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Dreams in a Charcoal Fire: Predictions about Giant Fullerenes and Graphite Nanotubes [and Discussion]

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Dreams in a charcoal fire: predictions about giant fullerenes and graphite nanotubes

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The early prediction of hollow graphite molecules suggested that they should be supercritical under ambient conditions. This is not true of C_{60}, but might still be true of higher fullerenes and graphite nanotubes of large diameter.

1. Introduction

My title refers to the celebrated vision of Kekulé, one of the founders of the concept of chemical structure. In 1865, staring drowsily one evening into the fire, he saw in a dream the cyclic structure for benzene, that fundamental unit of all aromatic molecules, and of graphite and the fullerenes. In his reverie, he imagined the atoms gambolling before his eyes... 'one of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes' (Kekulé 1890). In this paper I deal, not so much with the recent triumphs of the identification and bulk preparation of buckminsterfullerene, as with its imaginative prehistory. This begins with Dalton's atomic theory, elaborated from 1803 onwards. Despite a very promising start, atomic theory languished for decades as merely a sort of useful metaphor. One good reason was its failure to come up with consistent atomic weights for the elements and formulae for their compounds. Whether, for example, the atomic weight of oxygen was 8 and water was HO, or whether it was 16 with water as H_2O, remained uncertain for half a century.

And yet shortly after Dalton proposed his theory, the whole problem had been solved (Avogadro 1811). On the assumption that equal volumes of gas under the same conditions of temperature and pressure contained the same number of molecules, Avogadro was able to allocate consistent formulae to the known gases and vapours, and consistent atomic weights to the elements composing them. The one novel assumption he had to make was that the common elemental gases, hydrogen, oxygen, nitrogen and the like, were composed of double atoms: H_2, O_2, N_2 and so on.

Avogadro's solution seemed deeply repugnant to the chemists of the day; so repugnant that it was not so much argued against as simply ignored. At this distance in time, it is hard to see why. My guess is that monoelemental compounds like O_2 seemed completely incredible. All chemical experience, buttressed by the amazing successes of electrochemistry, suggested that elements combine because of some difference of polarity; the more dissimilar two elements were, the more likely they would be to combine. So how could two identical atoms react together? As a result of this mind-set, chemistry remained in needless confusion from 1811 till 1860, a whole working lifetime. Avogadro's hypothesis was finally accepted only after a special exposition of it (Cannizzaro 1858) was distributed at the conference of Karlsruhe in 1860. So I would like to propose Avogadro, the inventor of the whole concept of monoelemental compounds, as the ultimate godfather of buckminsterfullerene. His is the original insight which underlies our familiar acceptance of, for example, O_2, P_4, S_8, B_{12}, and now the latest and most striking example, C_{60}.

2. Early predictions of hollow graphite molecules

Carbon, of course, is the ideal element for simple-minded chemists. Obey a few elementary valency rules, and almost any organic structure you can doodle would exist, if you could make it. And this is perhaps the justification for my own simple-minded contribution to the story of C_{60}. For many years I have maintained a scientific *alter ego*, Daedalus, whose musings used to appear in *New Scientist* but now appear in *Nature*. Daedalus launches scientific proposals which are intended to fall in that uneasy no-man's-land between the clearly feasible and the clearly fantastic. His aim is inevitably rather erratic, and many of the attempts land on one side or the other. An account of some of Daedalus's chemical proposals has appeared in *Chemistry in Britain* (Jones 1987). His greatest moment came late in 1966, when he proposed the hollow-shell graphite molecule (Jones 1966).

All these years later, I can't remember just what triggered that particular proposal. But once I had the idea, it seemed to me that the physical properties of such structures would be highly unusual. I was thinking of what would now be called the giant fullerenes. These big, light molecules should be mainly empty space, and so would have a very low bulk density. In addition, I felt that they would interact with each other very weakly indeed. Despite their enormous molecular weight, they might be extremely volatile. After some naive calculations, I predicted for my hollow graphite molecules the properties below.

1. Bulk density intermediate between those of liquid and gas (e.g. 40 kg m^{-3}).
2. Supercritical at ambient pressure and temperature.
3. Pourable as light, loose liquids with an ill-defined surface.
4. Able to trap smaller molecules in their hollow interiors, and possibly to exchange them.
5. Able to act as lubricants, with the molecules rolling like ball-bearings.

