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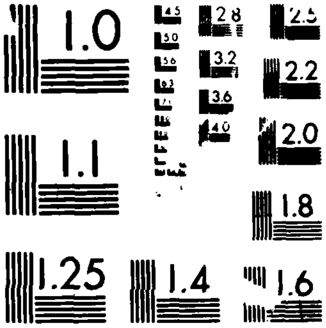
UNCLASSIFIED N00014-86-C-0043 F/G 20/5 NL



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Contract N00014-86-0043

TECHNICAL REPORT No. 58

Clusters: Link Between Molecules and Solids

by

Daniel A. Jelski and Thomas F. George

Prepared for Publication

in

Journal of Chemical Education

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

November 1987

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87 11 24 104

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SECURITY CLASSIFICATION OF THIS PAGE

AD-A188 170

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/87/TR-58	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York	6b. OFFICE SYMBOL (If applicable)
7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260	7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-0043	
8c. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217	10. SOURCE OF FUNDING NOS. PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT NO.

11. TITLE

Clusters: Link Between Molecules and Solids

12. PERSONAL AUTHOR(S) Daniel A. Jelski and Thomas F. George

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
	FROM ______ TO ______	November 1987	29

16. SUPPLEMENTARY NOTATION

Prepared for publication in Journal of Chemical Education

17. COSATI CODES

FIELD	GROUP	SUB. GR.

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

CLUSTERS, MOLECULES, SOLIDS, LINK, HÜCKEL MODEL, CARBON ~~60~~

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The physics and chemistry of clusters is discussed. First, clusters are compared with molecules, on the one hand, and then with solids on the other. It is found that clusters are an intermediate state, and therefore of special interest. The Hückel model is elucidated since this is the simplest of possible semi-empirical methods, and since it is readily applied to clusters. Two kinds of clusters are discussed in greater detail: alkali-metal clusters, because they are the obvious candidate for application of the Hückel model, and Buckminsterfullerene, which is a C_{60} cluster arranged in a soccer ball geometry.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson	22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410
	22c. OFFICE SYMBOL

DD FORM 1473, 83 APR

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SECURITY CLASSIFICATION OF THIS PAGE

Journal of Chemical Education, in press

Clusters: Link Between Molecules and Solids

Daniel A. Jelski and Thomas F. George
Departments of Chemistry and Physics & Astronomy
239 Fronczak Hall
The State University of New York at Buffalo
Buffalo, New York 14260

Abstract

The physics and chemistry of clusters is discussed. First, clusters are compared with molecules, on the one hand, and then with solids on the other. It is found that clusters are an intermediate state, and therefore of special interest. The Hückel model is elucidated since this is the simplest of possible semi-empirical methods, and since it is readily applied to clusters. Two kinds of clusters are discussed in greater detail: alkali-metal clusters, because they are the obvious candidate for application of the Hückel model, and Buckminsterfullerene, which is a C_{60} cluster arranged in a soccer ball geometry.

In this article we review some of the recent work reported with clusters of atoms, concentrating on the fundamental principles underlying cluster chemistry and physics. We begin by comparing clusters with molecules, on the one hand, and then with solids. Clusters are an intermediate state between individual molecules that make up gases and solids, and therefore of special interest. The Hückel model is elucidated since this is the simplest of possible semi-empirical methods, and it is readily applied to clusters. Two kinds of clusters are discussed in greater detail: alkali-metal clusters, because they are the obvious candidate for application of the Hückel model, and Buckminsterfullerene, which is a C_{60} cluster arranged in a soccer ball geometry. We shall also consider some of the practical consequences of this work.

Generally, when we refer to a cluster, we mean a group of atoms, usually three to several hundred, that exist in a solid state. An example is sodium, which is a quite stable solid, but we do not usually think of Na_5 or Na_7 as being a common species. These would be considered examples of clusters.

A special case is the class of clusters of carbon. Here we must distinguish between macromolecules and carbon clusters. Macromolecules are usually include carbon, hydrogen, oxygen, and nitrogen, among others. When we speak of carbon clusters, on the other hand, we mean a "molecule" that consists exclusively of carbon, such as C_{60} or C_{70}. (Even this can not be taken too literally, since one reads about clusters of benzene in the literature. However, we shall not consider this example further.) Obviously the distinction between cluster, molecule and solid is only one of convenience. Nevertheless, it is useful to discuss clusters separately because they have some of the properties of molecules and solids, and thus compose a state of matter distinct from that of solids or gases.

