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SANTA BARBARA · SANTA CRUZ

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY
LOS ANGELES, CALIFORNIA 90024

June 1, 1987

Professor Richard E. Smalley
Department of Chemistry
Rice University
P.O. Box 1892
Houston, Texas 77251

Dear Rick:

Thank you for sending the new preprints describing your work on carbon clusters. I'm sure they'll add incentive for further theoretical and experimental studies. On our part, we hope to return (with higher resolution) to the elastic scattering experiments in the near future; these are capable in principle of distinguishing open, planar structures from compact spheroids. At the same time, work on the C_{18} synthesis (Diederich's group) and on the theoretical description of fused monocyclic rings has accelerated.

I have a few comments on your preprints which you may wish to consider. First regarding the "Photophysics of Buckminsterfullerene ..." article, the following points occurred to me:

(i) In your description of the dynamics of the fragmentation process, you omit any mention of multiply charged ions as intermediates in the fragmentation process, although this would appear to be a very likely consequence of exciting large cluster ions with short-wavelength radiation. I realize why this is difficult to see directly in your data (because even-numbered carbon clusters are so much more stable in the large -N range), but some indirect evidence may come from your Figure 8 (middle frame) where C_{32}^+ is converted to an apparent C_{16}^+ (not known to be magic) with unusual efficiency. Why couldn't this be C_{32}^{2+}? A number of your other figures showing apparent small-cluster fragments, which you attributed to an explosion, may be similarly regarded. Recall that doubly or multiply charged cluster ions are seen everywhere when high energy excitation is used, (e.g. the work of Recknagel and colleagues) and we have found that multiply charged benzene cluster ions are efficiently (> 50 percent) formed by ArF or F_2 irradiation at fluences below 5 mJ/cm^2! I believe this may be important to your article because the dynamics of multiply-charged cluster fission could be very distinct from the RRKM-type mechanism you postulate: much of the absorbed radiation energy is lost to ionization steps (or effectively converted into Coulomb energy), and small singly charged fragments may be expected.

(ii) The major fragmentation process you find is C_2 loss (for N> 30 and even). I believe this could be accounted for by any model that can explain the preferential stability of even-numbered clusters, including the old carbyne model (Rohlfing, Cox, and Kaldor) or the fused-moncyclic rings model.* Therefore, one turns to the other observed fragment,and in particular your Figure 9 (upper) where one finds preferential loss from C_{36}^+ of (neutral) C_{10}, C_{14}, C_{18} and C_{22}. These are precisely the preferred fragments predicted by the fused-moncyclic-rings model, and provide compelling evidence that at least some of the C_{36}^+ clusters in your beam consist mainly of these units. [In fact, at Anaheim Peter Radi showed me data, taken in Bowers group at Santa Barbara, on the metastable decay of sputtered C_N^+ clusters and revealing the same result for the N = 30-50 range.] Many of your other arguments are now quite convincing for closed spheroidal shells, but it seems you need to concede still the possibility that some of the preferentially formed carbon clusters assume this type of structure.

I also had a small question about the topological results quoted: If I understand correctly, all C_N with N<32 must have at least a quartet of fused pentagons (I assume this means contiguous rather than two doublets), all with N<50 have a triplet, and all with N<60 have a doublet (N<70 or 68, if C_{60} is excluded). I suppose it's also true that the smallest possible shell in your model consists of the 12 fused pentagons (N=20 atoms, by my count). This pattern is now your key to explain the entire set of observed numbers; do you have a complete set of topological results yet?

My comment on the Accounts article regards the spheroidal growth model for soot formation and its compatibility with Iijima's results. Your argument that soot particles are defect structures grown from curved quasigraphitic sheets is very plausible, but it cannot yield the concentric circular structures of Iijina's micrographs. This result follows from a theorem regarding parallel transport on curve surfaces ("combing the hair on a sphere"); see the enclosed excerpt from H.J. Bernstein and A.V. Phillips Scientific American article (ca. 1982). The parallel arrows represent the growth front or edge that you describe. Each time the surface edge attempts to close it must find a local axis about which to spiral (the cowlick). If the growth maintains the same axis, one would observe a spiral structure (<u>not</u> concentric circle) by looking down that cylinder axis; if the growth continually switches axes, the spirals overlap and an amorphous appearance results. [By the way, structures spiraling about an axis are obviously chiral so that, if resolved, they would have optical activity.]