Of these predictions, 5 was pure provocation: I didn't believe it at the time, and indeed it is clearly absurd. At the molecular level, lubrication functions by sliding, not rolling. No molecule, certainly not a hollow one, could act as a frictionless undeformed rolling element, and in any case would need a molecularly smooth track on which to do so. The other predictions seemed to me about right for Daedalus: challenging, but not obviously beyond belief.

As with most of Daedalus's output, this suggestion met with no reaction from the scientific community. But some years later I published a book containing a number of Daedalus's better schemes (Jones 1982). Many of the articles were enhanced with diagrams and additional background material which had not been included in the original publications. Among these extended items was the article on the hollow graphite molecule. I have to salute the forbearance with which the editor, Michael Rodgers, tolerated the heavy technical additions to what was intended as basically a popular and light-hearted book. A sterner editor would have put a blue pencil through the lot: when my position among the originators of the hollow graphite

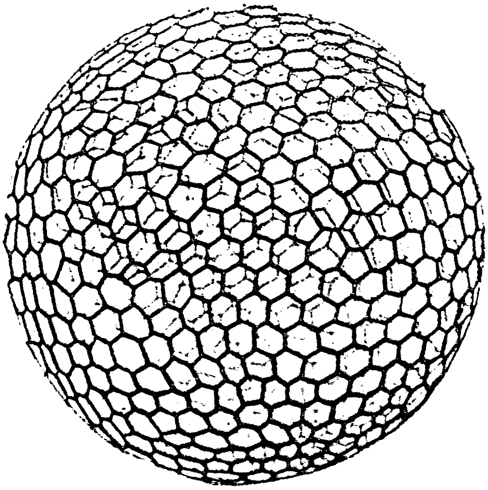

Figure 1. The diatom *Aulonia hexagona* is an almost perfect 100000-fold model of a giant fullerene with about 1200 carbon atoms. (From *On growth and form*, by W. D'Arcy Thompson. Courtesy of Cambridge University Press.)

molecule would have been far weaker. In the event, he allowed me to include a detailed discussion of these hypothetical molecules, including a biological analogy (figure 1) and some comments on the theory of polyhedra, in particular the rather surprising fact that any hexagonal mesh needs exactly 12 pentagons to make it into a closed shell; a rule discovered by Euler, but which I found in that wonderful book *On growth and form* (D'Arcy Thompson 1942). I was particularly concerned to find the largest size that hollow graphitic molecules could be made before they would collapse by inversion. A highly suspect calculation suggested that the biggest stable one would be C_{260000}, or thereabouts. It didn't occur to me to wonder how small they could be made; a sad and crucial failure of chemist's intuition!

3. Buckminsterfullerene arrives

In 1985 the remarkable predominance of the C_{60} fragment in the mass spectra of laser-ablated graphite was noticed, and the hollow buckminsterfullerene structure was suggested (Kroto *et al.* 1985). This brilliant proposal owed nothing to my musings in this area; in fact Harry Kroto only learnt of them later through Martyn Poliakoff at Nottingham University, who had a copy of the book. The only useful contribution which it made to the fast-developing saga was in pointing out the necessity for 12 pentagons in any closed-shell hexagonal structure: the C_{60} structure had been proposed without guidance from Euler's rule. None the less, Harry had the courtesy to telephone me with congratulations on a remarkable prediction. One of Daedalus's notions had turned out surprisingly close to possible reality.

Between 1985 and 1990, the structure and bulk properties of buckminsterfullerene remained uncertain. I was able to maintain an optimistic hope that predictions 2–4 would turn out to apply even to this small and compact molecule (prediction 1, a consequence of the empty space inside a large hollow molecule, could only be true of giant fullerenes). But when C_{60} was produced in macroscopic quantities (Krätschmer

