Probing C_{60}

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Experiments involving the laser vaporization of graphite have indicated that one particular cluster of carbon, C_{60}, is preeminently stable; this special stability may be evidence that C_{60} can readily take the form of a hollow truncated icosahedron (a sort of molecular soccerball). If true, this structure for C_{60} would be the first example of a spherical aromatic molecule. In fact, because of symmetry properties unique to the number 60, it may be the most perfectly spherical, edgeless molecule possible. Its rapid formation in condensing carbon vapors and its extreme chemical and photophysical stability may have far-reaching implications in a number of areas, particularly combustion science and astrophysics. For these reasons C_{60} and other clusters of carbon have continued to be the subject of intense research. This article provides a short review of the many new experimental probes of the properties of C_{60} and related carbon clusters.

THERE IS SOMETHING UNUSUAL ABOUT THE CLUSTERS OF carbon in the size range from 40 to over 100 atoms. The first evidence of this appeared late in 1984 in an article by Rohlfing, Cox, and Kaldor of Exxon Research and Engineering (*1*). Using a laser to vaporize a carbon target rod and a supersonic nozzle to form small clusters from the resulting hot carbon vapor, they examined the relative abundance of these clusters by mass spectroscopy. In addition to the small (2- to 20-atom) clusters studied many times before by earlier workers using less elaborate techniques, the Exxon group observed a distribution of carbon clusters in the 40- to 300-atom mass range. Remarkably, only the even-numbered clusters were present as though some unknown process in the supersonic nozzle sensed the "evenness or oddness" of each cluster and removed the odd.

Roughly a year later, experiments with carbon cluster beams were begun on a similar apparatus at Rice University. Stimulated by the interest of H. W. Kroto of the University of Sussex in modeling the formation of carbon molecules in circumstellar shells, we began with students James Heath and Sean O'Brien to study the chemical reactivity of the smaller (2- to 30-atom) carbon clusters. Our initial objective was to determine if some or all of these species had the same form as the long linear carbon chains known to be abundant in interstellar space. Although these experiments on the small clusters were ultimately successful (*2*), the most significant aspect of this research turned out to have little to do with the small clusters. It involved instead the discovery (*3*) that one of the large even-numbered clusters, C_{60}, was uniquely stable and led in the end to a general explanation of the dominance of the even-numbered clusters in this size range.

The Uniqueness of C_{60}, "Buckminsterfullerene"

Early in the study of the small clusters we noted incidentally that the large, even-numbered cluster distribution first reported by the Exxon group was very sensitive to nozzle and laser-vaporization conditions. This is shown in Fig. 1, which presents the measured relative abundance of carbon clusters when made under conditions that increasingly favored clustering reactions in the nozzle. The "evenness" aspect of these cluster distributions is clear. But most remarkable is the increasing prominence of one cluster, C_{60} (and to a lesser extent, C_{70}), as the nozzle conditions are changed. As seen in Fig. 1A, over the mass range detected in the experiment C_{60} accounts for more than 50% of all the clusters observed.

In the search for an explanation for this remarkable behavior, it was soon noted that a very special structure can be formed for a 60–carbon atom cluster (*3*). By placing atoms at each vertex of a truncated icosahedron as shown in Fig. 2, one generates a pattern of bonds generally familiar as the pattern of seams on a soccerball. For a carbon cluster it is an excellent solution to the problem of forming a surface with the vacuum while satisfying the valency demands of all atoms. It may be viewed as a hexagonal graphitic sheet, which, by

