offers a variety of properties not usually seen at a molecular level. Recent improvements in the large scale production of $C_{60}$ have encouraged research into its structure, properties, and applications. In fact, within the last decade so much work has been done with carbon 60 that entire books have been written about its chemistry alone, and the fullerenes have become the focus of many periodicals.

Several studies have been done using free electron-$C_{60}$ collisions which reveal Buckminsterfullerene as an efficient scavenger of electrons with energies up to $\sim 12$ eV via the reaction:

$$C_{60} + e^- \rightarrow C_{60}^-$$

(1.1)

The data also indicate a sharp decrease in the attachment rate for low electron energies, $\lesssim 200$ meV. This decrease is consistent with theoretical studies of the fullerene. Measurements using Rydberg atom-$C_{60}$ collisions show negative ion formation for very high principal quantum number $n$ of the Rydberg via electron transfer reactions of the form:

$$C_{60} + R(n\ell) \rightarrow C_{60}^- + R^+$$

(1.2)

(In an electron transfer reaction the excited Rydberg electron is captured by the target molecule.) This result is surprising because the mean kinetic energy of the Rydberg electron is on the order of a few meV or lower, well below the
onset attachment energy predicted by the theory and indicated by the free electron work. It is important to note that due to the special properties of Rydberg atoms, the Rydberg electron can be considered as a nearly free electron in collision studies. More detailed explanations of Rydberg atom properties and of the nearly free electron model follow, as well as a brief description of the structure and symmetry of carbon 60.

In the remainder of the thesis, Chapter 2 describes the experimental apparatus, and Chapter 3 discusses experimental procedures and data analysis. Presentation of the appropriate theory along with results for the free electron experiments and the Rydberg atom experiments is given in Chapter 4. Finally, speculative explanations for the discrepancies between theory and Rydberg atom experiments as well as between the free electron and the Rydberg atom data are offered in the Discussions section of Chapter 4. Following the Conclusion, a brief chapter on future studies completes the text.

1.1 Rydberg atoms

1.1.0 Properties

A Rydberg atom, named after the Swedish spectroscopist Johannes Rydberg, is nothing more than an atom with its outermost electron excited to a state of high principal quantum number, n. Before describing the use of Rydberg atoms as experimental tools, it is necessary to present some of the properties which make them so useful. Table 1 summarizes a few of the important properties. Numerical values are shown for the range of principal quantum numbers used in the present study.
Firstly, the size of the Rydberg atom scales as the principal quantum number squared, \( n^2 \), and thus such atoms can attain immense dimensions at the higher \( n \) values. The electron orbit increases with the size of the atom, making the core ion look more like a point particle. The Coulomb attraction between the core ion and the electron, acting as point particles, decreases with the square of the distance between them. Therefore, the attractive field can be easily overcome by a passing target molecule having a high electron affinity or having the characteristics of an electron scavenger.

The large electron-core separation (i.e. small Coulomb field) also causes the atoms to be strongly perturbed by stray electric fields. Thus it is necessary to minimize any external fields in order to create high \( n \) Rydberg atoms. For example, the critical field needed to ionize an \( n = 125 \) Rydberg is only a few \( \text{Vcm}^{-1} \). Hence, all Rydberg atoms have properties similar to highly excited hydrogenic atoms.

The unusual size of the Rydberg atom contributes to the second important characteristic, a low binding energy. The electron orbiting the core is bound by only a few meV instead of a few eV as is the case for ground state or low-lying excited-state atoms. Therefore, Rydberg atoms can be strongly perturbed by thermal energy collisions with neutral target molecules. State changing collisions can occur in which either the \( n \) or the \( \ell \) state of the Rydberg atom is changed, or ionization of the Rydberg atom can take place. Such factors need not be considered for ground-state atom collision processes.

The energy levels of a Rydberg atom are a function of the effective principal quantum number, \( n^* = n - \delta \ell \) where \( \delta \ell \) is the quantum defect. The energy is given by:
\[ E_{n,\ell} = -\frac{1}{2(n - \delta_\ell)^2} \] (1.3)

The quantum defect is a correction factor caused by the penetration of the electron into the core, which has a finite size, and \( \delta_\ell \) is determined by the angular momentum state. As the angular momentum quantum number \( \ell \) increases, the quantum defect decreases rapidly because for higher \( \ell \) states the probability of finding the electron inside the core becomes negligible. In essence, \( \delta_\ell \) is the result of incomplete screening by the core electrons and is most important for values of \( \ell \leq 3 \), for which the wave function of the valence electron is more likely to penetrate the core.

Finally, the third unusual Rydberg atom property is a long lifetime. Because the atoms have little tendency for radiative decay they survive long enough to study their collisional properties. The Rydberg atom lifetime is proportional to \( n^3 \) for low \( \ell \) values and, in general, is on the order of tens of microseconds.

<table>
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<td>Property</td>
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With the properties described above, Rydberg atoms are a valuable tool for studying collisions. Rydberg atoms allow the study of very low energy electron collisions, including electron attachment processes, because the time
averaged kinetic energy of the Rydberg electron is equal to its binding energy. Furthermore, as described below, interactions between a high n Rydberg atom and a target molecule can be represented as that of a free electron with the molecule, which allows comparison of the experimental data from the two types of collisions.

1.1.1 **Nearly Free Electron Model**

Since there is more than enough energy in thermal collisions to ionize a Rydberg atom, they can be strongly perturbed by interaction with neutral target molecules. As mentioned before, either state changing collisions or ionization can take place. Of interest in the present work is ionization. When a high n Rydberg atom collides with a neutral target molecule the Rydberg core and the Rydberg electron act as independent scatterers due to the large electron-core separation of the atom. In other words, the interaction is dominated by either a core-target or an electron-target collision.\(^1\) For large n, the Rydberg electron-target interactions can be considered in terms of free electron collisions with the target, completely neglecting the presence of the core. This free electron approximation has been used successfully to explain numerous Rydberg atom collision phenomena. In particular, numerous studies with free electrons have shown that Rydberg atoms provide a novel means to study electron capture.\(^2\) However, the free electron approximation loses validity for smaller values of n. The proximity of the core and electron at lower n necessitates the inclusion of core effects such as post attachment interactions between product ions. Use of the essentially free electron model can be effective even for low n values if the effects of such post attachment
interactions are included. In the present work, Rydberg atoms with $n \geq 35$ have been used so there is no need to account for such effects.

### 1.2 Buckminsterfullerene

Presentation of the discovery of a stable carbon cluster consisting of sixty carbon atoms appeared for the first time in a letter published in *Nature* in 1985, and the molecule was named Buckminsterfullerene after Buckminster Fuller, the architect who invented the geodesic dome. The same article describes procedures for $C_{60}$ production, hypothesizes the most probable structure for the molecule, and suggests potential applications.

The proposed structure of $C_{60}$ is that of a truncated icosahedron, i.e. a soccer ball shape. The stability of this shape has been compared with other possibilities such as a truncated dodecahedron which is also somewhat spherical but instead of hexagon and pentagon constituents has dodecahedrons and triangles. However, a simple Hückel calculation providing eigenvalues, degeneracies, and orbital energies for the molecule shows that the truncated icosahedral configuration is more stable. This structure can be easily modeled by the icosahedral ($I_h$) point group using group theory and reasonably approximated by spherical symmetry. The spherical approximation neglects lattice corrugation effects which are included in the icosahedron symmetry group, but such effects are relatively insignificant and do not influence the orbital degeneracies of the molecule. Thus, the use of spherical symmetry is a valid approximation.