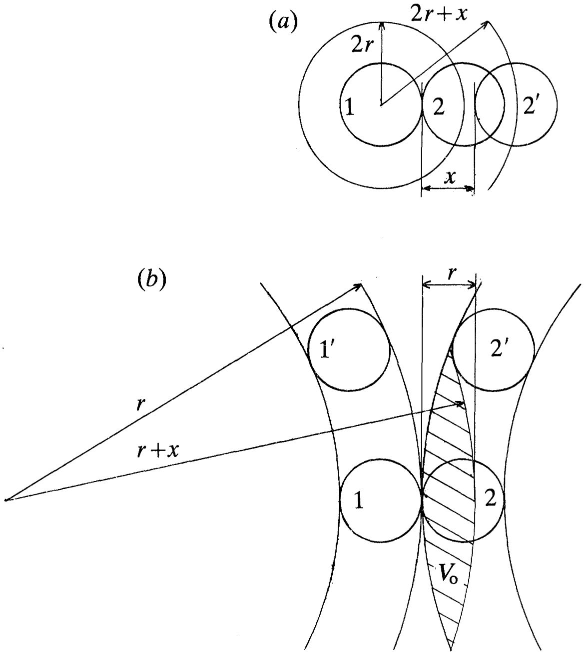

Figure 2. (*a*) Interaction of small spherical molecules. The molecule at 2, on the inner edge of a square potential well of width x, is 'in contact' with the central molecule 1. At 2′ it is on the outer edge of the well. The radius $2r$ defines the exclusion volume around the central molecule; the shell between radius $2r$ and $(2r+x)$ defines its interaction volume. (*b*) Interaction of spherical shell-molecules. Atoms 1 and 2 on their respective shells are 'in contact' on the inner edge of a square well of width x. Atoms 1′ and 2′ are beyond the outer edge of the well. If the shell-atoms are taken as uniformly 'smeared' around the shells, the energy of interaction between the molecules should be approximately proportional to the 'overlap volume' V_o, the region in which the shells are closer than x.

et al. 1990), it became clear how wrong I was. So far from being supercritical at ambient conditions, or even remarkably volatile for its molecular weight, C_{60} does not melt, and is so involatile that its variation of vapour pressure with temperature has to be measured by mass spectroscopy (Pan *et al.* 1991). Only prediction 4, the ability of a hollow graphite molecule to entrap small atoms or molecules inside it, has turned out correct (Heath *et al.* 1985; Weiss *et al.* 1988).

The determined theorist should make an orderly retreat in the face of the advancing facts. Giant fullerenes have not yet been made in bulk, so I am still free to maintain my original claims in respect of these as yet hypothetical substances. Predictions 2 and 3 were based essentially on my intuitions about the weakness of the expected interaction between big spherical molecules. I buttressed them with some highly over-simplified calculations, not hitherto published. They are more of a speculation than a rigorous argument.

4. Properties of giant fullerenes

Prediction 3 is a consequence of high molar mass. The 'scale height' of a gas in a gravitational field is that height for which its pressure decreases by 1/e. In the perfect-gas approximation, it is given by $h = RT/gm$, where m is the molar mass of the gas. For air at ambient temperature, $h = 8.8$ km. If my maximally sized giant fullerene $C_{260\,000}$ were a perfect gas, it should have $h = 8$ cm. Supercritical C_{260000} would be a very imperfect gas. It would therefore have $h < 8$ cm, and could be retained safely in a fairly tall open laboratory beaker.

Prediction 2, that such big molecules ought to be supercritical gases under ambient conditions, is supported by a more contentious argument based on their equation of state. The liquid state, and condensed phases in general, exist because of the short-range attractive forces between molecules. The simplest of all equations of state, Boyle's Law, $PV = RT$, makes no provision for attractive forces and does not predict condensed phases. The next approximation is Van der Waals' equation:

$$(P+a/V^2)(V-b) = RT.$$

This equation acknowledges that real molecules have size. They have an exclusion volume, defined as the region around the molecule from which the centre of any other molecule is excluded. This is allowed for by the constant b, which is usually taken as equal to half the molar exclusion volume. The equation also recognizes the existence of a sphere of influence around each molecule, an interaction volume within which any other molecule will experience a force of attraction. This force is usually represented by a Lennard–Jones 6–12 potential. The derivation below follows a simpler treatment (Flowers & Mendoza 1970) in which the potential is taken as a square-well function as deep as the Lennard–Jones minimum (figure 2*a*). Its width x is chosen to give the same volume-integral, and defines an 'interaction volume' V_x around the molecule, which will contain the centre of any molecule in the square well. This form of molecular pair potential then appears in the Van der Waals equation as the constant a, equal to half the product of the molar interaction volume and the molar interaction energy.