*In particular, your argument that large fused rings would eliminate C_3 rather than C_2 is spurious, because the only reason that C_3 is observed from small clusters is its neutral stability, in the absence of significant energetic differences among the possible ionic fragments. For large clusters this latter condition fails to hold in any of the models discussed

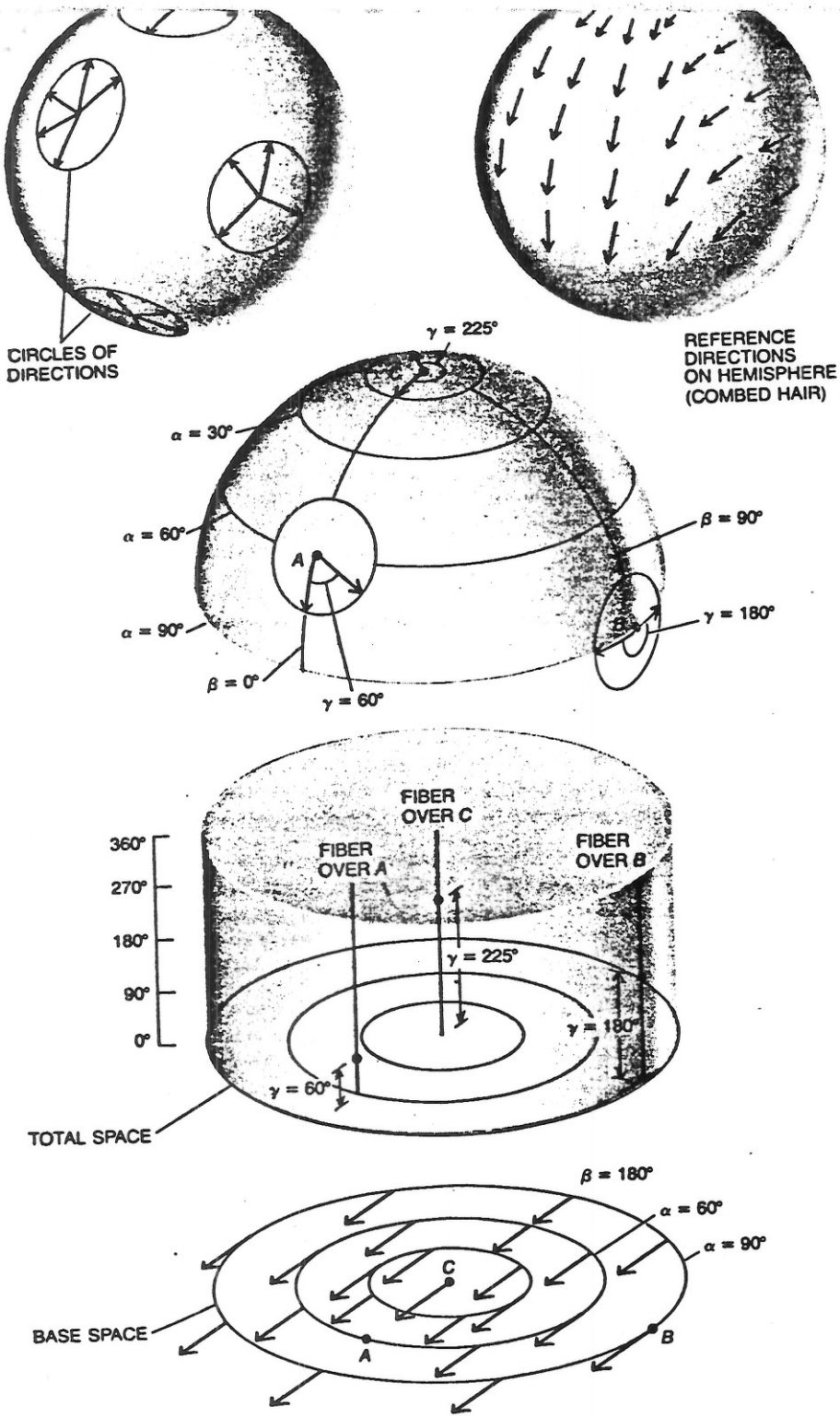
I hope these comments will be of use to you. It was good to see you in Anaheim and Washington (and Harry here at UCLA). See you in New Hampshire.