Clusters and Solids

In a solid crystal there are a huge number of atoms, which can be taken as infinite. It is thus possible to discuss the bulk properties of the material since the importance of the individual atom or electron is rather insignificant. Conversely, in a molecule there are few enough atoms that it is no longer possible to ignore the individual behavior. Let us look at the vibrational motions as an example. Consider a non-linear molecule with N number of atoms. Each atom can move in three directions, x, y or z, meaning that there are 3N degrees of freedom. In other words, we must specify 3N numbers before we can describe the motion of all the atoms in the molecule. However, we can make the problem somewhat simpler. First, suppose that the whole molecule is defined to be at rest. We can do this by using the position of one atom as the origin of this coordinate system. Then by definition, this atom cannot move. We have thus eliminated three degrees of freedom called translational degrees of freedom. Further, suppose we prevent the molecule from rotating around its origin. Since we have also assumed it to be non-linear, this assumption eliminates an additional three degrees of freedom, known as rotational degrees of freedom. We are thus left with 3N-6 degrees of freedom. These are called vibrational degrees of freedom in that they describe the vibrational motions of the system.

In the case of linear molecules, there are really 3N-5 vibrational degrees of freedom since there are only two rotational degrees of freedom.

The simplest possible molecule is one with two atoms. There are a total of six degrees of freedom -- three translational, two rotational and one vibrational motion. These are illustrated in Fig. 1.

[Insert Figure 1 about here]

For molecules it is relatively easy to calculate the various degrees of freedom, to write down the motions of each atom in terms of the so-called "normal modes" of the system, and then to do explicit calculations of the molecular motion. Normal modes are the fundamental motions of the system in terms of which all other possible motions can be expressed. As the system gets larger, this calculation rapidly becomes impractical. Certainly for a solid, with billions of atoms, it becomes impossible and even unnecessary, since we can then take advantage of the fact that we can ignore individual atoms.

When confronted with large systems, it is no longer possible to draw figures like Fig. 1. Instead of calculating the normal modes, we now assume that the atoms are arranged in some periodic repeating structure, called a unit cell. We can then calculate the motions of the unit cell, which may contain up to 20 atoms, and duplicate that for the entire system. But we also have to consider motions that involve several unit cells. In this case we have what is known as a collective motion of the solid. A good example is a rubber band. If one stretches it and then plucks it, it will vibrate. We can describe this motion without knowing the precise behavior of each atom. This is called the collective motion of the rubber band. For vibrational motions, which we have been discussing, these collective motions are known as phonons.

While we have been considering vibrational motions, we could just as easily have been considering electronic motions. For small atoms it is possible to write down the quantum mechanical Schrödinger equation for each electron and solve the result numerically. As the number of atoms (and electrons) increases, this becomes impractical, and so we instead write down the result in terms of collective motions. In the case of electrons, this collective motion is known as a plasmon.

The case of clusters falls in the middle, however. Clusters are generally large enough that a precise calculation, as for a small molecule, is not possible. However, they are still small relative to a bulk solid, and hence it can be dangerous to discuss collective motions in a cluster. The study of clusters is thus very interesting from a theoretical standpoint since they form a link between the macroscopic (bulk solid) and microscopic (molecular) points of view.

The pictures we have painted are at two opposite extremes. In actuality, our model for clusters is somewhere between an exact calculation (based on quantum-mechanical first principles and known as an *ab initio* calculation) on the one hand, or a purely phenomenological calculation (that treats matter as if it were a continuum) on the other hand. In reality there are several intervening possibilities which are characterized as semi-empirical. These sorts of calculations start with quantum mechanical principles, but are then simplified by making some approximations. These approximations usually involve insertion of parameters into the calculation that are chosen solely because they reproduce the experimental data, and hence the name semi-empirical.