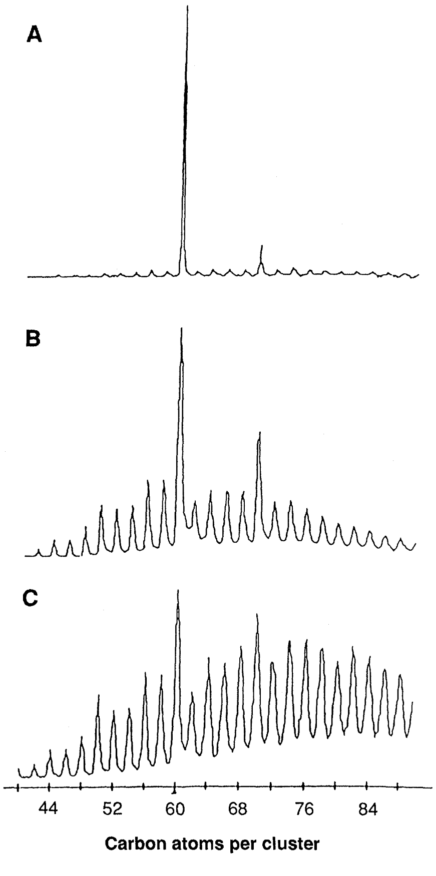

Fig. 1. Mass spectra of carbon cluster distributions in a supersonic beam produced by laser vaporization under conditions of increasing extent of clustering (**C** to **A**). [Reprinted from (*3*) by permission from *Nature*, copyright 1985, Macmillan Journals Limited]

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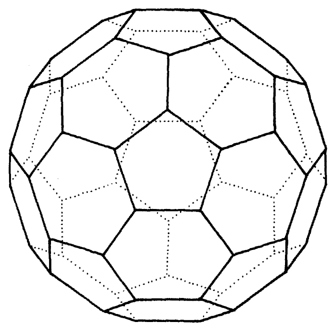

Fig. 2. Truncated icosahedral structure proposed for C_{60}.

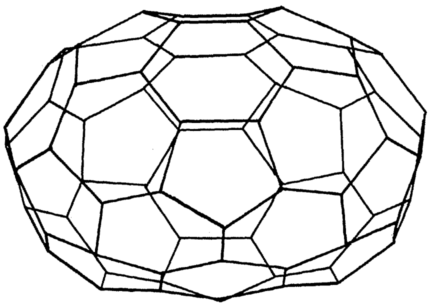

Fig. 3. A possible fullerene structure for the cluster C_{72}. [Reprinted from (*8*) with permission from *Journal of Physical Chemistry*, copyright 1986, American Chemical Society]

incorporating pentagons, has been able to curl into a ball, perfectly tying up all dangling bonds.

A key aspect contributing to its unique stability is the fact that, by symmetry, the truncated icosahedron arranges the maximum possible number of atoms uniformly on the surface of a sphere. As a consequence, the strain of distorting what would ordinarily be a planar conjugated double-bond system is then distributed with perfect evenness. Because this geodesic strain distribution is reminiscent of the geodesic domes of Buckminster Fuller, the rather tortuous but appropriate name "buckminsterfullerene" was chosen in the initial announcement (*3*) of the possible detection of this species.

The idea that carbon may form a stable soccerball molecule was not new. It had been conceived in the imaginations of chemists long before these supersonic beam studies (*4*) and had several times been the subject of approximate molecular orbital calculations (*5*). Over the past few years, a flurry of more modern quantum chemical calculations have confirmed the stability of this structure. However, the synthesis of buckminsterfullerene by classic organic chemical methods has so far been unsuccessful. It is reasonable, therefore, to regard with some skepticism the claim that the prominent peak in the mass spectrum of Fig. 1A is the result of a carbon soccerball. If the directed efforts of sophisticated organic chemists have not yet succeeded in synthesizing this species, how feasible is it that such a symmetrical, low-entropy form is generated spontaneously from the random condensation of carbon vapor?

Before discussing more detailed probes of C_{60} itself, we begin by addressing this question of feasibility. One plausible mechanism for the spontaneous formation of soccerball C_{60} is outlined below. It requires consideration of the other even-numbered clusters and leads to a hypothesis concerning the active nucleus for the growth of soot.

The Other Even Clusters: The "Fullerenes"

The structure proposed in Fig. 2 is only one of an infinite number of possible closed nets composed of five- and six-membered rings. Starting at C_{20} (in the form of a dodecahedron) and with the sole exception of C_{22}, any large even-numbered carbon cluster can be formed into a closed network. By means of a theorem attributed to Euler it is easy to show that all such structures must have exactly 12 five-membered rings. As an example, Fig. 3 shows a possible closed spheroidal net structure for C_{72}. Such closed spheroidal structures for the even-numbered carbon clusters have come to be called "fullerenes," of which C_{60}, buckminsterfullerene, is prototypical.

