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Photophysics of Fullerenes: Thermionic Emission

R. N. Compton[1,2], A. A. Tuinman[1] , and J. Huang[3]

1. The University of Tennessee. Knoxville, Tennessee 37996
2. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6125
3. Ames Laboratory, Iowa State University, Ames, Iowa 50011

INTRODUCTION

The high degree of symmetry and large number of endohedral and exohedral π-type electrons of the hollow cage fullerene molecule give rise to many interesting photophysical properties of this new allotrope of carbon. Of the many possible isomers of a given fullerene, those satisfying the rule that the twelve pentagons be isolated (i.e. do not share a bond) are the lowest in energy. The isolated pentagon rule (IPR) isomers are also the structures found to be most prevalent in the synthesis of fullerenes. Of the 1812 possible isomers of C_{60} only the I_h form is produced in the arc discharge or laser ablation method. Reminiscent of a Georges Seurat *pointillism* painting, C_{60} at a distance appears as a spherical "atom" of K_h symmetry. Upon closer inspection the carbon atom "imperfections" give rise to the lower icosohedral symmetry of the cluster. The photophysical properties of C_{60} can be discussed by analogy to the "particle on a sphere" (see Savina et al.[1]). The energy levels for the 60 π electrons of C_{60} occupying the degenerate levels representing "electrons on a sphere," along with the filling of empty orbitals in I_h symmetry are shown below in Figure 1.

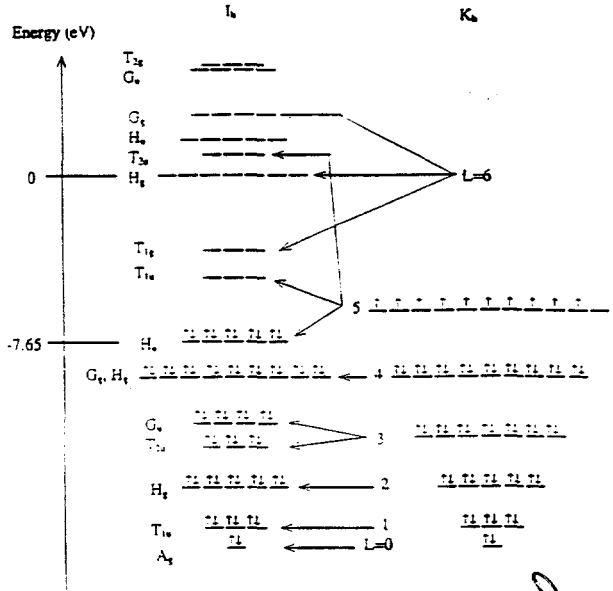

Figure 1. Energy levels occupied by 60 electrons on the surface of a sphere in K_h or I_h symmetry.

DISCLAIMER

The energy level of the highest filled molecular orbital, H_u, is located at the known ionization potential of C_{60}. Although the atomic (K_h) particle on a sphere model provides a reasonable HOMO-LUMO, gap the known degeneracy of the HOMO (5-fold) and LUMO (3-fold) as well as the diamagnetism of C_{60} is accounted for by assuming I_h symmetry, as inferred from single-line NMR and four-line IR spectra. The diamagnetism of C_{60} is driven by ring currents in the twelve isolated pentagons.[2] Fullerene double bonds are more localized than that of a purely aromatic system, a property that governs its addition chemistry as well. Photoabsorption of most fullerenes occurs as a result of transitions in the UV since the high degree of symmetry renders the low-lying transitions to be forbidden. The beautiful purple color of most C_{60} solutions results from the lack of photoabsorption in the blue (424-492 nm) and red (650 nm) region of the spectrum.[3] However, perturbations with the solvent and between fullerene solutes can make transitions more allowed and change the color of the solution greatly. Solvent effects on the optical limiting action of C_{60} solutions have been considered by Koudoumas et al.[4]

Photoabsorption in C_{60} is dominated by collective electronic motion, i.e. plasmons. Bertsch et al.[5] predicted these Mie-type plasmons which have been observed in many experiments at ~ 6 eV (π plasmon) and ~ 22 eV (π plus σ plasmon). Yoo et al.[6] and Hertel et al.[7] show a weak onset at the known ionization potential (7.65 eV) of C_{60} followed by a large peak in the cross section at ~ 25 eV which contains almost all of the expected oscillator strength (60). Although less well studied, plasmons may also strongly influence the electron impact ionization of C_{60}. As shown in Figure 2, we find a weak intensity threshold in the cross section for electron impact ionization for C_{60} as well.