With Best Regards,

Robert L. Whetten

Robert L. Whetten
Assistant Professor

RLW;sts



BUNDLE OF DIRECTIONS on the surface of a sphere is an important example of a fiber bundle. At each point on the sphere there is a circle of directions along which one can look on the surface. To label these directions with angles one must assign a reference direction to each point. If the reference directions could be assigned everywhere in a continuous manner, one could "comb the hair" on the sphere, but that is not possible; there must always be a "cowlick." Hair can be combed, however, over any region smaller than the entire surface. For example, on a flat map of the northern hemisphere the description "downward and to the left" specifies a direction at each point and so defines a continuous set of reference directions on the hemisphere. A picture of the bundle of directions on the hemisphere can be made by adopting the flat map as a base space. Every direction at a point on the hemisphere appears on the vertical coordinate line above the corresponding point on the map, and at a height that corresponds to the angle the direction makes with the reference direction. Heights 0 and 360 correspond to the same direction. The total space of the bundle is a cylinder where points at the top and the bottom of each vertical fiber are identical. The arrows that represent the reference directions on the map are parallel, but their counterparts on the sphere do not represent parallel transport.

define the average curvature of a region as its total curvature divided by its area. By convention the sign of the average curvature is given correctly when the arrow is transported along the path counterclockwise, so that the region is on the left of the path. The curvature of a surface at a point can be defined as the limiting value of the average curvature of progressively smaller regions containing the point.

Parallel transport makes it possible to define a path-lifting rule from the surface of the sphere to the total space of all directions. In the total space the angular excess is represented as the angular distance along the fiber that corresponds to the point on the closed path where the circuit of parallel transport begins and ends [*see illustration on opposite page*]. Hence the total curvature of the region enclosed by a path in the base is represented by a distance along one of the fibers in the lifted path. It turns out that replacing parallel transport by an arbitrary path-lifting rule generalizes the notion of curvature to other bundles on which the operation of parallel transport does not make sense. Such path-lifting rules have to be formulated without any reference to geodesics or angles.

Instead of focusing on the geometry of the base space, as one does in parallel transport, it is possible to lift a path by imposing structure on the total space. One way of doing this is to associate a set of parallel, sloping planes with each fiber. The slopes of the planes determine how fast a lifted path rises or falls as it moves from fiber to fiber in the total space. The planes must never be parallel to the fibers. Their slopes must vary continuously from point to point, and they must have the same slope at every point along a given fiber. The latter condition is an analogue of the guarantee provided by parallel transport that the angular excess (and thus the curvature) is independent of the initial direction of the arrow being transported. Such a set of continuous planes in the total space is called a connection in the fiber bundle. At the point on a fiber where a lifted path crosses the fiber the path must be tangent to the sloping plane associated with the point. This is how the plane defines the slope of the lifted path at the point. The illustration on the opposite page shows the connection that lifts paths on the sphere in the same way that parallel transport does.

The curvature of a connection can be defined by a procedure similar to the one employed for measuring the curvature of a surface. The aim of the procedure is to assign to each point in the base a number that represents the curvature at that point. (For higher-dimensional spaces the curvature is specified not by a single number but by a collection of

Sean

Sent 6/25/87

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June 23, 1987

Dr. F. W. McLafferty
Accounts of Chemical Research
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Cornell University
Ithaca, New York 14853-1301

Dear Fred:

I returned from a short trip yesterday and have just seen your letter of June 17. In view of your trouble with getting a response from a second referee you might try Dick Zare, Roald Hoffman, or Marshal Newton (at Brookhaven), all of whom have followed the carbon cluster story in detail and are fully capable of an impartial but substantive review. They have each seen an advance copy of the ACCOUNTS article already, so they should be able to respond rather quickly.

In response to your notion of another ACCOUNT article where Andy Kaldor presents his side of the carbon cluster story, my colleagues and I feel very strongly that

(a) we want absolutely nothing to do with it,

(b) it should be very carefully reviewed on its own merits,

and (c) it should not delay appearance of our ACCOUNT in any way.

We feel so strongly about this because Andy (at least so far) has simply not acted as the fair, truth-seeking critic he has made himself out to be. These experiments with supersonic cluster beams are extremely complex and clearly need careful examination, testing and verification. The primary journals of our field have well-established and effective mechanisms for achieving these ends using carefully reviewed articles, comments, and notes. But Andy has not carried out his side of the carbon cluster controversy in this way. Instead, he has been fighting somewhat of a guerrilla war. Aside from one (not very carefully reviewed) short letter-to-the-editor in JACS, Andy's entire response to our carbon cluster work has taken the form of oral remarks in private conversations and meetings -- remarks which often appear to us to be designed primarily to discredit and confuse.

We are definitely not trying to supress competing points of view. If Andy has alternative explanations for our experiments, or new experiments of his own, we would love to see them written in the primary literature -- written in full enough detail that they can be examined fairly. Don Cox and he are working now on a large paper for JCP that may fill this need, but it's not out yet and we have not been able to respond. The version we have seen would have been easy (but rather tedious) to refute.

Since he has written some of his arguments here in his review of our manuscript, I can give some of our counter-arguments. I'll just focus on two main topics for now. If you want to hear more, just give me a call.