Note that unlike the carbons in C_{60}, the carbon atoms in the C_{72} fullerene structure of Fig. 3 are not all equivalent. In general, for all fullerenes the strain of closure tends to concentrate at the vertices of the pentagons. Only for C_{20} and C_{60} can this strain be distributed uniformly over all atoms. Schmaltz *et al.* (*6*) have demonstrated that to first order the net strain of closure is constant independent of the fullerene size; hence the average strain per carbon atom will increase as the cluster gets smaller. The C_{20} dodecahedron would probably be too highly strained to be stable as a bare molecule (although the hydrogen-saturated form $C_{20}H_{20}$, dodecahedrane, is a known and very stable species). Electronic structure calculations (*7*) have estimated that the closed fullerene structures begin to be more stable than the alternative open graphitic sheet somewhere in the C_{30} to C_{40} region. These calculations would then predict that somewhere in the cluster distribution above C_{30} one might begin to observe the fullerenes.

The "evenness" of the large carbon cluster distribution seen originally by the Exxon group may result from the fact that only the even-numbered clusters can close to form a fullerene. Odd-numbered clusters can begin to curl so as to tie up dangling bonds, but there will always be at least one atom in such a cluster with a remaining dangling bond. The odd-numbered clusters would then be too reactive to survive long in a condensing carbon vapor. Supersonic beam experiments (*8*) probing the reactivity of carbon clusters have verified this: all small clusters and all large clusters with an odd number of carbon atoms are highly reactive. In contrast, C_{60} and all the even-numbered clusters in the size range larger than C_{40} are virtually inert, in good accord with the suggestion that they are closed fullerenes.

Simply by considering the placement of the pentagonal rings and the degree to which the strain of closure is concentrated at any particular atom, it is possible to explain why some members of the fullerene distribution such as C_{70} and C_{50} should be specially stable as well. These points are discussed in more detail by Kroto (*9*).

Formation of Fullerenes and Graphitic Soot

Even if one grants that fullerenes may be stable, why should such curved, hollow carbon nets be formed? The answer is thought to involve the tendency of the growing clusters to curl in order to minimize the number of dangling bonds.

It has long been known that graphite vaporization either by pulsed lasers or by electric discharge in high vacuum initially produces just the small clusters of carbon in the C_1 to C_{20} size range (*1*). These small carbon radicals are highly reactive and presumably drive the growth of the large clusters seen in the supersonic beam experiments. Clusters in the 2- to 20-atom size range are expected to be linear chains or monocyclic rings. As the clusters grow larger, polycyclic structures similar to the hexagonal "chicken wire" pattern of bulk graphite may be expected to form. However, any such graphitic hexagonal net will be terminated around its edges by a large number of dangling bonds, and the flat sheet will probably not be the most stable possible form. Instead, we have noted (*8*) that incorporating a pentagon into the periphery of an otherwise flat graphitic sheet will cause the sheet to curl, with the benefit that at least one new strong carbon-carbon bond will be formed from two

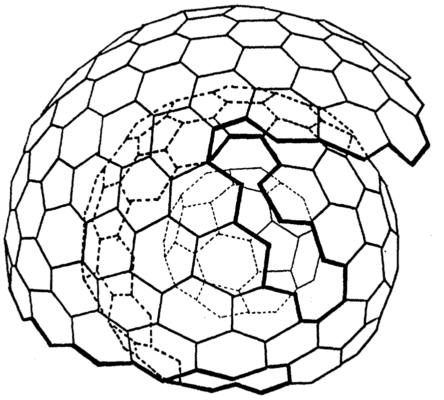

Fig. 4. Spiraling graphitic soot nucleus believed to form from imperfect closure of a growing curved network during carbon condensation. [Reprinted from (*8*) with permission from *Journal of Physical Chemistry*, copyright 1986, American Chemical Society]

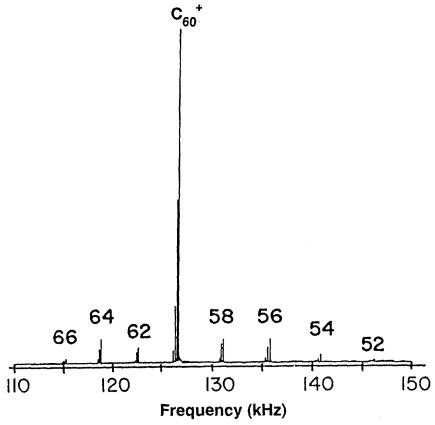

Fig. 5. Mass spectrum of carbon cluster positive ions trapped in the high magnetic field of the FT-ICR spectrometer.

previously dangling bonds. This reduction in the number of dangling bonds serves as a local driving force toward curvature.