The cage-like shape of $C_{60}$ offers interesting possibilities for molecular interactions, and its extreme stability implies that it may be present
throughout the universe.³ Therefore, interest in studying the fullerene's chemistry and properties has soared. However, until 1990 and the development of a technique to produce $C_{60}$ in macroscopic quantities by Krätschmer et al.,⁶ experimental studies of it were limited by cost and availability. Naturally, after such a breakthrough, investigations increased dramatically and have already determined many of the fundamental characteristics of the molecule. An entire realm of experiments examining the chemical and collisional interactions involving the carbon 60 have shown that what was originally thought to be a completely nonreactive, stable molecule is in fact highly reactive (forming methylene and oxygen adducts, for example)⁷ and an intriguing source for further study. Various calculations provide information about the carbon-carbon bond length in $C_{60}$ ($r_1 ≈ 1.434 \text{ Å}$ and $r_2 ≈ 1.403 \text{ Å}$, corresponding to the edges of pentagons and the edges of hexagons not lying on a pentagon, respectively) and about the molecular geometry like the radius of the cage, $R ≈ 3.53 \text{ Å}$.⁸ Vaporization studies have determined some of the thermodynamic properties including an equation for the vapor pressure as a function of temperature.⁹ Also, the large polarizability of carbon 60 has been investigated both computationally¹⁰ as well as through experimental determination of the bulk dielectric constant.¹¹ Finally, and most importantly for this thesis, the electron attachment properties of Buckminsterfullerene have been investigated using both free electron and Rydberg atom techniques. The results of the studies will be discussed in Chapter 4 of this thesis.
CHAPTER 2: 
Experimental Apparatus

The basic apparatus consists of: a vacuum system, a laser system, a dual time-of-flight mass spectrometer equipped with two position sensitive detectors (PSD), a data acquisition and analysis system, an alkali oven, and an effusive source of $C_{60}$. A more thorough discussion of each of the six components follows.

2.1 Vacuum System

The vacuum system consists of two stainless steel chambers - an oven chamber and an experimental chamber. These are connected by a $\sim 0.040''$ (0.10 cm) diameter aperture, which provides the inlet for the potassium beam, from the oven region into the experimental region. Each chamber has numerous flanges allowing access to the potassium oven, the dual time-of-flight mass spectrometer, and the interior of the chambers, as well as feedthroughs for power, thermocouples, and bias potentials. A Brewster window is used to introduce laser light into the experimental region. The chambers are evacuated by a mechanical, roughing pump in combination with three diffusion pumps: two 6" and one 4". The pressure in the main experimental chamber is monitored by a Bayard-Alpert-type ion gauge. The pumps maintain a base pressure of approximately $1 \times 10^{-7}$ Torr.
2.2 Laser System

The laser system used is a Coherent CR-699-21 ring dye laser pumped by a Coherent Innova 400 (I-400) Argon ion laser. Coherent describes the CR-699-21 as a single frequency, tunable, actively stabilized, unidirectional traveling wave, ring dye laser capable of locked scanning across a 30 GHz range. As with all dye lasers, the primary advantage of the system is tunability. The operational frequency range of the laser is determined by the specific dye used, in this case Rhodamine 6G with an optical fluorescence range from ~ 560 nm to ~ 625 nm. The dye enters the laser cavity via a jet which produces a "ribbon" of dye oriented at Brewster's angle. The dye is then optically excited by approximately 10 W of 514.5 nm light from the I-400. To obtain UV output, a Potassium Dihydrogen Phosphate (KDP) frequency doubling crystal has been added inside the cavity of the dye laser. The crystal converts \( \sim 1 \times 10^{-3}\% \) of the fundamental radiation circulating in the laser into the UV by second harmonic generation. Using Rhodamine 6G, UV radiation at the wavelengths necessary to excite potassium atoms into Rydberg states from \( n \approx 10 \) to \( n \approx 1000 \) can be generated. Figure 1 offers a helpful reference for the following description of the internal elements of the dye laser cavity.

Stabilization of the system requires several different elements. To maintain unidirectional operation, an optical diode found on a Faraday rotator is included inside the ring dye laser. Controlling changes in frequency requires a pressure and temperature controlled, scanning, confocal interferometer which acts as a reference cavity for the CR-699-21. A feedback loop from the reference cavity operates a piezoelectric mounted folding
Fig. 1 Schematic diagram of the internal elements of the CR-699-21 ring dye laser cavity.
mirror to eliminate the high frequency jitters and a scanning Brewster plate to adjust for low frequency drifts.\textsuperscript{12,13} The $\sim 40$ MHz/ hour, long term drift of the reference cavity necessitates an external stabilization device, called 'Superlock'. Superlock improves the stability to 1 MHz/ day (2 MHz UV) by locking the dye laser frequency to an ultra-stable commercial helium-neon laser via a temperature-stabilized confocal Fabry-Perot etalon.\textsuperscript{14} This system allows a stable scan range of 500 MHz which can be controlled manually or by computer.

Single frequency operation is obtained through the adjustment of a combination of three internal filters which also act as the tuning elements for the dye laser. The filter stack is designed such that only a single longitudinal mode is allowed to oscillate in the ring cavity. Coarse tuning is provided by a crystalline quartz, birefringent filter which could be tuned continuously through the entire available bandwidth if used alone, but, in conjunction with the other two elements, it is limited to steps of 20 GHz increments. The finer tuning is accomplished using the two remaining filters, a 0.5 mm thin etalon and a 10 mm thick etalon. The three filter combination produces an effective line width of $\sim 250$ kHz. Without including Superlock, it is possible to scan over a 30 GHz range while maintaining mode-locked operation. Such tuning is accomplished by changing the length, and therefore frequency, of the reference cavity by using the galvo-driven Brewster plate located within the reference cavity.
2.3 Dual Time-of-Flight Mass Spectrometer

As shown in figure 2, the present apparatus consists of two nearly identical time-of-flight mass spectrometers configured in vertical symmetry about the interaction region. Parallel fine mesh copper grids define acceleration and drift regions within each, and the spectrometers both terminate in a position sensitive detector.

The grids are separated by macor spacers to isolate each region, except the drift region grids which are electrically coupled through a stainless steel tube. Each region can be individually biased to allow more accurate time focusing of the ion signals. To obtain good focus the electric fields must be well defined and uniform. The condition of the grids is a principal factor in determining this uniformity. To prevent field penetration from region to region the mesh for the grids needs to be fine, 300 lines per inch (lpi) is used for the interaction region and nothing less than 70 lpi is used for any grid. To create a homogeneous electric field, the mesh must be smooth, without tears or holes, and must lie parallel to the adjacent grids. To obtain such consistency, a tensioning device is used to stretch the mesh taut over a copper grid ring, and then, the fragile mesh is electroplated onto the ring. Each ring mounts to a copper plate to which the appropriate bias voltage is applied.

Ion arrival positions and times are measured using position sensitive detectors which consist of two microchannel plates and a resistive anode. The plates are oriented such that no particle can pass through without contacting at least one of the plates. The resulting cascade of electrons strikes the anode which formulates the position data. The anode determines the position from data read by sensors located its the four corners. By measuring
Fig. 2 Schematic diagram of the dual time-of-flight mass spectrometer including beam orientation
the relative current pulse magnitudes at each corner, the PSD can provide the impact position with a spatial resolution of \( \sim 0.15 \) mm for \( C_{60} \). The timing signal is determined using the current pulse from the back of the second microchannel plate.

As shown in figure 2, two extra closely spaced grids are included in the lower mass spectrometer to create a high-field region. The grids are again copper mesh and electrically isolated. The separation is reduced from \( \sim 3/8'' \) (0.95 cm) to 1/8'' (0.32 cm) which allows production of a large electric field between them, up to 20 kVcm\(^{-1}\). (The grid rings have been rounded at the edges to prevent arcing.) This electric field is used to determine the field detachment characteristics of the product ions.

2.4 Data Acquisition and Analysis System

The data acquisition and analysis system consists of a Motorola VME 131 XT computer that communicates with the experimental hardware via a CAMAC (Computer Automated Measurement And Control) system along with various NIM modules. This combination produces the various triggers, delays, and gates necessary for controlling the experiment and records the data. The actual timing of an experimental cycle will be discussed in the experimental procedures section 3.3, but the various crate components and their uses will be described here. Figure 3 shows a block diagram of the electronic components and is helpful reference.