I. IP's and EA's

Andy's most important argument seems to be that all this stuff we claim about C_{60} being special is an ionization potential effect:

> "Let me repeat, the enhanced C_{60} signals observed in the photoionization of the neutrals arise from differences in ionization processes ...".

This is a remarkable argument which we have never heard before -- let alone seen in print. But now that he has made it, its easy to refute. We are certain that all the large carbon clusters (n>40) are cleanly one-photon ionized by the F_2 excimer laser when they are cold. The temperature dependence of the apparent IP thresholds Andy mentions is seen only in the weakest supersonic expansions-- we never operate under such hot conditions. By adjusting nozzle conditions in our apparatus we can actually even generate carbon cluster beams cold enough to form van der Waals cluster adducts like C_{60}-benzene (an advance copy of a quick paper on the spectroscopy of this molecule is enclosed). Under these beam conditions all carbon clusters can be seen to be ionized with efficiencies linearly dependent on F_2 laser power. There is no evidence of a detectivity bias in the C_{60} experiments that we know of. If Andy thinks there is, we challenge him to prove it.

Andy's explanation requiring an abnormally low IP, and a correspondingly high electron affinity for C_{60} comes at a particularly convenient time for us since we have just succeeded in obtaining the photoelectron spectrum of the negative ions of all these clusters. In direct contradiction of Andy's new model, C_{60} has the <u>lowest</u> EA (2.5 eV) and largest HOMO-LUMO gap (1.8 eV) (and therefore probably the highest IP) of any carbon cluster in the 40 - 80 carbon size range. This is perfectly in accord with *ab initio* calculations for the spheroidal carbon shell model. We'll be writing this up next week for a short letter to Chem. Phys. Lett., and I'll send you a copy.

The key point here is not so much that Andy is wrong, but that he's claiming he has alternative explanations that are so beautiful that they deserve publication in a back-to-back ACCOUNT with ours. His alternative explanation has not yet even appeared in the primarly literature! Is it really your intention to have Accounts in Chemical Research be the <u>first</u> place people publish their research?

II. Comparison to Alternate Structure Models

Although Andy keeps talking about other structure models, he never proposes one explicitly and works out its details. If he's got one he should try to get it in the open literature. Simply saying "3d-carbyne structure" doesn't make it a model. What does this thing really look like? Why is 60 special? How does it explain all the published experimental results?

The structural model of Rob Whetten that Kaldor mentions does have some appeal and we would be happy to discuss it briefly. But even Whetten himself has not yet seen fit to put it in the literature. We don't think it's close to being a viable alternative structure, but it would be rather unfair to criticize Whetten's baby before he has shown he likes it himself.

There are many other aspects of this Exxon/Rice controversy we can talk about if you're interested, but I suspect this is already probably far more than you have time or interest to go through.

As we discussed over the phone when you first received our manuscript, I realize we have some cutting to do. Even in its current form we really haven't been able to devote enough space to cover all the aspects Kaldor feels need attention -- for example our discussion of the hydrogen content of soot, or Kaldor's famous "Deflated Soccerball" JACS paper and the apparently rather subtle points he continues to find unbelievable. But we're not writing the ACCOUNT for Kaldor -- it was written for the general chemical community with the intent of showing the evidence so far accumulated for Buckminsterfullerene. In this I think we succeeded fairly well.

By the middle of July we should have a tightened version of our ACCOUNT for you. Knowing now a bit more of the situation existing between ourselves and Kaldor, I hope you'll understand our resistance to any notion of an arrangement for back-to-back ACCOUNTS with a delay while Andy sorts his part out. You can feel free to discuss any of the contents of this letter to Andy -- I've sent him a copy myself. We used to be great friends once. I hope we can be again.

With best regards,

R. E. Smalley
Hackerman Professor of Chemistry

RES:jat

Enclosure

cc. R. F. Curl
H. W. Kroto
J. R. Heath
S. C. O'Brien ✓
A. Kaldor

Jim + Sean

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AMERICAN CHEMICAL SOCIETY

Accounts of Chemical Research

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Fred W. McLafferty, *Editor*

July 1, 1987

Prof. Richard E. Smalley
Department of Chemistry
Rice University
P. O. Box 1892
Houston, Texas 77251

Dear Rick:

Your June 23 letter greatly clarifies the points raised by Andy Kaldor, and we will try to proceed expeditiously with publication of your ACCOUNT. I am on my way to Japan for two weeks, so any reviews that arrive will just be forwarded to you.