Incorporation of additional pentagonal rings causes continued curvature until the sheet has grown back on itself and closure becomes possible. In some cases a closed fullerene structure may result, tying up all remaining dangling bonds and precluding further growth. More generally, though, the growth process will be too fast to follow the minimum energy pathway. It seems likely that most growing nets will not close at all; instead, the growing edge will overrun and bury the opposite edge as it curls. Once this burying occurs, there is no ready way to terminate the growth process and spiral structures of the sort shown in Fig. 4 seem likely to form (*8*). Such spirals could be a key factor in particle formation in the condensation of carbon vapor ("graphitic soot") and may also be important to soot formation in flames. The nature of such spirals and their possible relevance in combustion and astrophysical settings are discussed in more detail in (*9*).

Probing the Reactivity of C_{60}^+

In order to probe more directly the nature of C_{60}, we have begun to apply a few of the new techniques recently developed for the general study of cluster surfaces. One of these involves the generation of a beam of the cold cluster ions, mass selecting a small region of the overall cluster distribution and injecting these clusters into the magnetic trap of a Fourier transform ion cyclotron resonance (FT-ICR) (*10*) apparatus. A detailed discussion of this powerful new technique has appeared elsewhere (*11*). Initial applications have included study of the dissociative chemisorption of H_2 on transition metal clusters and the systematic measure of chemisorption rates on silicon clusters as a detailed function of cluster size (*12, 13*).

One of the virtues of the cluster FT-ICR technique is that the clusters may be trapped without perturbation for minutes. The result of chemical reactions or photophysical fragmentation of particular clusters may be observed at mass resolutions exceeding 10^5. For example, Fig. 5 shows a section of the FT-ICR mass spectrum of positive carbon cluster ions as measured in such an apparatus. The fine substructure on each major peak is due to isotopic variants arising from the 1.1% natural abundance of ^{13}C in the graphite disk used in the supersonic laser-vaporization cluster source.

Note that C_{60}^+ is by far the dominant cluster ion in the magnetic trap, and that only even-numbered carbon clusters are present. Just as with the initial experiments that showed the neutral carbon cluster distribution ultimately became dominated by C_{60} under conditions of increasing clustering, the positive carbon cluster ion distribution from these laser-vaporization sources is similarly dominated by C_{60}^+.

With C_{60}^+ in the magnetic trap, its chemical reactivity could be readily probed by exposing it to a neutral reactant gas over a set time period, pumping the reactant gas away, and performing an FT-ICR detection cycle. Evidence for reaction was to be sought by looking both for the depletion of the C_{60}^+ parent ion signal and for the appearance of new mass peaks corresponding to reaction products. As with the neutral reaction studies (*8*), not only C_{60}^+ but all the fullerene ions were found (*14, 15*) to be completely unreactive in these ICR studies. This was true even when the cyclotron motion of the fullerene ions in the magnetic trap was excited to over 100 eV in the presence of such reactive gases as O_2, NH_3, and NO. These conditions were maintained sufficiently long for the typical cluster to suffer over 10^4 collisions. No evidence of reaction was ever detected. The fullerenes are the most inert clusters ever studied by such a technique.

A particularly relevant contrast is provided by positive silicon clusters. Unlike carbon, silicon clusters show no evidence of any selective behavior in the cluster ion distribution as they are injected into the FT-ICR trap. In particular, there is no evidence that Si_{60}^+ is special. Also in marked contrast with fullerenes, the large silicon cluster positive ions are generally quite reactive. With some reagents such as NH_3 the reactivity is sharply sensitive to cluster size (*13*), and there is currently much interest in seeing if these reactivity patterns provide a clue to the nature of silicon surface restructuring and its consequent effect on surface chemistry.