Semi-empirical methods can be quite complicated and also quite accurate. Their big advantage is that they can be readily applied to relatively large systems, and while still retaining some of the mathematical rigor of quantum mechanics, they yield relatively accurate results in a short period of time. One of the most popular of these methods is known as MNDO, which stands for Modified Neglect of Diatomic Overlap.[1] This method, available as a series of computer programs, can be used on the ubiquitous VAX computer (among others), and can easily calculate parameters such as the heat of formation for molecules containing up to 40 atoms, an impossible task for an *ab initio* calculation.

The Hückel Model

The simplest and one of the first of these semi-empirical methods is called the Hückel[2] method, which was first developed[3] (in the 1930's) to describe conjugated systems, i.e. molecules that can be written as an alternating series of double and single bonds (see Fig. 2). In what follows, we shall describe the simple Hückel method and then demonstrate its application to cluster chemistry. To illustrate the fundamental idea behind the Hückel model, suppose we have a group of identical atoms in a molecule. For each atom we can distinguish between the valence electrons and the inner-shell electrons. From the standpoint of chemical bonds we can treat the inner-shell electrons by assuming that the valence electrons feel some average charge, that is, the valence electrons are attracted to the nucleus but repelled from the surrounding electrons. Hence the total charge felt by a valence electron will be the difference between the attraction and the repulsion, and this can be taken as a constant, called α, also known as the

Coulomb integral. On the other hand, α can be chosen as zero since where we define the zero-point of energy is arbitrary, and it is sensible to think of isolated, individual atoms as having no energy.

The bond between the atoms, however, is due to the interaction between two valence electrons, one on each of two neighboring atoms. Since the atoms are all identical, this interaction can also be considered a constant, called β, also known as the resonance integral. This parameter is in units of energy, and as long as one is not picky about which units are used, it is possible to simply set $\beta = -1$. It is the only parameter required by the Hückel model. Since we are assuming that the atoms are bonded, it follows that the energy of this interaction must be exothermic, and hence β must be a negative number. The parameter β tells us the strength of the interaction between two electrons on two neighboring atoms and is thus related to the bond strength. We can easily relieve our condition of all identical atoms by choosing different β's for each species.

[Insert Figure 2 about here]

The obvious question is what happens when there are two valence electrons on one atom? In this case the Hückel model no longer works since we have no way to account for this interaction. Electrons on neighboring atoms are relatively far away from each other and hence interact relatively weakly. Under this circumstance it is possible to consider an average electronic configuration and call that β. But if the electrons are on the same atom, this is no longer true and the Hückel model breaks down. How then can we apply the Hückel model to carbon systems with conjugated bonds, since carbon has four valence electrons?

The key to this question is the notion of molecular orbitals. Bonds in conjugated systems consist of two types, σ-bonds and π-bonds; σ-bonds are localized between two atoms, where each carbon atom contributes one electron to each of three σ-bonds, and the bond is made by the neighboring atom contributing the second electron. π-bonds, on the other hand, are delocalized in that, in a fully conjugated system, the π-electrons move around the whole molecule. The essential principle is that each carbon atom contributes only one π-electron, and furthermore that the π-electrons are of significantly higher energy than the σ electrons. Hence we can think of the π-electrons as being the valence electrons for the molecule, whereas the σ-electrons are thought of as inner-shell. Thus β stands for the energy of interaction between two π-electrons on neighboring atoms.

For some simple systems this method works quite well. By making other additional approximations, it is possible to calculate bond lengths, charge densities and other physically measurable quantities. Table 1 shows some of the results of these calculations compared with experimental data. Given the simplicity of the technique, it is amazing that the results are as accurate as they are. It should be pointed out that the actual calculation is quite simple and can be carried out for small molecules on a microcomputer. The procedure is described in full in standard texts on quantum chemistry.