The electronic modules have three main functions - gating pulses, converting signals, and monitoring the timing. Several simple 416A Gate and Delay units or in-house delay modules are used to achieve the
Fig. 3 Block diagram of the data analysis and acquisition system
appropriate experimental timing. Also, a dual coincidence unit (DCU), built
in-house, allows gating of the signal from the position sensitive detector
(PSD). The input of the DCU is only output when the gate, a second input, is
held high. Two separate signals can be gated by the DCU simultaneously. In
addition to the module delay units, a Wavetek pulse generator acts as an
inhibit or gate for the scalar module used to record the positive ion signal.
Converting the signals is accomplished using both a LeCroy Quad
Discriminator which discriminates and transforms the output pulse from the
PSD into NIM outputs and also a 12 bit Jorway analog to digital converter
(ADC) which digitizes the 0-5 volt analog position signal from the bottom
PSD. A quad event timer (QET) reads the time data in the form of TTL pulses
and converts it to a digital signal for the computer. The QET uses a single
initiate but allows monitoring of four timing signals with separate stop
pulses.

2.5 Potassium Oven

Within the smaller of the two vacuum chambers, a stainless steel oven
provides the effusive potassium beam from which Rydberg atoms are
formed. One gram of potassium metal is placed inside the oven body, and
the oven is heated to about 300°C, well above the melting point of
potassium which is ~60°C. Its temperature is monitored and maintained
using two thermocouples in conjunction with a temperature controller. A
0.040" (0.10 cm) diameter aperture collimates the beam before it passes into
the interaction region of the dual mass spectrometer. The aperture can be
heated by a tungsten wire coiled around a macor mount. Heating is not
necessary during operation and is not recommended due to production of a background electron signal. But the aperture is heated while cooling the oven to prevent potassium condensing on the aperture and hence clogging it.

2.6 \textit{C}_{60} Oven Design

As shown in figures 4a and 4b, the \textit{C}_{60} source is constructed from an effusive copper oven that sits in a boron nitride crucible which electrically insulates it from the heating filament, a tungsten basket. Both the crucible and the filament are commercial products. \textit{C}_{60} is loaded from the front of the oven, through a 0.05" (0.13 cm) diameter aperture located approximately 3/4 of the diameter from the bottom of the oven face. Because the aperture is offset from center the holding capacity of the oven is dramatically increased; about 450 mg of \textit{C}_{60} constitutes a full load. The oven also has attachment points for a thermocouple and a biasing wire.

Heating the filament requires a high current, between 25 and 30 amps. Two straight copper bars, to which the filament is screwed down, provide adequate means of conducting such current. The power leads attach to the bars through in-line connectors affixed to copper posts protruding from the back of each bar. The copper bars are fastened to 1/2" (1.27 cm) ceramic spacers and are mounted on a 1/4" (0.64 cm) thick aluminum baseplate, which has numerous through holes for the various other attachments.

Two heat shields surround the assembly. The inner shield is made of molybdenum and screens the top, bottom, and sides of the oven. The shield attaches directly to the copper bars and has two parts. The upper section curves over the filament but does not contact the opposite copper bar. The
Fig. 4 Schematic diagram of the $C_{60}$ oven and support assembly
lower section attaches on the other copper bar and extends underneath the filament. The outer heat shield attaches to the aluminum baseplate using 1/2" (1.27 cm) ceramic spacers and surrounds the oven assembly. It is made of stainless steel 0.010" (0.25 mm) shim and is bent to minimize radiative loss from the front and sides.

The defining aperture for the $C_{60}$ beam is outside the outermost shield and consists of an aluminum mount to which a stainless steel shim with a rectangular aperture of dimension $\sim 0.156" \times 0.05"$ (0.40 cm $\times 0.13$ cm) is spot welded. The rectangular aperture produces a beam width of $\sim 1/2"$ (1.27 cm) at the center of the interaction region and is aligned with the 0.05" (0.13 cm) aperture on the copper oven before welding to insure maximum $C_{60}$ flux in the interaction region.

To prevent any spurious ions or electrons produced by the filament or the oven from entering the interaction region, two sets of deflection plates mount to the baseplate beyond the aperture. The inner set of deflection plates are electrically isolated, using ceramic spacers, from the baseplate and from each other. Therefore, the voltage on each plate can be controlled independently. The outer set of deflection plates are connected directly to the baseplate which is maintained at ground. The inclusion of these plates generates a field "wall" between the $C_{60}$ oven apparatus and the interaction region. Hence, any ions or electrons which escape from the fields created by the other biased elements (the outer heat shield, the oven, or the filament) are removed and do not affect the observed signal.

The oven mount requires multidimensional alignment. The baseplate assembly attaches to a 4" (~10 cm) post in a 3" (~7.6 cm) post holder. The post holder fastens to a slotted baseplate, which provides forward and backward
positioning capabilities. Both the vertical adjustment and the angular adjustment are controlled through the post and holder and are locked by a set screw. The slotted baseplate attaches to a 5" (12.7 cm) X 5" (12.7 cm) X 1/4" (0.64 cm) aluminum bottom plate with tapped holes drilled in a 1/2" (1.27 cm) interval grid to allow lateral positioning.

The alignment procedure for the assembly as well as the bias conditions will be described in section 3.1.
CHAPTER 3:
Experimental Procedures

In preparation for the experiment, the carbon 60 oven is aligned and any residual electric fields present in the interaction region are minimized. Following the description of these initial steps, the general operation and timing of the experiment along with the procedure for data analysis is presented.

3.1 C$_{60}$ Beam Preparation

The C$_{60}$ oven and support assembly have been described previously, but the correct alignment of the beam, the preparation of the sample, and the biasing of the various components are essential to maximize the signal and to minimize spurious backgrounds. The alignment of the C$_{60}$ oven, both vertically and horizontally, determines how much and what part of the beam intersects the potassium beam. Slight shifts in the C$_{60}$ beam orientation can produce drastic effects on the signal observed. If the height is incorrect, the C$_{60}$ beam will lie in a different plane than the K-beam and no interaction can occur. The vertical height of the beam is aligned with the center of the interaction region by using the symmetrical slots in the μ-metal shield as reference. The horizontal and angular alignment determine where the carbon 60 interacts with the potassium. If the beams cross before the region where excitation of the potassium occurs, no Rydberg atoms will be available for collisions. If the intersection is too far in front of the excitation location,
the product ions from the $C_{60}$-Rydberg atom reaction have enough time to drift laterally beyond the edge of the PSD and thus to not be detected. The horizontal and angular adjustments are accomplished in conjunction such that the oven apparatus does not electrically short to the $\mu$-metal shield or extraction plates and so that the $C_{60}$ beam crosses the potassium beam at an oblique angle. The angle of intersection is such that maximum $C_{60}$ flux passes through the K-beam slightly forward, as seen by the K-beam, of the excitation region. The rectangular aperture of the $C_{60}$ beam allows for small errors in angular alignment. Once the appropriate arrangement is obtained the vertical, horizontal, and angular positions are maintained by set screws and reference markings.

After the 99.5% pure $C_{60}$ sample, produced by SES Research Inc. using the contact-arc method, is loaded into the copper oven (i.e. Knudsen cell) and aligned in the chamber, the sample is pretreated by baking at $\sim 200^\circ$C for $\geq 12$ - 18 hours. Following the baking process, which is necessary to eliminate any high vapor pressure contaminants and is suggested by previous experiments, which also sublimate $C_{60}$ using a Knudsen cell, the sample is ready to use. Prior to heating to the $\sim 600^\circ$C needed to create an effusive beam, the oven is allowed to cool to near room temperature. Furthermore, after each 6-7 hour data run a thorough cleaning of the oven is necessary before reloading to remove a residue leftover after sublimation. The residue is suggested to be the result of polymerization of a portion of the $C_{60}$ during heating.

During the experiment various elements of the $C_{60}$ apparatus, including the filament, the outer heat shield, the copper oven, and the individual deflection plates, are biased to minimize the background signal.
The background signal can be distinguished from the $C_{60}^-$ signal by noting its location on the position sensitive detector.