Probing the Photophysics of C_{60}^+

One of the most useful general probes of any new cluster species is to see how it fragments upon laser excitation. The rigid, highly symmetrical structure proposed for C_{60} would be expected to be extremely difficult to fragment because its atoms are so effectively interconnected. To explore such photophysical aspects of C_{60} and other carbon clusters, a tandem time-of-flight (TOF) spectrometer was used. This is another of the new experimental devices recently developed for the general study of refractory clusters. It permits a single mass-selected cluster ion prepared in a supersonic beam and sorted by an initial TOF mass analysis to be irradiated with a probe laser and then have its photofragment daughter ions detected in a second TOF analysis. The results of such experiments for all the positive carbon clusters up to over 70 carbon atoms (*16*) reveal striking new aspects of C_{60}^+ that were quite unexpected but that turn out to be fully in accord with the fullerene model.

When any carbon cluster ion with 31 or fewer atoms is irradiated in the ultraviolet in the tandem TOF apparatus, the clusters fragment readily and a single primary fragmentation route is followed: loss of C_3 (*17*). These smaller carbon clusters are thought to take the form of either linear chains or monocyclic rings. Quantum chemical calculations confirm that C_3 is a particularly stable fragment (*18*), and C_3 loss is likely to be the lowest energy dissociation process from such small carbon clusters.

However, starting at C_{32}^+, the photodissociation process changes drastically for all higher clusters. The large even-numbered clusters (the fullerenes) are extremely difficult to photodissociate. When ultimately they are irradiated with sufficient laser intensity to begin to fragment, they do so by the loss of C_2. This is surprising because C_2 is much less stable than C_3. Nonetheless, only C_2 loss is observed in the primary photoprocess. Interestingly, the C_{32}^+ cluster acts as a sharp dividing line in the photofragmentation of carbon clusters (*16, 19*). For all lower clusters only C_3 loss is observed, whereas all higher even-numbered clusters lose C_2 and all higher odd-numbered clusters lose C_1. The C_{32}^+ cluster itself follows neither fragmentation route. Instead it fissions into fragments in the 10- to 19-atom range.

Of all the clusters yet probed in our laboratories, including tightly bound clusters of such refractory elements as tantalum and niobium, C_{60}^+ is by far the most difficult to photodissociate. In the tandem TOF apparatus with an ArF excimer laser for photodissociation (1930 Å, 6.3-eV photon energy), measurements of the fluence dependence of the C_{58}^+ daughter ion intensity showed the fragmentation of C_{60}^+ to be at least a 3-photon process (and probably higher) (*16*).

As higher photolysis laser fluences are used on any particular mass-selected fullerene, the C_2 loss process appears (*20*) to continue in successive steps. Remarkably, in the course of the extensive fragmentation from a large fullerene such as C_{80}^+, the cluster fragments at C_{70}^+, C_{60}^+, and C_{50}^+ are particularly prominent. The fragmentation process appears able to sense that specially stable structures are available to these clusters. With sufficiently intense laser excitation this loss process continues, but, as seen in Fig. 6, it breaks off abruptly at C_{32}^+.

These photofragmentation results constitute a stringent test for any model of the structure of C_{60}^+ and the other large clusters. The fullerene model passes this test if one invokes a concerted C_2 loss mechanism (*16*) in which the next smaller closed cage is formed as the C_2 leaves. Upon further C_2 loss, the fullerene cage becomes increasingly smaller and therefore increasingly strained. Ultimately, the C_2 loss process would be expected to terminate abruptly as the final fullerene cage becomes so strained that it shatters. This is precisely the behavior exhibited at C_{32}^+.

Photophysics of Metallofullerenes

If this photophysical model of successive shrinking of the closed fullerene cage is correct, the critical point where the cage bursts might be affected if a fairly large metal atom is placed inside [to make a "metallofullerene" (*21*)]. Figure 7A shows evidence (*15*) that this is what happens. Here a $C_{60}K^+$ cluster prepared by laser vaporization of a graphite disk treated with KCl has been trapped in the FT-ICR apparatus along with a similar amount of the C_{64}^+ bare fullerene ion. Figure 7A shows the result when these species were irradiated with 200 shots of an ArF excimer laser. The bare fullerene fragments seen here originated from the C_{64}^+ parent. Like the bare fullerenes, $C_{60}K^+$ is highly photoresistant, and when it fragments it does so by C_2 loss producing first $C_{58}K^+$, then $C_{56}K^+$, and so forth. The bare fullerene fragment distribution extends down through C_{42}^+ (it continues to C_{32}^+), while the C_nK^+ fragments break off abruptly at $C_{44}K^+$ (Fig. 7A).