[Insert Table 1 about here]

The Hückel model has several implications. First, all atomic attributes are expressed in the constant β. Once β has been determined, the specific nature of the atoms is irrelevant. Secondly, in its simplest form, the Hückel model is independent of bond length. Only the fact of whether or not atoms are bonded is of significance. (A modification of the simple technique allows one to calculate bond lengths.) Therefore, once β has been determined, the results of the Hückel model depend ONLY on the topology of the molecule and on nothing else. Topology is like geometry, only simpler. The topology of a molecule depends only on which atoms are bonded to each other. It makes no difference how long each bond is, what the bond angle is, or how close or how far apart the atoms are. Figure 3 contains examples of different topologies for three and four atom molecules. Recalling that N is the number of atoms in the molecule, we can express the topology in a very simple way called the adjacency matrix, a square, N by N matrix with zeros along the diagonal. The ij-component (the number in the i^{th} row and the j^{th} column of the matrix) is unity if atom i is bonded to atom j; otherwise it is zero. An example of an adjacency matrix is given in table 2. Once we know the adjacency matrix and β, then the Hückel results are determined.

[Insert Figure 3 about here]

[Insert Table 2 about here]

The fact that the Hückel model depends only on geometry is both a blessing and a curse. Obviously if one is interested in phenomena that depend sensitively on the precise configuration around an individual atom, or the precise length of a bond, then the Hückel model is not very useful. If, on the other hand, one is interested in comparing the effects of different geometries, then the Hückel model is very useful indeed.

Alkali Metal Clusters

One of the difficulties of cluster chemistry is that many of the clusters are very short lived, and hence it is difficult to determine the geometry of a given species. In many cases, the only evidence for the existence of such clusters is mass spectroscopy, which is a technique which allows the accurate measurement of the molecular weight of cluster ions. But it tells nothing about cluster structure and geometry. While we have considered conjugated carbon systems in our description of the Hückel model, we could just as easily have considered alkali metal systems, each of which contributes only one valence electron to the molecular system. In fact, alkali metal clusters have been an ongoing area of research for many years,[4] both from an experimental and theoretical point of view, and it is here that the Hückel model can be used with effectiveness.

Let us consider small alkali metal clusters, ranging in size from three to ten atoms. What is their geometry? Given that there are only a few atoms, it would seem possible to do a more sophisticated calculation. The problem is that there are a huge number of different possible geometries to check. In principle (and here we acknowledge that many of the possible structures are physically unreasonable), there are two ways of connecting three atoms, six ways to connect four atoms (see Fig. 4), 853 ways to connect 7 atoms, 261,080 ways to connect 9 atoms and 11,716,571 ways to connect 10 atoms! Clearly it is impossible to do complex calculations to determine the most obvious structure for all but the simplest of molecules.

Recently research has been done to calculate the most stable structure for alkali metal clusters, both in neutral and cationic form, with up to nine atoms. The principle is to consider all possible structures from graph theory, eliminate those which were physically impossible (the computer did this), and then do a Hückel calculation to determine which was most stable (the computer did this too). The results are shown in Fig. 4. The second most stable structures have also been calculated but are not presented here. With this information it should be possible to make some predictions about which structures these clusters assume, and also to narrow the field down sufficiently so as to make more sophisticated calculations possible. Similar research has also been carried out for larger alkali metal clusters, ranging in size from 10 to 14 atoms, albeit not by going through every possible geometry. Instead, the workers did a Hückel calculation for likely geometries, i.e. for geometries that existed for other types of molecules.

[Insert Figure 4 about here]

The most interesting results from this research are the conclusions that the authors draw concerning the behavior of these clusters. There is a close similarity between the Hückel model results and those of the spherical jellium model. Without going into the details, the jellium model is one of the macroscopic ways of looking at a solid, which is very commonly used in solid state physics. However, it would not be expected to apply very well to such small clusters, and the fact that it does is surprising. Furthermore, this research shows that there are fairly distinct breaks in the pattern. Small clusters, six atoms or less, are arranged in a primarily two-dimensional way. Clusters from 7 to 11 atoms in size seem to have predominately three-dimensional geometry. Clusters larger than 12 atoms in size contain "body" atoms, that is, atoms that are entirely surrounded by neighbors and do not lie on the surface of the cluster. Hence, one can conclude that clusters with 12 or more atoms begin to behave more and more like bulk solids.