### 3.2 Field Minimization

As mentioned briefly before, electric and magnetic fields strongly affect Rydberg atoms, especially for higher $n$ values. At $n = 125$ an electric field of $\sim 1.3$ Vcm$^{-1}$ is sufficient to completely ionize the Rydberg atom, and electric fields with much smaller magnitudes can Stark shift the atomic states enough to prevent formation of Rydberg atoms at the expected laser frequency. Therefore, elimination of all unwanted fields is essential for working in the high $n$ regime. The \(\mu\)-metal shield surrounding the entire dual mass spectrometer protects from stray magnetic fields, but strong residual electric fields require compensation through external biasing.

The technique used to determine the magnitude of the stray electric fields involves the Stark effect. When the atom is placed in an electric field, the Stark effect splits a single Rydberg state into a manifold or continuum of states. In other words, the electric field breaks some of the energy degeneracy. The energy shift caused by the Stark effect is proportional to the square of the applied field. Application of the effect for finding the residual field present in a region is described in detail in reference 17, but a brief description of the process follows. The laser is slightly detuned to the red of a specific $4s-np$ transition, and the Rydberg production is monitored as a function of an external bias applied between the grids defining the interaction region. Typical results for $n = 100$ Rydberg atoms are shown in figure 5. The two
Field Zero at n=100
Signal vs. Applied Voltage

Fig. 5 Electric field minimization using the Stark effect. Rydberg atom formation signal in arbitrary units shown as a function of applied electric field in eV.
separate peaks in figure 5 correspond to the applied bias values which shift the Rydberg state into resonance with the new laser frequency. If no residual fields exist in the interaction region, the peaks should appear symmetrically about zero energy because the absolute value of the field strength in the interaction region is what causes the np state of the Rydberg atom to Stark shift. However, if the peaks center about a value other than zero, a stray field is present, and the offset from zero represents the magnitude of the residual field.

After determining the magnitude of the stray field, a bias is applied to the interaction plates to null this. Therefore, the center of the interaction region is sufficiently field free to allow production of Rydberg atoms with principal quantum numbers up to \( n = 150 \).

3.3 *Experimental Operation*

The apparatus has been described previously and figure 2 shows the dual time-of-flight mass spectrometer and the orientation of the beams. The experiment is operated in a pulsed mode, and the timing diagram in figure 6 shows the progress of a typical data acquisition cycle. Both diagrams, as well as the block diagram in figure 3, are helpful references for the subsequent description. The cycle begins with the computer initiating a system start pulse. The system start triggers both a pulse generator and, after a delay, the acousto-optic modulator (AOM). The pulse generator applies a -600 V voltage pulse to the upper of the two planar fine-mesh grids defining the interaction region while the lower is maintained at ground. The resulting
TIMING DIAGRAM

System Start

High Voltage Sweep Pulse

Light Pulse

Extraction Pulse Trigger

High Voltage Extraction Pulse

Quad Event Timer Start

Bottom PSD Strobe Gate

Scalar Initiate

Quad Event Timer Stops
For K⁺

For C₆₀⁻

System Stop

Time

0 μs  10 μs  20 μs  30 μs  40 μs  50 μs  60 μs

Fig. 6 Timing diagram representing one data acquisition cycle.
field removes any spurious ions or electrons from the region. Then, the output of the intra-cavity doubled CR699-21 ring dye laser, which is chopped into pulses of typically ~5 µs duration with a pulse repetition frequency of ~5 kHz by the AOM, crosses the potassium beam at normal incidence. The length of the laser pulse determines the duration of Rydberg formation. Rydberg atoms are formed through single photon excitation of the potassium atoms into a selected np state. Excitation occurs in near-zero electric field at the center of the interaction region.

The C\textsubscript{60} beam crosses the Rydberg beam at an oblique angle and slightly forward of the excitation position (as seen by the K-beam). Interactions are allowed to occur for a further specified time period (on the order of two microseconds) after the end of the laser pulse. After the specified collision time, the pulse generator is again triggered, and any charged products are expelled from the interaction region by application of a second -600 V voltage pulse to the upper grid. This creates a field in excess of 300 Vcm\textsuperscript{-1}, which also is sufficient to ionize any remaining Rydberg atoms. The extraction pulse trigger also signals the quad event timer (QET) to start and enables the bottom position sensitive detector strobe gate which determines how long the detector looks for data. The extraction pulse accelerates the K\textsuperscript{+} ions into the upper mass spectrometer, and the K\textsuperscript{+} signal is recorded by a counter because no specific position or time distribution data is needed. Similarly, the negative ions are accelerated into the lower time-of-flight mass spectrometer. When an ion strikes one of the position sensitive detectors, the QET is triggered to stop and, in the case of the top PSD, the scalar is initiated. Finally, the system stop pulse arrives at the computer after a ~60 µs delay.
Time-of-flight techniques are used to identify the product ions and to ensure that they result from the reaction of interest. The observed signal is identified as $C_{60}^-$ using the mass spectrometer which has an uncertainty of $\sim \pm 5$ amu for carbon 60. Furthermore, systematic tests support the identification of $C_{60}^-$ ions as products from potassium Rydberg atom - $C_{60}$ collisions. The signal vanishes if either the carbon 60 beam or the potassium beam are absent. Also, if the laser is either detuned from resonance or completely absent, thereby eliminating Rydberg excitation, the $C_{60}^-$ signal disappears. These simple tests imply that the source of the $C_{60}^-$ signal must be a $C_{60}$ - Rydberg electron interaction. Another test of the validity of the signal is to increase the collision time and note the effect. Logically, the collision time should be proportional to the number of $C_{60}^-$ ions produced, and in fact a linear relationship is observed. In addition, the position information indicates that the $C_{60}^-$ ions are formed in the location where the $C_{60}$ and Rydberg beams cross.

3.4 Data Analysis

On the basis of the nearly free electron model, the reaction rate for the interaction of carbon 60 with a Rydberg electron should equal the reaction rate for the interaction of carbon 60 with a free electron having a velocity equal to that of the Rydberg atom (for a population of electrons the velocity distributions must be equal). This reaction rate is calculated from the total probability per unit time that a reaction will occur. The probability of reaction with $C_{60}$ for an electron with velocity $v$ traveling a distance $dx$ through the $C_{60}$ beam with density $\rho$ is given by:
\[ dP = \rho \sigma \, dx \]  \tag{3.1}

where \( \sigma \) is the cross section and is a function of \( v \). Noting that \( dx = v \, dt \) the probability per unit time becomes:

\[ \frac{dP}{dt} = \rho \sigma(v) \, v \]  \tag{3.2}

To obtain the total reaction probability per unit time, i.e. reaction rate, equation 3.2 must be averaged over the velocity distribution \( f(v) \) of the entire electron population:

\[ \frac{d\bar{P}}{dt} = \rho \int_{0}^{\infty} v \sigma(v) f(v) \, dv \]  \tag{3.3}

Thus, if equation 3.3 represents the total probability per unit time that a \( C_{60}^- \) Rydberg electron reaction will occur, the rate at which \( C_{60}^- \) ions are formed per unit time is given by:

\[ \frac{dS}{dt} = \rho \, k \, N \]  \tag{3.4}

where \( N \) is the number of Rydberg atoms (i.e. electrons), \( S \) is the number of \( C_{60}^- \) ions observed and \( k \), the rate constant, is given by:

\[ k = \int_{0}^{\infty} v \sigma(v) f(v) \, dv \]  \tag{3.5}
Note that creation of a $C_{60}^-$ destroys a Rydberg atom. Thus, the change in the number of Rydberg atoms available for reaction per unit time must be equal and opposite the rate of $C_{60}^-$ formation given in equation 3.4 and is given by:

$$\frac{dN}{dt} = -\rho k N$$

(3.6)

The differential equation 3.6 has a simple solution:

$$N(t) = N(0)e^{-\rho kt}$$

(3.7)

which shows that the Rydberg atom population will decay exponentially with time. Substituting equation 3.7 into 3.5 gives:

$$\frac{dS}{dt} = \rho k N(0)e^{-\rho kt}$$

(3.8)

which also has a simple solution:

$$S(t) = N(0)\left[1-e^{-\rho kt}\right]$$

(3.9)

Assuming $\rho kt \ll 1$, $e^{-\rho kt}$ can be approximated by $(1-\rho kt)$. This assumption is valid for this work because the estimated values of $\rho$ (the $C_{60}$ beam density), $k$ (the absolute rate constant), and $t$ (the time of the extraction pulse) give $\rho kt = 10^{-5}$. Finally, equation 3.9 becomes:

$$S(t) = N(0)\rho kt$$

(3.10)

Equation 3.10 provides a means of calculating the rate constant for the $C_{60}$ - Rydberg electron reaction studied here with $N(0)$ equal to the total
number of Rydberg atoms initially formed and \( S(t) \) equal to the total \( C_{60}^- \) produced in a time \( t \).