Figure 7B shows the result of a similar experiment with a metallofullerene with a larger metal ion, $C_{60}Cs^+$, trapped in the FT-ICR magnet along with the bare fullerene C_{72}^+. Here the break in the C_nCs^+ fragment distribution occurs at $C_{48}Cs^+$, in excellent accord with a model such that these clusters consist of a singly charged metal ion completely trapped within a closed fullerene cage.

Photoelectron Spectroscopy of C_{60}^-

If C_{60} really does have the geometry suggested in Fig. 2, its electronic structure would be greatly simplified by the high symmetry. A direct view of a molecule's electronic structure can often be best obtained from the ultraviolet photoelectron spectrum (UPS). This powerful spectral technique has recently been adapted for the study of refractory clusters. The cold, mass-selected negative ion is

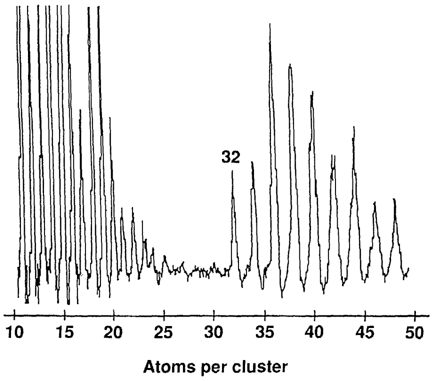

Fig. 6. Low-mass portion of the daughter ion fragments produced by intense laser excitation of C_{60}^+. [Reprinted from (*16*) with permission from *Journal of Chemical Physics*, copyright 1988, American Institute of Physics]

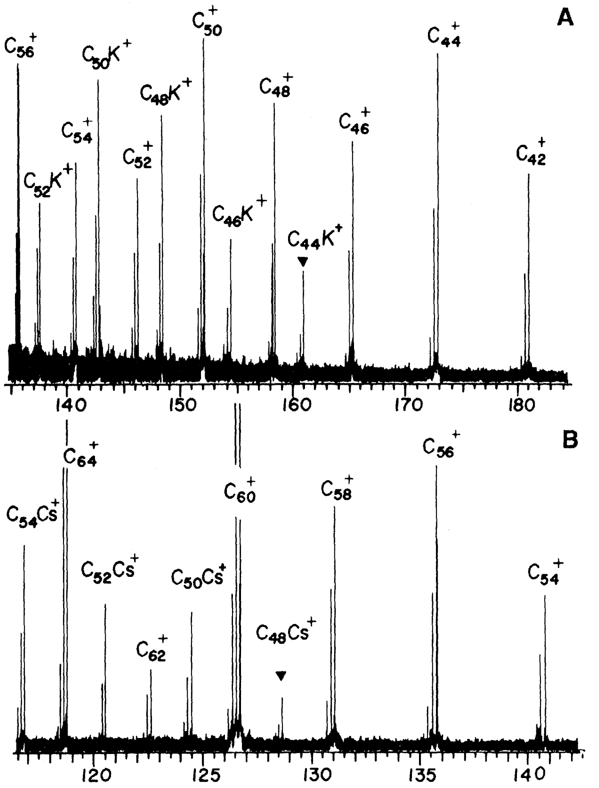

Fig. 7. Low-mass portion of the daughter ion fragments produced by intense laser excitation of $C_{60}K^+$ (**A**) and $C_{60}Cs^+$ (**B**) in the FT-ICR trap. The bare carbon cluster fragments seen in these panels are fragments of large bare fullerene ions trapped simultaneously with the metal species. [Reprinted from (*15*) with permission from *Journal of the American Chemical Society*, copyright 1988, American Chemical Society]

prepared for the desired cluster, electrons are detached by means of a far-ultraviolet laser of known photon energy, and the energy of each photoelectron is analyzed by TOF spectrometry.

Extensive cluster UPS experiments have now been reported (*22, 23*) for carbon clusters throughout the C_2 through C_{84} size range. The photoelectron spectrum of C_{60}^- is shown in Fig. 8. As expected, it is unique among carbon clusters in this mass range. The electron affinity of C_{60} (given by the threshold energy for the appearance of photoelectrons) appears to be the lowest of any fullerene, and the UPS pattern for C_{60}^- exhibits by far the most structure.