Buckminsterfullerene

Buckminsterfullerene (Bucky ball) is a C_{60} cluster named after R. Buckminster Fuller, a famous architect who designed the Geodesic Dome, and who incidentally was appointed in 1962 as Charles Eliot Norton Professor of Poetry at Harvard University. It has the geometry of a soccer ball (see Fig. 5) with a carbon atom at each vertex. There are 60 identical carbon atoms, where each atom is a part of one pentagon and two hexagons, and each atom is connected by three bonds in a sp^2 hybridization. There are 12 pentagons and 20 hexagons in the structure.

[Insert Fig. 5 about here]

Bucky ball was first discovered by researchers at Rice University[5] using mass spectroscopy. When they first did the experiment, they found a range of carbon clusters with sizes from about 32 atoms up to about 80 atoms or more (the limit of measurement). But only even numbers of carbon atoms appeared to form clusters; there were no clusters with an odd number of atoms. A typical mass spectra from one of these experiments is shown in Fig. 6.

[Insert Fig. 6 about here]

The researchers then allowed the clusters to react as much as possible. They did this by prolonging the time before the clusters entered the mass spectrometer, and also by mixing free radicals (reactive chemicals) into the chamber. They then found that all clusters essentially disappeared except for C_{60} and, to a much lesser extent, C_{70}. Thus C_{60} appears to be a remarkably stable species. The question then arises as to what accounts for this stability.

To answer that question we digress for a moment and discuss some geometry. Euler's rule states that for any solid polygon the number of faces plus the number of vertices, minus the number of edges, must equal 2. Stated symbolically,

$$F + V - E = 2 \quad . \tag{1}$$

For a cube, for example, F = 6, V = 8 and E = 12. For a triangular pyramid, F = 4, V = 5 and E = 7. The reader can verify that the rule holds for a square pyramid or any other figure (it must be a solid polygon without holes; donut-like shapes do not follow this rule).

The most stable structure for carbon is that of benzene, a hexagon. Benzene is stable because of the sp^2 hybridization between the carbon atoms, with the extra valences occupied by hydrogen atoms. Pure carbon is most stable in the form of graphite, or a large number of benzene rings in a plane. But at the point where the graphite plane is truncated, there are loose valences which would tend to make the molecule unstable (unless there are hydrogen or other atoms to occupy the extra valences). From this reasoning, it makes sense to think that the pure carbon clusters form closed spheres so that, as in Bucky ball, all valences are occupied. The benefit of this is that there are no loose valences, but the cost is an increase in strain energy due to the fact that the molecule has to curve around on itself. Since a structure of only hexagons is planar, it is impossible to make a spherical structure that contains only hexagons.

If a structure made up only of hexagons is impossible, then the next most stable structure for carbon is the pentagon. The strain energy is somewhat larger in this case, but pentagonal structures are known to exist. If we permit a molecule with both pentagons and hexagons, and insist that it be a closed polygon, then Euler's rule applies, and we can derive the following:

Let n_6 be the number of hexagons, n_5 the number of pentagons, and N the total number of atoms. Then the total number of faces, F, is the sum of pentagons and hexagons, the number of vertices is the same as the number of atoms, and the number of edges is $\frac{3}{2}N$. The latter number is due to the fact that each atom has three bonds, but that each bond is shared amongst two atoms. We can then rewrite Eq. 1 as

$$n_5 + n_6 + N - \frac{3}{2}N = n_5 + n_6 - \frac{1}{2}N = 2 \quad . \qquad (2)$$

Another condition is the limitation on the total number of atoms. Each atom is a member of one pentagon and two hexagons, i.e. three "gons". There are five atoms in a pentagon and six atoms in a hexagon. Putting this together we get

$$\frac{5}{3}n_5 + \frac{6}{3}n_6 = N \quad . \qquad (3)$$

Using Eqs. 2 and 3 to solve for n_5 and n_6, we can easily derive the following:

$$n_6 = \frac{N}{2} - 10, \qquad n_5 = 12 \quad . \tag{4}$$

The astonishing fact here is that no matter how large N is, if we insist that there be only hexagons and pentagons in the polygon, then there can be ONLY 12 pentagons -- no more nor less. (The reader may like to show that if one constructs a polygon consisting only of hexagons and triangles, then there will be only 4 triangles. The reader can also show that structures containing only hexagons and heptagons, or hexagons and octagons, are impossible.)