An absolute rate constant for \( C_{60}^- \) production cannot be obtained because the \( C_{60} \) beam density cannot be measured directly. However, the beam density at the center of the interaction region can be estimated using published vapor pressure information and knowledge of the oven geometry. The number density along the beam line is given by:

\[
\rho_b = \frac{\rho_0 A}{4\pi r^2}
\]

where \( r \) is the distance from the aperture, \( A \) is the cross sectional area of the oven aperture, and \( \rho_0 \) is the number density inside the oven. The Ideal Gas Law gives:

\[
\rho_0 = \frac{P}{KT}
\]

with \( K \) as the Boltzman constant, \( T \) as the temperature and \( P \) the pressure in the oven. Over the range from 600 K to 800 K, the relationship between pressure and temperature is found experimentally to be given by:\(^9\)

\[
\log P = -\frac{9777}{T} + 11.582
\]

with the pressure measured in Pascals and the temperature in Kelvin. The experimental data for equation 3.13 is shown in figure 7 as a plot of \( \log P - \log s \) vs. \( 1/T \). Although the temperatures used in the present experiment exceed the temperature range used to determine equation 3.13, figure 7 shows little deviation of the fit from the data even at the endpoints.
Vapor Pressure Data for \( C_{60} \)

Log (P) - Log(s) vs. 1/T

Fig. 7  Thermodynamic determination of vapor pressure as a function of temperature for \( C_{60} \) from reference 9. Log (P) - Log (s) versus 1/T where s is an experimental constant.
Thus, extrapolation seems reasonable. Use of equations 3.11 - 3.13 yields a beam density in the center of the interaction region on the order of $\sim 10^9$ cm$^{-3}$, from which the absolute $C_{60}^-$ production rate constant, $k$, is estimated to be $\sim 10^{-8}$ cm$^3$s$^{-1}$ which is small but is comparable with that for many other electron-attaching targets. For example, $k$ is $\sim 6 \times 10^{-8}$ cm$^3$s$^{-1}$ for $C_7F_{14}$.$^{19}$ Also, $k \sim 10^{-8}$ cm$^3$s$^{-1}$ for $C_{60}^-$ is in accord with the value obtained in earlier Rydberg atom work using Cs($\eta p$) atoms.$^{18}$

Monitoring the $C_{60}^-$ production over an extended period of time of 5 - 6 hours shows that the $C_{60}^-$ signal decreases in time following what appears to be an exponential decay, as seen in figure 8. Because no other parameter changes during the time period of data acquisition, the $C_{60}$ beam density is assumed to be decreasing. The same characteristic decline has been observed repeatedly with each oven load and has been accounted for in the data analysis, as described below. No exact reason for the decay can be given, but the geometry of the oven is suspected to create a changing surface area for sublimation.

Monitoring the $C_{60}$ oven also provides a second means of estimating the absolute rate constant. The beam flux a distance $r$ along the beam axis from an effusive oven is given by:

$$F(r) = \frac{N_a}{\pi r^2} \quad (3.14)$$

where $N_a$ is the number of atoms escaping from the aperture per second. The average value of $N_a$ can be determined experimentally from the total mass of $C_{60}$ per oven load divided by the total runtime. Substituting this value into equation 3.14 and dividing by the average velocity, $\bar{v}$, of $C_{60}$ atoms gives $\rho_b$.
Fig. 8 Normalized $C_{60}^-$ signal as a function of time at $n = 40$. The solid line represents an exponential fit to the data.
along the beam line which can be used as before to determine the absolute rate constant. $\bar{v}$ can be determined thermodynamically by:

$$\bar{v} = 2 \sqrt{\frac{2kT}{\pi m}}$$

(3.15)

where $K$ is the Boltzmann constant, $T$ is the temperature in Kelvin and $m$ is the atomic mass. This method results in a value of $k \sim 10^{-8}$ cm$^3$s$^{-1}$ which agrees with the previous estimates.

Although an absolute rate constant cannot be measured, the $n$-dependence of the relative rate constants can be determined. From equation 3.10, taking a ratio of the $C_{60}^-$ signals formed in the same time interval by atoms with $n = n$ and $n = 40$, we obtain:

$$\frac{k_n}{k_{40}} = \frac{S_n}{S_{40}} \frac{N_{40}\rho_{40}}{N_n \rho_n}$$

(3.16)

where $S_n$, $N_n$, $S_{40}$, and $N_{40}$ are all measurable quantities and $\frac{\rho_{40}}{\rho_n}$ is the ratio of the beam densities. $S_n$ is obtained by recording the $C_{60}^-$ signal. By using computer software to window the $C_{60}^-$ signal in both time and position, the background signal can be reduced to an acceptable level, $\sim 4\%$ of the total signal. Because field-ionization and interactions with $C_{60}$ both produce a $K^+$ signal, the number of $K^+$ ions recorded is equivalent to the total number of Rydberg atoms, $N_n$, created by the laser pulse. These values provide the ratio $S_n / N_n$, which in essence is the $C_{60}^-$ signal normalized to the number of Rydberg atoms.
Several consecutive measurements are taken at each \( n \) value. Each set of data at a particular \( n \) is bracketed by data taken at \( n = 40 \) to account for the time dependence of the \( C_{60} \) beam density. By fitting the \( n = 40 \) data with an exponential (as a function of time) as shown in figure 8 and interpolating, the ratio of the beam densities can be obtained thereby giving the relative rate constants shown by equation 3.16. This ratio provides the \( n \)-dependence of the relative rate constants which is shown in figure 9. Figure 9 also includes the results of the earlier Rydberg electron transfer work using Cs(\( \eta \)p) atoms. The two sets of data have been normalized to each other at \( n = 40 \). Further discussion of the data is presented in section 4.3.

As a final test, fields of up to 20 kV cm\(^{-1}\) are applied in an attempt to induce electron detachment from the \( C_{60}^- \) ion. No effect is observed indicating that the electron is bound in an orbit which is not conducive to detachment by electric fields less than 20 kV cm\(^{-1}\). Further discussion of the electron binding characteristics can be found in section 4.4 of this thesis.
Fig. 9 Rate constant for formation of $C_{60}^-$ ions as a function of effective principal quantum number $n^* = n - \delta$, where $\delta$ is the quantum defect. ■, present measurements, $K(np)$; ▲, earlier measurements, $Cs(np)$. The two sets are normalized to each other at $n = 40$. 
Chapter 4
Results and Discussion

The electron attachment characteristics of Buckminsterfullerene have been investigated experimentally, using both free electron and Rydberg atom techniques, and theoretically. The free electron results point to p-wave attachment at low electron energies, which is consistent with the theory. Theoretically, symmetry arguments indicate the absence of an available $C_{60}^-$ valence state with angular momentum quantum number $\ell = 0$ to which the electron can bind. Therefore, s-wave attachment (i.e. into an $\ell = 0$ bound state) is not expected. With strictly p- and higher- wave attachment, a potential barrier exists which must be overcome for the electron to bind. The free electron experiments suggest this is indeed the case because a sharp decrease in the attachment rate constant is observed at low electron energies. However, the Rydberg atom work reveals no such sharp decrease. The following section briefly describes the experimental and theoretical studies demonstrating the discrepancy and discusses possible explanations to account for it.