The Van der Waals equation is one of those happy approximations which somehow make reasonable predictions well outside the region in which their assumptions are valid. It can even be used to predict the critical constants of a gas. A Van der Waals gas should have a critical pressure and temperature given respectively by

$$P_{c,\,vw} = a/27b^2 \quad \text{and} \quad T_{c,\,vw} = 8a/27Rb.$$

Reasonable choices of a and b can often predict the critical constants of real gases to within 10 or 20% of their observed values.

An estimate of the critical constants of a substance composed of large hollow-shell molecules can therefore be obtained from its values of a and b. Consider two such molecules in contact (figure 2*b*). An atom in one shell finding itself close to an atom in the other, will experience an attractive force; pairs of atoms further apart will feel a much smaller force and will contribute little to the interaction. If each shell is taken as a uniform distribution of atoms exerting a square-well potential, the energy of interaction reduces to the product of the energy-density of the potential well and a lenticular volume of overlap V_o. The central width of this volume is x, the square-well width. For r much greater than x, V_o (and therefore the energy of interaction) increases linearly with r. The interaction volume V_x is defined as in figure 2*a*: a shell of radius $2r$ and thickness x. For r much greater than x, it equals $16\pi r^2 x$ and therefore increases as r^2. The constant a is half the product of the molar interaction energy and the molar interaction volume. So it increases as $r^2 r$, i.e. as r^3. The constant b, proportional to the exclusion volume of the shell-molecule, also increases as r^3.

Thus for large shell-molecules the factor a/b, which determines the Van der Waals critical temperature $T_{\mathrm{c,vw}}$, should be constant with change of radius. Extending the treatment to the case of figure 2a in which r is comparable with x (in fact $r = 0.922x$, after Flowers & Mendoza), and making the simplifying assumption that x is effectively unchanged, gives this constant as about 0.45 times the value of a/b for the equivalent small molecule. By contrast, a/b^2, which determines the critical pressure $P_{\mathrm{c,vw}}$, should decline as r^3. Accordingly, a hollow molecule of reasonable size, say five times the radius of a simple fully dense molecule, should have a T_{c} of about half the normal value, and a P_{c} about 1% of it. T_{c} and P_{c} for common simple fluids seldom exceed 500 K and 70 atm, so reductions of this magnitude might well bring them down to ambient temperature and pressure or below. Hence a substance consisting of hollow spherical molecules could quite plausibly exist as a supercritical fluid under ordinary conditions. The low critical pressure seems a more secure prediction than the low critical temperature.

It is worth noting that this calculation pays no attention to the mass of the molecule. The liquid or gaseous state of the material, and its critical constants, depend only on the molecular radius and pair potential. This runs counter to our chemical intuition; it is natural to imagine that big molecules form involatile solids or high-boiling liquids because they are too heavy to take off. This cannot be true. Big molecules have low volatility because they interact strongly with their neighbours. Even a heavy molecule like UF_6 can be surprisingly volatile; its spherical symmetry and weak pair-potential reduces its interaction with its neighbours. Molecular mass must have some restraining influence on volatility; after all, critical temperature and pressure increase slightly along the series H_2, D_2, T_2. The low densities of hollow-shell molecules like the giant fullerenes should at any rate make them more volatile than fully packed molecules of equivalent radius.

The above calculation is clearly too impressionistic to support precise predictions. The case of the giant fullerenes can be studied more carefully in the light of a recent calculation of a 6–12 potential function for C_{60} molecules based on values for graphite (Girifalco 1992). Contrary to my expectations, the C_{60} molecule interacts very strongly with its nearest neighbours: its second virial coefficient $B(T)$ is two orders of magnitude greater than for the common gases. A Van der Waals gas has $B(T) = b - a/RT$. Values of a and b for C_{60} can be derived by fitting an equivalent square well to Girifalco's potential function, but they do not reproduce his $B(T)$. The best agreement is obtained from a square well with an outer limit rather beyond that suggested by the potential function. The resulting values of a and b then predict $T_{\mathrm{c}} = 1300$ K at $P_{\mathrm{c}} = 12$ atmospheres, and fit $B(T)$ in the neighbourhood of this T_{c}. These critical constants do not seem unreasonable for C_{60}. A fullerene with five times the radius, say C_{1500}, should then on the argument above have $T_{\mathrm{c}} = 650$ K at $P_{\mathrm{c}} = 0.1$ atmospheres. The high critical temperature is a little disappointing. A fluorinated or hydrogenated giant fullerene, whose molecules would attract each other less strongly, should have a lower one.