With apologies for the hasty letter,

FW McLafferty

F. W. McLafferty
Editor

ATTB

cc: A. Kaldor

Accounts of Chemical Research

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Fred W. McLafferty, *Editor*

July 1, 1987

Dr. Andrew Kaldor
Corporate Research Science Laboratories
Exxon Research and Engineering Company
Clinton Township, Route 22 East
Annandale, New Jersey 08801

Dear Andy:

The enclosed is my response to Smalley's June 23 letter, which you should have also received. Although we do ask that differences of opinion be aired first in primary journals, ACCOUNTS does not shy away from controversy. Thus we would still welcome an article concerning your views on this subject when the time is appropriate.

Thanks again for you helpful review.

Best regards,

F. W. McLafferty
Editor

cc: R. E. Smalley

Sean

Accounts of Chemical Research

PUBLISHED BY THE
AMERICAN CHEMICAL SOCIETY

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Fred W. McLafferty, *Editor*

July 22, 1987

RECEIVED
JUL 27 1987

Prof. Richard E. Smalley
Department of Chemistry
Rice University
P.O. Box 1892
Houston, TX 77251

Dear Rick:

Our fourth request has finally generated the enclosed second review of your manuscript. If any others arrive, we will forward them promptly. I agree with the reviewer that this is a very exciting topic, presented in an attractive and persuasive fashion. However, we also agree that a careful revision is imperative.

As noted in my letter of May 8, and also discussed with you by telephone, the manuscript length must be reduced by a full third in order to comply with our target maximum of six journal pages. Removing the more speculative or superficial material in this will also provide a response to the reviewer's request. Please consider carefully the other points raised by the reviewer, but I recognize that your final version will still reflect Kaldor's views poorly. I recognize that he has published little, but you should point out this controversy in the introduction and emphasize your evidence that contradicts his conclusions. Although the C_{60}-soccer ball structure will surely attract reader interest, it might be better to leave the extensive discussion of the appropriateness of the structure and soot formation until after all of the experimental evidence is presented. I would also suggest a little more description of your nifty apparatus, except that this would surely make it much more difficult for you to get down to our six page limit.

In retyping the manuscript, please be sure that it is entirely double spaced (including references and figure legends), that the legends are on a separate page, and that superscript reference numbers follow punctuation marks. We look forward to publishing your revised manuscript.

Best regards,

FW McLafferty

F. W. McLafferty
Editor

ATB

FWM:cni
cc: Reviewer report

ACCOUNTS OF CHEMICAL RESEARCH

Report of:

Reviewer - 3

MS# : AR870034F-0-1-0
AUTHOR: James R. Heath, Sean C. O'Brien, Robert F. Curl , Harry W. Kroto and Richard E. Smalley
TITLE: Buckminsterfullerene and Other Clusters of Carbon

RETURN BY: July 14, 1987

This is a well written paper clearly outlining the recent developments by the Rice Group on C_{60} and related clusters. This is definitely suitable for publication in the Accounts of Chemical Research. However, a few more comments about other possible structures such as graphite or carbyne forms will improve the paper.

References 1-10 are incomplete in the version which I received.

ACCOUNTS OF CHEMICAL RESEARCH

Report of:

Reviewer - 4

MS# : AR870034F-0-1-0
AUTHOR: James R. Heath, Sean C. O'Brien, Robert F. Curl, Harry W. Kroto and Richard E. Smalley
TITLE: Buckminsterfullerene and Other Clusters of Carbon

RETURN BY: July 22, 1987

This is a very interesting paper that will be widely read. The work described here has captured the imagination of theoretical, physical, and organic chemists. It has already received a wide, if cursory, press, so that there will be great interest in an Account.

However, I cannot recommend publication in its present form. First of all, the references numbered 1-3, 5-7, 9, 10, 32a and 57a are incomplete. Since, for example, the last of these references takes an opposing point of view, it should at least be given a full citation.

Secondly, Section III starting on page 10 and covering soot and spontaneous growth of carbon shells is, to my reading, very superficial and speculative. Yet it is presented as if it had the same experimental backing as the rest of the work. I would urge the authors not to mislead their readers. Why not label this section more clearly as speculation?

Finally, the authors claim on page 19 that their model is "fully supported by all known experiments and theoretical calculations." However, my reading of reference 57b (entitled "$C_{60}La$ - A Soccer Ball Deflated") is that there is another side of the story that is not being given much more than lip service in this article.

Admittedly, the last two points might be considered matters of taste; even a cautious editor would probably accept the response that soot is important, that the authors of reference 57b have not done as many control experiments as have the Rice group, etc. However, the overselling of C_{60} has done little to enhance the reputation of the current authors. A little humility on their part and a lot more scientific honesty in presenting the evidence would be gratefully received by the readership of Accounts.