4.1 $C_{60}$ Theory

A general background including the calculated internal structure and bonding of neutral $C_{60}$ is necessary before the anomalous effects involving anion formation can be discussed. Several papers have addressed the structure of $C_{60}$, including its electronic energy levels and the distribution of
electrons to obtain a stable configuration.\textsuperscript{8,21} Each carbon atom must have four bonds. In the Buckminsterfullerene, three of those bonds lie on the surface of the sphere and are $\sigma$ bonds. The final bond is a $\pi$ bond, and to zeroth order approximation the sixty electrons involved can be considered as a sea of electrons on the inner and outer surfaces of a sphere.\textsuperscript{3,8} The electrons must fill thirty orbitals and create closed shells to ensure stability of the molecule. In the free-electron-molecular-orbital approach, the energy levels have a degeneracy of $2\ell + 1$ where $\ell$ refers to the angular momentum quantum number of the level. The free-electron-molecular-orbital model alone predicts an unstable structure with the following electron distribution:

\begin{equation}
(l = 0)^2(l = 1)^6(l = 2)^{10}(l = 3)^{14}(l = 4)^{18}(l = 5)^{10} \quad (4.1)
\end{equation}

The $\ell = 5$ orbital has a degeneracy of 11, and can accommodate 22 electrons. Thus, it is not a closed shell. However, Buckminsterfullerene has icosahedral symmetry which offers a solution to explain the stability dilemma.

Without delving too deeply into the fundamentals of group theory, the basic resolution evolves from the symmetry of $C_{60}$ which allows decomposition of the $\ell$ orbitals into the irreducible components of the icosahedral group, $I_h$.\textsuperscript{8} Transforming from spherical to icosahedral symmetry divides the orbitals into narrower levels. The degeneracies of the new levels sum to the appropriate value for the total degeneracy of the original $\ell$ orbital. For example, the $\ell = 5$ orbital breaks into three levels, the $t_{1u}$, $t_{2u}$, and $h_u$ with degeneracies of 3, 3, and 5 respectively. Similar level splittings occur for $\ell = 0$ to $\ell = 4$. The ten electrons in the $\ell = 5$ orbital can fill the $h_u$ level, the lowest of the three, resulting in a stable closed shell. The remaining $t_{1u}$ becomes the
lowest unoccupied molecular orbital (LUMO). The $t_{1u}$ level has an angular momentum of $\ell = 1$. Consequently, no $\ell = 0$ state is available for attachment, which implies no s-wave attachment. The same result exists when including electronic-vibrational coupling within the molecule.

The details of Jahn-Teller coupling are beyond the scope of this work, but a brief description is necessary for demonstrating the null effect it has on the angular momentum of the LUMO level. The Jahn-Teller theory basically proposes that electronic orbital degeneracy of the electrons essential to the binding of a molecule automatically implies nuclear instability of that molecule. In other words, it is impossible for the nuclei to remain in a stable configuration if the binding electron orbitals are free to oscillate between arrangements while maintaining the same energy. The nuclear instability manifests itself in forces which tend to destroy the molecular symmetry. The forces can be viewed as resulting from electronic-vibrational coupling, i.e. the Jahn-Teller effect/Jahn-Teller distortion.\textsuperscript{7} In the case of $C_{60}$, theorists have determined, by applying group theory once again, that a d-wave-like, fivefold-degenerate, vibrational mode couples strongly to the LUMO $t_{1u}$ level. Semiclassical calculations of the electron-vibron interactions are shown in detail in Ref. 5 including calculation of the Hamiltonian and eigenfunctions representing the distortions caused by the coupling. The result of these computations is the selection rule for the molecular angular momentum, $L$. As a consequence of the rotational part of the wavefunction needing to be invariant under inversion, the selection rule becomes:

$$(-1)^{L+n} = 1$$

(4.2)
Obviously, in the ground state, $n = 1$, $L$ must equal 1, not 0. Therefore, regardless of whether coupling is taken into account, no valence $C_{60}^{-}$ state should exist with angular momentum equal to 0 which can provide a means for s-wave attachment.

### 4.2 Free Electron Experiments

Several free electron experiments\textsuperscript{18,22,23,24} have been done with $C_{60}$ which support the theoretical prediction of the absence of s-wave attachment. Most of the published work consists of a chronological set of experiments which consistently introduce improvements, either instrumental or analytical, over the previous studies. A summary of the central group of experiments and their results follows and provides a basis for comparison with the Rydberg electron transfer results presented in section 4.3.

All the free electron studies use a "hot" $C_{60}$ beam which implies a wide distribution of vibrational and rotational levels. The first\textsuperscript{22} free electron-$C_{60}$ experiment used a crossed-beam arrangement and an electron multiplier to detect the collisional products. The data showed electron attachment to $C_{60}$ at electron energies up to $\sim 12$ eV. An analysis of the dependence of the attachment rate on electron energy was attempted, but due to a limited beam resolution, on the order of $\sim 0.2$ eV, the low energy regime could not be explored in detail.

As a follow-up investigation, a flowing afterglow/Langmuir probe (FALP) experiment\textsuperscript{23} was used to study attachment at lower energies, from 30 meV to 0.5 eV. The results of the FALP study reveal a decrease in the rate constant for electron capture by $C_{60}$ at energies below $\sim 0.26$ eV. This decrease
implies an apparent "activation energy" or potential barrier which the electrons must overcome to attach suggesting a p-wave attachment process which agrees with the theoretical predictions.

Motivated by such findings, the initial crossed beam experiment was repeated\textsuperscript{24} using an electron monochromator to improve the resolution and thereby allow lower energy electron attachment studies. Analysis of the data, which involved an "unfolding" process and a calibration against the FALP results (neither method is adequately described), suggested an activation energy of $\sim 0.24 \text{ eV}$. This agrees well with the FALP result as well as with theory.

Recent independent work by Huang et al.\textsuperscript{18} includes results from a crossed-beam free electron experiment as well as data from a Rydberg atom-$C_{60}$ attachment study. In both cases, the $C_{60}$ is "hot" as in the previous investigations. The crossed beam data are consistent with p-wave capture. However, where the previous results show a $\sim 0.26 \text{ eV}$ potential barrier, Huang et al. report a threshold of $0.15 \pm 0.05 \text{ eV}$. Huang et al. claim the ion extraction field present in the earlier studies changed the energy distribution and resolution at low energies and hence accounts for the differences between the two sets of data. The interesting aspect of the recent work involves the Rydberg electron transfer results which will be discussed, in conjunction with the current Rydberg atom study, in the next section.

Overall, the general consensus of the free electron work, in agreement with theory, is that $C_{60}^-$ formation occurs through a p- or higher-wave process. The attachment appears to have an activation energy in the range $\sim 0.15 - 0.26 \text{ eV}$. A comparison of these results with the Rydberg data is presented in section 4.4.
4.3 Rydberg Electron Transfer Experiments

Rydberg atom-$C_{60}$ collisional studies were first undertaken using cesium Rydberg atoms\(^{18}\) with effective principal quantum numbers, \(n^* = n - \delta_e\), in the range \(25 \leq n^* \leq 40\), and the present work extends these data using potassium Rydberg atoms with \(35 \leq n^* \leq 125\). Both experiments indicate that \(C_{60}\) attaches electrons from even high \(n\) Rydberg atoms, i.e. attaches low energy electrons. Figure 9 presents the experimental results for both studies in the form of the relative rate constant as a function of \(n\).