Despite the tenuity of the argument, I continue to feel that large enough hollow spherical molecules should show very low critical constants, or at any rate a very low critical pressure. But even if fullerene molecules large enough to test this claim are ever obtained in bulk, they could still escape on a technicality. Molecular models (Kroto & Mackay 1988) show them not to be spherical, but distinctly icosahedral. Their mean interaction energy, averaged over all orientations of molecular collision, might not be the same as that of spheres of an equivalent diameter; though the difference should not be great. In any case, such molecules when synthesized may well turn out to be spherical or nearly so, being inflated by trapped internal gas like tiny footballs.

5. Predictions of giant graphite nanotubes

Shortly after the mass-spectroscopic identification of the C_{60} fragment, and the proposal of its spherical structure, Daedalus attempted to maintain his lead in the field by suggesting the synthesis of what would now be called giant graphite nanotubes (Jones 1986). He proposed to make these molecules by a mechanism which has since been disproved for C_{60} (O'Keefe *et al*. 1986; McElvany *et al*. 1987), the laser-detachment from a graphite surface of single graphite sheets, which subsequently curl up. A laser interference-pattern of closely spaced lines, he claimed, would detach long thin graphitic strips; these would roll or curl up into cylinders. Again I was intrigued by the possible volatility and even supercriticality of these large, empty, cylindrical molecules. A calculation like that of §4 should apply to them as well. I further suspected that, like high polymers in liquid solution, such long volatile molecules would make the air extremely viscous, even if present in very low concentrations. They could thus be used as a blanketing agent to slow cars on motorways, as a sound-damping medium, and as a shield against bullets and missiles.

Graphite nanotubes have since been identified by electron microscopy of the products of carbon-arc synthesis (Iijima 1991); another successful prediction for Daedalus. But the bulk synthesis of giant nanotubes, like that of giant fullerenes, is still beyond us. Such large single-sheet graphite cylinders (they should perhaps be called microtubes, or even millitubes) might possibly be grown, or even blown. Graphite is made commercially by heating carbonized precursor material to 3000 °C. At high-temperatures dislocations in a graphite sheet become quite mobile (Scott & Roelofs 1987). The small disordered sheets of the starting material can grow and seek the thermodynamic advantages of large-scale order (Maire & Mering 1960). They can be oriented and extended by simple stretching; oriented graphite fibres are made by the controlled simultaneous stretching and graphitization of a polymeric precursor fibre. So Daedalus imagines (Jones 1991) that at a high enough temperature, a graphite sheet approaches a condition something like a liquid soap-film. It could be stretched in two dimensions, so that a giant fullerene molecule might even be expanded like a soap-bubble. With still more help from some as yet unimagined natural micro-phenomenon, a giant nanotube could perhaps be cylindrically extruded and inflated like blown polyethylene film. Such a tube would have to be rapidly quenched, for a cylindrical liquid film becomes unstable if its length exceeds π times its diameter. It breaks up into a chain of bubbles, which in this case would be giant fullerene molecules.

At this stage, however, my argument has degenerated from defensible speculation into a pure dream in a charcoal fire. I look forward to the eventual bulk production, by unguessed chemistry, of giant carbon fullerenes and nanotubes. Even if they do not have the properties I originally imagined for them, I am sure they will be fascinating substances.

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Discussion

E. Wasserman (*The DuPont Company, U.S.A.*). When you talk about the possible phases of something like C_{60} (is it a gas, a liquid or a low density liquid of high compressibility), we really have to compare it with another phase which may be accessible under the same temperature and pressure conditions. In many such cases, some of the features of C_{60} are due to intermolecular interactions, in some of the more condensed phases, rather than to individual molecular properties that you were concentrating on. For example, the very strong tenacity of one C_{60} molecule to bond to another, as well as to incorporate solvent molecules in the interstitial spaces, depends critically on how well they seem to fit together, as well as to the intrinsic forces that may be found in smaller molecules. We find that if you have small degrees of substitution of C_{60}, for example, alkyl groups, the volatility increases dramatically.