Although detailed analysis of this UPS pattern for C_{60}^- is still in progress, it is already clear that—at least in coarse measure—the spectrum is nicely in accord with expectations for the buckminsterfullerene structure. Even though C_{60} is a very large species having 240 valence electrons, the high symmetry of the truncated icosahedron geometry causes these electrons to organize into a simple, well-spaced pattern of molecular orbitals, each with high degeneracy. Near the highest occupied molecular orbital (HOMO), this pattern is calculated (*5*) to look like that sketched beside the UPS data of Fig. 8. The extra electron in the C_{60}^- ion is forced to occupy the threefold degenerate t_{1u} lowest unoccupied molecular orbital (LUMO) because the HOMO of the neutral molecule is already filled with 10 electrons. The first feature in the UPS pattern near 3 eV corresponds to removal of this most weakly bound electron. The next most tightly bound electrons would come from the h_u symmetry HOMO where there are 10 equivalent electrons, followed at higher binding energy by a group of 18 electrons in the nearly degenerate g_g and h_g orbitals. Taking reasonable account of configuration interaction corrections to this picture (*24*), the observed UPS pattern is in excellent accord with this expectation. The UPS feature in the 4- to 5-eV range has about the right intensity and position to be assigned as electron detachment from the h_u HOMO, the larger feature in the 5.5- to 7-eV range reasonably being assigned to the next deeper molecular orbitals.

More detailed spectral information is expected soon from UPS probes of C_{60}. Recent spectra taken with improved cluster cooling have begun to resolve what appears to be vibrational structure on the detachment threshold feature near 3 eV. Of the 174 vibrations of C_{60}, only two are totally symmetric, and only these two will be active in forming progressions in the UPS data.

The Optical Spectrum of C_{60} and C_{60}^+

One of the very best ways to probe the electronic and vibrational structure of a cluster is to record the optical absorption spectrum, particularly if this can be done at high resolution in an ultracold supersonic beam. Unfortunately, the standard approach most likely to succeed, laser-induced resonant photoionization, has not worked with C_{60}. Apparently radiationless transitions proceed so rapidly in this molecule that the excited electronic state relaxes before a second photon can be absorbed.

Even so, an initial view of the absorption spectrum of this molecule has been successfully obtained by a technique that relies on the laser-induced fragmentation of a cold van der Waals complex (*25*). A single narrow absorption feature, 50 wavenumbers in width, has been detected at 3860 Å. This is in reasonable agreement with the predicted position of the first allowed electronic transition calculated for C_{60} in the soccerball geometry (*24*). The fact that it is a single feature with no vibrational activity is consistent with the expected rigidity of such a molecule.

If C_{60} is abundant in space, the most important form of this molecule to study may turn out to be the positive ion, C_{60}^+. Because the interstellar medium is bathed in radiation with energies up to 13.6 eV and the ionization threshold for C_{60} is between 6.4 and 7.9 eV (*8*), most C_{60} present in this environment would be in the ionized form, C_{60}^+. In order to survive unshielded in the interstellar medium, C_{60}^+ would have to be extremely stable with respect to ultraviolet photolysis.

When a vacuum ultraviolet photon is absorbed in such a large molecule, it is generally expected that internal conversion will take place rapidly, producing a molecule that is highly excited vibrationally. If photodissociation is to be avoided, the lifetime for unimolecular decay must be long compared with the time required to reradiate in the infrared the excess energy above the activation energy for unimolecular fragmentation.

As discussed earlier, C_{60}^+ is extremely photoresistant. In the course of the FT-ICR probes it was found that C_{60}^+ could survive over 1500 pulses of ArF excimer radiation (6.4 eV) at 0.5 mJ cm^{-2} in a 30-s period without any fragmentation at all. From other experiments the absorption cross section for this radiation is known to be roughly 10^{-16} cm^2, so during this 30-s irradiation the average C_{60}^+ ion absorbs over 100 photons of this 6.4-eV laser light. Infrared emission must be a very efficient cooling mechanism for this large molecule in order to prevent fragmentation in such an experiment.