The other interesting fact is that for the structure to be closed, there must be an even number of atoms. It is experimentally observed that, for clusters larger than about 32 atoms, only even-numbered clusters exist! This gives strong supporting evidence that these clusters do, in fact, form closed shells. Otherwise there is no reason why the odd numbered clusters should not exist.

Clearly the Hückel model should work very well for Bucky ball. The cluster is highly conjugated, with one π-electron for every atom. In fact, a Hückel calculation of Bucky ball does show that it is energetically stable, a fact later substantiated by MNDO calculations,[6] with further analysis in terms of vibrational motions.[7] But it should be pointed out that so far the only evidence for the existence of Bucky ball is mass spectroscopic (though there is a very recent article describing an X-ray crystallographic study that verifies its existence). No one has managed to synthesize it in the laboratory, nor isolate it in a bottle, though if the theoretical calculations are correct, that should be possible. Nevertheless, the discoverers of Bucky ball have proposed a possible situation of where it might occur naturally.

Fire oxidizes carbon. The basic reaction, using methane as an example, is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad . \qquad (5)$$

However, most fires do not burn very cleanly. Some of the material is simply vaporized and leaves the scene as smoke. In particular, individual carbon atoms may be vaporized and eventually form soot. These individual atoms, or small clusters of atoms, are inherently unstable and reactive, and so they would tend to grow in size, a process known as "upclustering." Many would become very large and would become the soot particles that accumulate in chimneys. But suppose that in individual cases these particles did manage to come together in a closed sphere. Then, as Bucky balls, they would be relatively stable and continue up the chimney as an element of smoke.

Conclusion

We have discussed the current status of cluster chemistry and have also considered some of the techniques which can be used to learn more about clusters. We have considered two important types of clusters: alkali-metal clusters and carbon clusters.

Acknowledgments

The portion of this research presented in this article which was carried out by our group at Buffalo was supported by the Office of Naval Research, the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, and the National Science Foundation under Grant CHE-8620274. The United States Government is authorized to reproduce and redistribute reprints for governmental purposes notwithstanding any copyright notation hereon.

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FIGURE CAPTIONS

1. A diagram illustrating the degrees of freedom for a diatomic molecule. The molecule can move in any of three dimensions, x, y and z. In addition, it can rotate in the plane of the page, and also in a plane at right angles to the page (can you see how a non-linear molecule would have another rotational degree of freedom?). Finally, the molecule has one vibrational motion.

2. Examples of conjugated molecules. Carbon atoms occupy each of the vertices. In the case of benzene, the hydrogen atoms are shown explicitly. In the case of naphthalene they are not shown (though they are still there), and the carbon atoms are numbered. The adjacency matrix for this molecule is shown in Table 2.

3. All possible graphs that can be drawn from groups of three or four atoms. Each of these structures has a different topology since the number of bonds connecting the atoms are different.

4. The most stable alkali-metal clusters as determined by Hückel calculations. These clusters, nine atoms and fewer, were found by showing that all other possible graphs were either of higher energy or were geometrically impossible. "M" refers to an alkali-metal atom, with the subscript denoting the stoichiometry. The other notation denotes the symmetry of the molecule and is too complicated to describe here (see texts on inorganic chemistry).

5. A drawing of Buckminsterfullerene. There are carbons at each vertex, and no other atoms in the molecule. For a three-dimensional model, look at a soccer ball.