We see mass spectra at much lower temperatures than we do for C_{60} itself. So, if the packings of the condensed planes are interfered with, you may be able to increase volatility, and go towards some of the directions you were referring to.

D. E. H. JONES. My original feeling was that the individual graphite planes have very little feeling for one another, and that is why graphite is a lubricant. I had guessed the interaction between graphite sheets was quite low. Clearly, if that is true, it does not transfer to the fullerene structures, which is a surprise, but I am glad that there is a way of getting around it by suitable substitution.

E. WASSERMAN. I think one of the reasons that graphite is a lubricant, is that as one sheet moves relative to another, you don't lose interactions. The key point is the ease of rotation of C_{60} in the solid.

E. J. APPLEWHITE (*Washington, U.S.A.*). I enjoyed your comments on the giant fullerenes, which reminded me of one of Buckminster Fuller's most way out ideas. Please don't judge Fuller on this particular idea, but I will tell you about it in the spirit of interdisciplinary interaction. If geodesic balls are built big enough, the weight of the construction materials are minuscule, compared to the weight of air contained within the structure. If the sun heated the interior of the dome, then the weight of the air inside the dome, plus the weight of the structure, would be less than the weight of air normally, and the structure would float. Control of the heating procedure would control the altitude of the bucky-ball.

D. E. H. JONES. A nice notion; a flying greenhouse!

H. W. KROTO (*University of Sussex, U.K.*). When we attempted to extract C_{60} we were not sure of the state, solid, even a gas. It might have been volatile, because UF_6 is volatile, and C_{60} is like a rare gas in many ways. Radon is only half the weight, so we thought that if we were producing it, it might have evaporated before you could 'catch it'. So there are interesting aspects of volatility, especially where C_{60} is concerned. The second point is that at ICI, Margaret Steel has produced something similar to your 'pipe'. I believe her group used a CO_2 laser on a spinning graphite cylinder, and spun off some small balls. They were not hollow, but this convinced me that these were ways of making the concentric shell structures that Iijima observed for the first time many years ago. I am unhappy that we were not able to collaborate further with that group at the time, because the evidence she had was that they were concentric shell structures. She was interested in producing carbon fibres, and spinning these things, but they were very close.

S. IIJIMA (*NEC Corporation, Japan*). The giant fullerene structures are not as you mentioned. Already I, and other groups, have done similar experiments that involved having the metal in a small cluster, for example nickel or iron, and carbonising the metal. I have made thin graphitical films all around the metal particle, so it is similar to the structure you have mentioned.

R. C. HADDON (*AT & T Bell Laboratories, U.S.A.*). The question of what holds C_{60} together, and just how strong the forces are, is a very interesting one. Work we have done recently has shown that it is possible to make membranes of C_{60}, i.e. a free standing film of C_{60} molecules. It is not obvious that this is possible, because you are asking a sheet of C_{60}, a few thousand ångstroms thick, to support itself in a free standing arrangement, which is composed of C_{60} molecules, each of which is spinning in space millions of times a second. So I am particularly interested in learning about the forces that hold C_{60} together, and whether or not they differ from those that hold other Van der Waals's solids together.

D. E. H. JONES. I would not expect C_{60} to have any tensile strength at all. It is intriguing and remarkable. This phenomena is not seen with other spinning solids, such as camphor.

C. T. PILLINGER (*Open University, U.K.*). People have talked about inflating C_{60}, but what happens when you compress? I have heard reports that diamonds are produced. What are your thoughts on the subject?

D. E. H. JONES. In my original suggestion, I was worried that the structure would collapse in on itself, and that you would gain a lot of surface energy of interaction. I did some rather unbelievable calculations to see how big it would be, before it would spontaneously invert. My feeling is that a structure enclosing a large empty space will be unstable, and that it will not tolerate compression. That again applies to the notion of the giant fullerenes. C_{60} itself looks small enough and neat enough to withstand any such deformation, but one might expect the IR spectra of the larger fullerenes to show some worrying modes, before the thing collapses.