Calculations for C_{60} show that there are many excited electronic states of this molecule spread through the visible and near-ultraviolet, but for the neutral cluster the ground electronic state is of ${}^1A_g$ symmetry and transitions to most of these are forbidden by symmetry (*24*). For the positive ion, on the other hand, the ground state will be of ${}^2H_u$ symmetry and many more transitions will be allowed, including five to ten distributed throughout the visible region of the spectrum. As discussed in (*9*), it may be these absorption transitions of C_{60}^+ that are responsible for the so-called "diffuse interstellar lines."

To test this hypothesis the laboratory spectrum of C_{60}^+ is needed. The same kind of van der Waals complex fragmentation spectroscopy used successfully to obtain the spectrum of C_{60} should work for C_{60}^+. However, in this case, it is a bit more challenging to ensure that formation of the complex is only a weak perturbation. The complexing agents used for the neutral species (benzene and methyl-

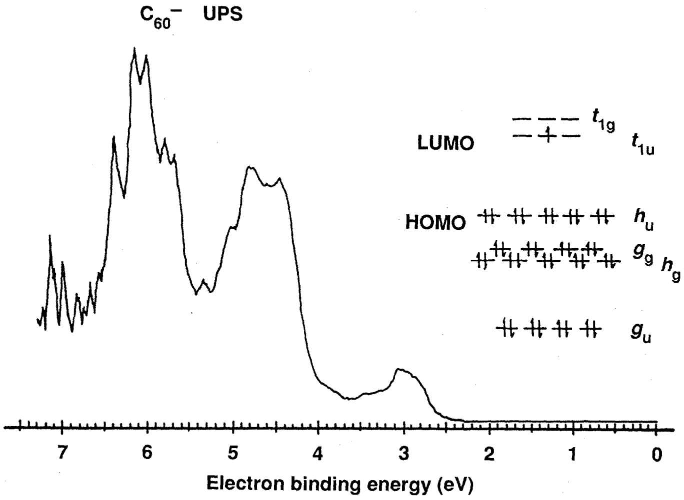

Fig. 8. Ultraviolet photoelectron spectrum (UPS) of C_{60}^-. Also shown is a portion of the molecular orbital pattern expected for the soccerball structure of C_{60}^-. The near-threshold feature near 3 eV corresponds to removing the electron from the C_{60} LUMO; the band in the 4- to 5-eV range is thought to arise from electron removal from the C_{60} HOMO.

ene chloride) interact far too strongly with the ion. Experiments to obtain the spectrum of C_{60}^+ using the argon van der Waals complex, $C_{60}Ar^+$, are currently under way, but it is quite possible that even argon is too strong a perturbation. It may be a while yet before the full story is known.

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Research Articles

Artificial Airglow Excited by High-Power Radio Waves

P. A. BERNHARDT, L. M. DUNCAN, C. A. TEPLEY

High-power electromagnetic waves beamed into the ionosphere from ground-based transmitters illuminate the night sky with enhanced airglow. The recent development of a new intensified, charge coupled–device imager made it possible to record optical emissions during ionospheric heating. Clouds of enhanced airglow are associated with large-scale plasma density cavities that are generated by the heater beam. Trapping and focusing of electromagnetic waves in these cavities produces accelerated electrons that collisionally excite oxygen atoms, which emit light at visible wavelengths. Convection of plasma across magnetic field lines is the primary source for horizontal motion of the cavities and the airglow enhancements. During ionospheric heating experiments, quasi-cyclic formation, convection, dissipation and reappearance of the cavities comprise a major source of long-term variability in plasma densities during ionospheric heating experiments.

IN 1938, BAILEY PROPOSED THAT A MEGAWATT OF POWER radiated from a ground-based radio transmitter could maintain a glow discharge in the lower ionosphere that would be "about fifty times as bright as the night sky on a moonless night" (*1*). Although sky brightening of this magnitude has not been achieved, excitation of airglow below the threshold of visual detection, along with a number of other interesting phenomena, has been produced by ionospheric modification by high-power radio waves.

Ionospheric heating experiments require the use of powerful ground-based transmitters to feed a high-gain antenna radiating a beam of electromagnetic waves into the upper atmosphere. The typical effective radiated power (ERP) in these experiments is 200 MW. The radio wave is partially absorbed near a resonant point where the wave frequency is equal to the plasma frequency. In this interaction region, ordinary mode electromagnetic waves parametri-

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