In accordance with the independent particle model described previously in section 1.1.1, the rate constants for high \(n\)-Rydberg electron transfer should be equal to the rate constants for attachment of free electrons having the same velocity distribution as the Rydberg electrons.\(^{1,25}\) Thus, the rate constant should be given by:

\[
k = \int v\sigma_e(v)f(v)dv
\]  \hspace{1cm} (4.3)

where \(\sigma_e(v)\) is the cross section for attachment of free electrons with velocity \(v\), and \(f(v)\) represents the Rydberg electron velocity distribution. The electron velocity distribution for Rydberg atoms is dominated by the orbital motion of the electron about the Rydberg core which is much faster than the relative motion of the core for the \(n\) values used in this work. It is obvious from figure 9 that the relative rate constant appears to be independent of \(n\), i.e. the Rydberg electron velocity distribution, for the higher \(n\) values. Examination of equation 4.3 reveals that the cross section must be proportional to \(1/v\) if \(k\) is independent of \(n\). According to the Wigner threshold laws, s-wave
attachment (i.e. into an \( \ell = 0 \) bound state) is characterized by a \( 1/v \) cross section. Other electron-attaching targets, for example \( SF_6 \) or \( C_7F_{14} \), have shown the same behavior. However, free electron studies using the other targets support the Rydberg electron transfer results indicating s-wave capture which is not the case for \( C_{60} \). The free electron experiments described above indicate that \( C_{60}^- \) forms through a p-wave process, which is characterized by a cross section varying as \( v \) and vanishing as \( v \to 0 \). The experimental inconsistency merits discussion and gives rise to speculation about possible mechanisms allowing s-wave capture by \( C_{60} \).

4.4 Discussion

The comparison of Rydberg and free electron experiments requires careful consideration of the electron energies involved. The extremely small energies in the Rydberg attachment experiments are estimated using the median velocity \( v_m \) of the electrons attached at each \( n \). The median velocity is determined such that the value of equation 4.3 integrated from 0 to \( v_m \) is half the value over the range 0 to \( \infty \). The median collision energy is given by \( m v_m^2/2 \), assuming s-wave capture, and the range of median electron energies encompassed in figure 9 is from \( \sim 7 \text{ meV} \) (\( n = 20 \)) to \( \sim 170 \mu\text{eV} \) (\( n = 125 \)). (The mean kinetic energies of the Rydberg electrons are somewhat larger than the collision energies.) The electron energy distributions appropriate to the free electron studies are difficult to measure precisely, due to the limited experimental resolution. Also, the presence of even weak residual fields can accelerate the electrons and thereby discriminate against low energy attachment. Because of the inherent difficulties at very low
energies in free electron work, it is feasible that the Rydberg electron transfer studies could identify an extremely low energy structure that the free electron studies may overlook. In fact, such a discrepancy is not unprecedented. Previous research using $c\cdot C_7F_{14}$ indicates discrepancies between data obtained using electron swarm techniques $^{26,27}$ and Rydberg electron transfer $^{19}$ or low energy photoelectron methods. $^{28}$ The sharp decrease in cross section at low electron energies reported in the swarm work is not seen in the other studies, which suggest an s-wave process.

Nonetheless, s-wave attachment to $C_{60}$ remains an intriguing result since the theory predicts no available $\ell = 0$ state into which the electron can bind. An explanation must be presented that points out any possible inadequacies of the theory or any theoretical oversimplifications leading to the discrepancy.

Dissociative attachment to a contaminant in the $C_{60}$ sample should be considered since Buckminsterfullerene has been observed to form adducts with oxygen and methane, as well as a number of other compounds. $^{29}$ Plus, the electron affinity of $C_{60}$ is 2.65 eV which is sufficient to provide energy for dissociation. However, the $C_{60}$ used is specified to be $\geq 99.5\%$ pure. Supposing the signal is due to electron attachment to one contaminant comprising the remaining 0.5%. This would imply that the rate constant for the reaction involving the contaminant species would be $\sim 2 \times 10^{-6}$ cm$^3$s$^{-1}$. A rate constant on the order of $\sim 10^{-6}$ cm$^3$s$^{-1}$ is enormous for such a reaction. This also assumes the contaminant in the sample consists of only one species, which is unlikely. It is much more feasible that several different contaminants contribute to the $\leq 0.5\%$ impurity, not all of which will attach electrons. This implies an even larger rate constant than $\sim 10^{-6}$. Also, $C_{60}^{-}$
formation is seen for several different $C_{60}$ samples, each of which is prebaked to reduce the high vapor pressure contaminants. Taking all these details into consideration, dissociative attachment seems a highly unlikely source for the signal observed.

To explain this observation of $C_{60}^-$ formation in Rydberg atom-$C_{60}$ collisions, Huang et al. suggested that the electric field due to the presence of the Rydberg core-ion is sufficient to break the symmetry of the $C_{60}$ molecule and thereby allow low energy electron attachment. However, the current research extends the Rydberg data to much higher $n$ values. As $n$ increases from $n=40$ to $n=125$ the core-electron separation increases by a factor of ~1000. (Refer to Table 1.) If attachment is related to the presence of the core, the observed signal would be expected to change as separation between the core and the electron-$C_{60}$ interaction is increased. As seen in figure 9, no such $n$-dependence is apparent. Therefore, the argument citing symmetry breaking due to the presence of the Rydberg core seems unlikely.

Another possibility is that centrifugal distortion caused by molecular rotation of the $C_{60}$ molecule is important. There is a significant population of the high rotational states in the $C_{60}$ beam used here. The theory assumes spherical symmetry, but the molecular rotation could cause polar flattening. The inclusion of rotation in the theory would involve a rigorous and complicated analysis using group theory and is beyond the scope of this thesis. However, the effects of the distortion cannot be dismissed. The symmetry breaking caused by rotation could easily produce rovibronic coupling which might provide a low-energy $\ell = 0$ state for attachment.

Finally, the most intriguing explanation for the discrepancy is that $C_{60}^-$ formation results from a process in which the electron binds to its own image
charge. Image-charge-bound negative ions are not unprecedented; a previous study reports observation of such a state for Au$_6$. The mechanism of image-charge-binding results in a state which is similar to that seen in dipole-bound negative ions. For molecules with a sufficiently large dipole moment, it is possible for an electron to attach in a localized orbit about the positive end of the dipole. Similarly, for molecules with a large polarizability, the electron can induce a dipole moment. Binding to the induced dipole is basically equivalent to the electron binding to its own image charge. Such states are to be expected for C$_{60}$ if the binding energy of the lowest image-charge state is negative, for the appropriate range of parameters.

In order to examine this possibility further, C$_{60}$ is modeled as a dielectric sphere of radius R. The binding energies of the image states are found from a numerical solution of Schrödinger's equation outside the sphere. Solving the boundary value problem of a point charge in a vacuum a distance a away from the center of the sphere determines the correct electrostatic potential to use in the Hamiltonian. First, choose the coordinate axes for the problem such that the center of the sphere is at the origin and the point charge lies along the z-axis at z = a. The potential of the system consists of two terms: the potential due to the point charge and that due to the induced surface charge distribution of the dielectric sphere. Thus, at a location a distance r from the origin, the potential is given by:

\[
V(\bar{r}) = \frac{Q}{4\pi\varepsilon_0 |\bar{r} - \bar{a}|} + \frac{Q}{4\pi\varepsilon_0} \sum_p P_p (\cos \theta) \begin{cases} 
A_p r^p & \text{for } r < R \\
B_p r^{-(p+1)} & \text{for } r > R 
\end{cases}
\] (4.4)
where $Q$ is the magnitude of the point charge and $\varepsilon_0$ is the permittivity of free space. The unknown constants $A_p$ and $B_p$ are determined by applying the boundary conditions - that $V(r)$ and $\varepsilon \frac{\partial V}{\partial r}$ must be continuous at the surface of the sphere - to obtain a set of simultaneous equations:

$$B_p = A_p R^{2p+1}$$

$$\frac{\kappa p R^{p-1}}{a^{p+1}} + \kappa p R^{p-1} A_p = \frac{p R^{p-1}}{a^{p+1}} - \frac{(p + 1)}{R^{p+2}} B_p$$

where $\kappa$ is the dielectric constant of the sphere. The solution of equations 4.5 and 4.6 is:

$$A_p = \frac{1}{\kappa p + (p + 1)} \left( \frac{1 - \kappa}{\kappa} p \right)$$

$$B_p = \frac{\left( \frac{1 - \kappa}{\kappa} p \right) R^{2p+1}}{\kappa p + (p + 1)}$$