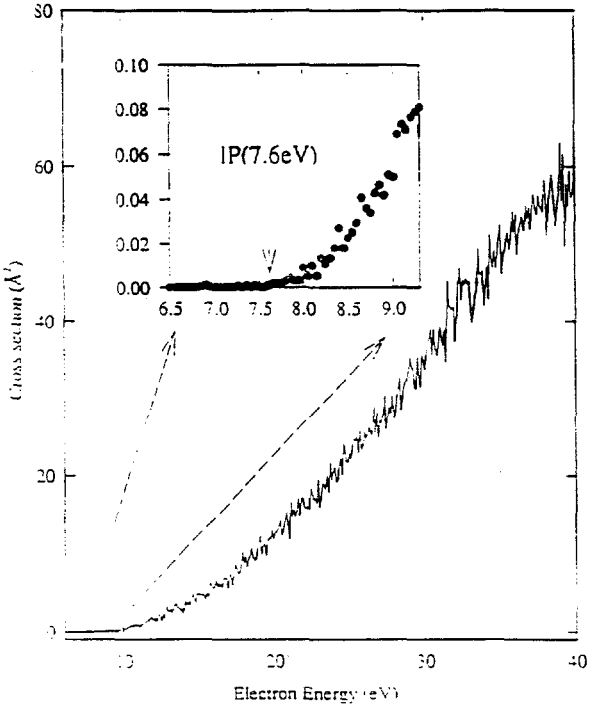

Figure 2. Relative cross section for the Electron impact ionization of C_{60}. Notice the apparent delayed onset is actually a weak cross section at threshold.

The energy scale for the high resolution electron beam (hemispherical sector electron energy analyzer) was calibrated using the onset of argon ions at 15.76 eV. Thus the presence of the plasmon at ~25 eV appears to affect the appearance of the threshold for electron impact ionization of C_{60}.

Thermionic Emission

Multiphoton ionization of fullerenes using long-pulse length (> n sec) lasers occurs mainly through vibrational autoionization. In many cases the laser ionization can be described as thermionic in analogy to the "boiling off" of electrons from a filament. Thermionic emission manifests itself as a "delayed" emission of electrons following pulsed laser excitation. The delayed emission of electrons for microseconds following multiphoton absorption of pulsed laser light has been reported for molecules,[3] metal clusters[9,10] fullerenes,[11-15] and metcars.[16] Klots[17,18] has employed quasiequilbrium theory to calculate rate constants for thermionic emission from fullerenes which seem to quantitatively account for the observed delayed emission times and the measured electron energy distributions.[16] The theory of Klots also accounts for the thermionic emission of C_{60} excited by a low power CW Argon Ion laser.[19] Figure 3 summarizes the mechanism believed responsible for thermionic emission in fullerenes. The triplet state offers a pathway (ISC) to the "heat bath" of the S_o ground electronic state.

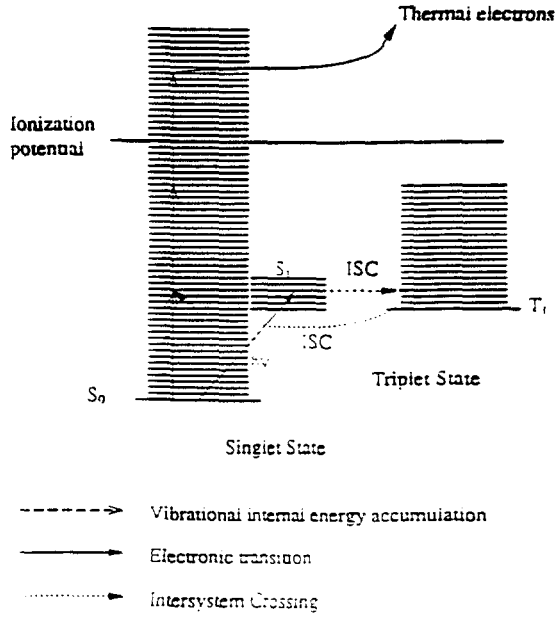

Figure 3. Mechanism leading to thermionic emission in C_{60}.