By substituting these values back into the potential in equation 4.4 and replacing the point charge term by its multipole expansion a complete solution is obtained covering three different regions of space: inside the sphere, between the sphere and the point charge, and outside the point charge. For the present purposes only the regions outside the sphere are of interest:
\[
V(\vec{r}) = \frac{Q}{4\pi\varepsilon_0} \left[ \sum_p \left( \frac{r^p}{a^{p+1}} + \frac{(1 - \kappa)p}{\kappa p + (p + 1)} \frac{R^{2p+1}}{a^{p+1}} \frac{1}{r^{p+1}} \right) P_p(\cos \theta) \quad R < r < a \right]
\]

\[
\left[ \sum_p \left( \frac{a^p}{r^{p+1}} + \frac{(1 - \kappa)p}{\kappa p + (p + 1)} \frac{R^{2p+1}}{a^{p+1}} \frac{1}{r^{p+1}} \right) P_p(\cos \theta) \quad r > a \right]
\]

(4.9)

It is clear that this potential satisfies the conditions that the two expressions share a common representation at \( r = a \), the location of the point charge. The potential experienced by the electron, or the point charge in our model, is the value needed for substitution into Schrodinger's equation. Using equation 4.9, the value of \( V(a) \) can be obtained by subtracting out the term due to the point charge because it cannot act on itself and by dividing the remaining term, representing the induced polarization potential, by two. The latter modification is a subtle effect due to the difference in potential energy between a static dipole and an induced dipole. The potential of an induced dipole, as with any electrostatic potential, is the effect of charge interaction and therefore, the potential energy is shared between the interacting charges. Thus, to determine the potential at the location of the point charge, the self-interaction must again be eliminated which necessitates using only one half the induced polarization potential. The final form of the potential experienced by the electron a distance \( z = a \) from the center of a dielectric sphere becomes:

\[
V(a) = -\frac{1}{2} \sum_{p=1}^{\infty} \frac{(\kappa - 1)p}{\kappa + 1} \frac{R^{2p+1}}{a} \quad (4.10)
\]

in atomic units, where \( \kappa \) is the dielectric constant of the sphere and \( R \) is the sphere's radius. The values for \( \kappa \) and \( R \) which define the appropriate parameter space are determined as follows.
The radius of the $C_{60}$ molecular cage is known to be 3.53 Å. However, to model image-charge binding, the radius of importance is the distance from the center of the sphere to the image plane. The image plane above a metal surface is located at one half the lattice constant plus 0.1 Å above the outermost surface layer. The average carbon-carbon bond length of 1.4 Å can be considered the lattice constant for $C_{60}$. Therefore, the appropriate range for $R$ extends from 4.2 to 5.2 Å.

For each $R$ value, the dielectric constant, $\kappa$, is calculated using the following equation:

$$\alpha = \frac{(\kappa - 1)R^3}{(\kappa + 2)}$$  \hspace{1cm} (4.11)$$

such that the polarizability, $\alpha$, of the sphere equals that of $C_{60}$. Calculations provide a lower limit of ~ 560 bohr$^3$ on the polarizability of $C_{60}$. A value of ~ 612 bohr$^3$ can be inferred using the Clausius-Mossotti equation (which relates the bulk dielectric constant to the molecular polarizability) and the measured values for the dielectric constant.

Figure 10 shows the calculated energy of the lowest ($\ell = 0$) image-charge-bound state as a function of $R$ for several values of $\alpha$. Within the defined parameter space, the binding energies are indeed negative and are on the order of tens of meV. This implies that $C_{60}$ should support an $\ell = 0$ image-charge state which could explain the $s$-wave process observed using Rydberg atoms. The long negative ion lifetimes could be explained by a rapid energy transfer into the vibrational modes of the $C_{60}$ core preventing autodetachment. Also, the results of the high field detachment tests described previously imply that the binding energies for image-charge states must
exceed a value of ~5 meV in order to withstand the 20 kVcm\(^{-1}\) fields applied, unless the image-charge state further decays into a valence state. This classical estimate supports the values seen in figure 10.
Fig. 10 Calculated energy of the lowest ($\ell = 0$) image-charge-bound state as a function of $R$ for the values of $\alpha$ indicated.
CHAPTER 5

Conclusion

In summary, Rydberg atoms have been used as a source of nearly free electrons in collisional studies with $C_{60}$. The electron scavenging properties of carbon 60 have been investigated through studies of the reaction:

$$C_{60} + R(n\ell) \rightarrow C_{60}^- + R^+$$

and the data indicate that attachment occurs even at very low electron energies. Furthermore, the independence of the relative rate constant on principal quantum number $n$ for high $n$ values indicates that $C_{60}^-$ formation is the result of an s-wave process. This observation disagrees with the results of earlier studies using free electrons, as well as with the theoretical work, both of which suggest the absence of an $\ell = 0$ state of $C_{60}$ to which the electron could attach. However, several mechanisms have been suggested to account for the discrepancies between theory and experiment. Possible explanations include centrifugal distortion which could break the symmetry of the fullerene. The effects of rotation are not included in the theory. Also, though unlikely, both dissociative attachment to a contaminant as well as symmetry breaking due to the presence of the Rydberg core have been considered. Finally, the existence of an image-charge-bound state is suggested. Model calculations representing $C_{60}$ as a dielectric sphere provide binding energies for the lowest ($\ell = 0$) image-bound state. The binding energies are negative and on the order of tens of meV and indicate that s-wave attachment of the electron by its own image charge may be possible. Although the above
mentioned mechanisms are only speculations, they provide legitimate explanations for the discrepancies observed in the various electron-$C_{60}$ collision experiments.
CHAPTER 6
Future Work

The process of image-charge-binding is intriguing and inspires exploration into similar attachment mechanisms, including quadrupole-bound states or image-charge states of different molecular systems. The methods presented in this thesis can easily be applied to other electron attachment studies. Previously, for example, Rydberg atom collisional studies have been performed with a number of targets resulting in observation of comparable states like dipole-bound negative ions.

Further investigation of electron capture by molecules with particular symmetry could be of interest. The spherical or icosahedral symmetry of $C_{60}$ provides a unique opportunity for modeling the image-charge-binding process. The question of whether other icosahedral molecules similarly support an image bound state is a natural extension of this work. The most logical choice for a target is $C_{70}$ which has a nearly spherical symmetry and shares the electron attachment characteristics of $C_{60}$. Also, $C_{20}H_{20}$ is a synthesized dodecahedrane with $I_h$ symmetry which could be an interesting target.

Another proposed investigation involves searching for higher multipole-moment binding. For example, a molecule having little or no dipole moment and a large anisotropic quadrupole moment would be a candidate for indication of a quadrupole-bound negative ion species. Previous studies using $CS_2$ show anomalous results which could possibly be attributed to such a bound state. $CS_2$ is a linear molecule with no dipole moment and a sizable quadrupole moment which is oriented appropriately
for binding an electron, i.e. with the positive charges on either end flanking a central negative charge. Further investigation of $\text{CS}_2$ is necessary to substantiate the binding mechanism, and other molecules having similar characteristics, like $\text{C}_4\text{H}_2$, diacetylene, would provide interesting comparisons to learn more about the properties of such a species. Another option is looking for quadrupole binding in non-linear molecules which have symmetries eliminating the dipole moment and encouraging a quadrupole, for example $\text{SF}_4\text{Cl}_2$. The extra dimension might affect the shape of the electron orbital or the binding energies and lead to other interesting possibilities.

In general, the future holds a plethora of opportunities for applying the methods of the present experiment to similar, unexplored attachment mechanisms.
REFERENCES


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