Recently Klots and Compton[20] have reviewed the evidence for thermionic emission from small aggregates where mention was also made of experiments designed to determine the effects of externally applied electric fields on thermionic emission rates. Such effects are well characterized in bulk metals and semiconductors. We have measured the fullerene ion intensity as a function of the applied electric field and normalized this signal to that produced by single photon ionization of an atom in order to correct for all collection efficiency artifacts. Figure 4 shows a Schottky plot for the ion intensity ratio C_{60}^-/Cs^+ produced by XeCl pulsed laser light (308 nm). 308 nm light efficiently ionizes cesium directly into the continuum, thus any variation in the Cs^- ion signal with electric field should represent a collection efficiency change.

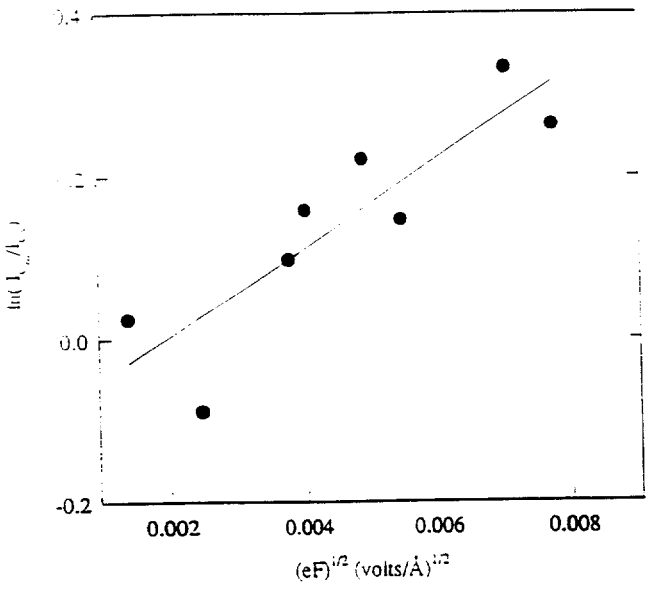

Figure 4. Shottky plot for field enhanced ionization of gas phase C_{60} at 308 nm.

The increase in fullerene ion signal relative to that of Cs^+ is attributed to field enhanced thermionic emission. From the slope of the Schottky plot we obtain a temperature of approximately 1000 K. This temperature is comparable to but smaller than that estimated from measurements of the electron kinetic energies (~1600 - 3700 K). This result for field enhanced thermionic emission is discussed further by Klots and Compton.[21]

Thermionic emission from neutral clusters has long been known for autodetachment from highly excited negative ions.[22] Similarly, electron attachment to C_{60} in the energy range from 8 to 12 eV results in C_{60} anions with lifetimes in the range of microseconds.[23,24] Quasiequilibrium theory (QET) calculations[20] are in reasonable accord with these measurements. More recently we have observed the sequential attachment of two electrons to C_{84} in the gas phase, i.e.,

$$e^- + C_{84} = C_{84}^{-**}$$

Followed by

$$e^- + C_{84}^{-**} = C_{84}^{=***}$$

After mass selecting the metastable $C_{84}^{=**}$ ion, we have observed its autodetachment into the C_{84}^- anion. This is the first observation of the decay of a doubly-charged anion.

The observed magnitude of the $C_{84}^=$ signal relative to that of C_{84}^- implies that the cross section for the attachment of the second electron is as large as that for attachment of the first electron. This is a surprising result since the long range interaction between the incident electron and C_{84}^- is repulsive. The capture of electrons into a state of high angular momentum might be facilitated by the excitation of vibrations (phonons) in the C_{84}^- anion. The possibility that of the formation of a "Cooper-pair" in the gas phase is intriguing. The fact that alkali atom doped C_{60} (3:1) is a known superconductor strengthens this argument.

The two extra electrons in $C_{84}^=$ are calculated to form a bound state (Mark Pederson, private communication). The dissociation of $C_{84}^=$ into C_{84}^- + e is further inhibited by the presence of a Coulomb barrier (see Ref. 25). The decay of $C_{84}^{=**}$ into C_{84}^- over the top of the Coulomb barrier occurs mainly as a result of thermionic emission and from tunneling through the barrier to a much lesser extent. Again, the measured lifetime of $C_{84}^{=**}$ can be accounted for by QET.

ACKNOWLEDGMENTS

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