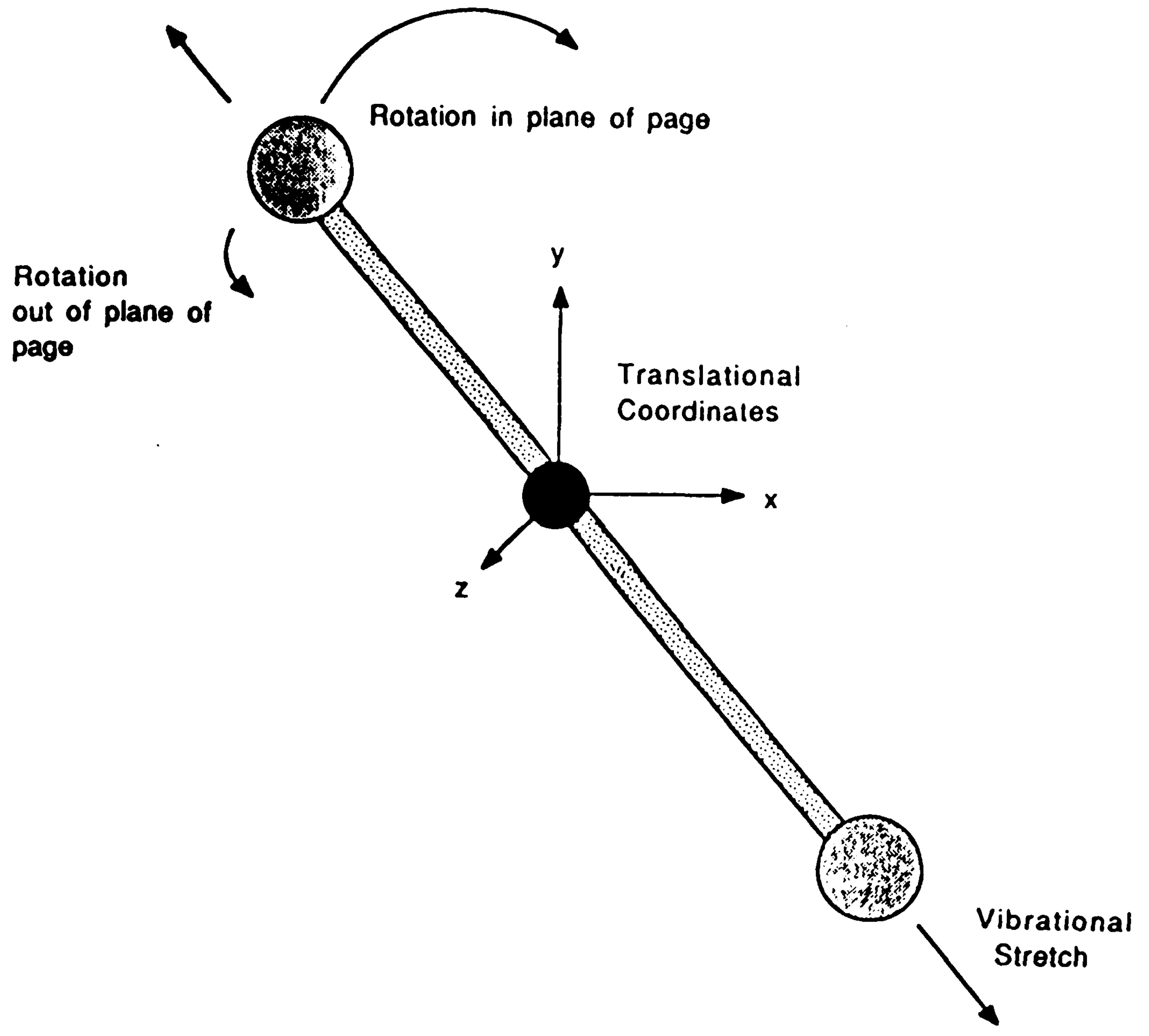
6. A typical mass spectrum for carbon clusters. The peak height is approximately proportional to the quantity of that particular cluster detected. Note that C_{60} is the most prominent. Other experiments have demonstrated that C_{60} is, in fact, much more stable than any of the others. Note also that odd-numbered clusters are non-existent. (This was reproduced from the first paper listed in Ref. 5 with permission of the authors.)

	Bond Length in Å			
Bond	1-2	2-3	1-9	9-10
Modified Hückel	1.382	1.414	1.420	1.419
Experimental	1.368	1.414	1.422	1.419

TABLE 1. The bond lengths of naphthalene as measured by experiment and as calculated by a modified version of the Hückel model. The numbering system is shown in Fig. 2 (taken from Ref. 2, p. 146).

0	1	0	0	0	0	0	0	1	0
1	0	1	0	0	0	0	0	0	0
0	1	0	1	0	0	0	0	0	0
0	0	1	0	0	0	0	0	0	1
0	0	0	1	0	0	0	0	0	1
0	0	0	0	1	0	1	0	0	0
0	0	0	0	0	1	0	1	0	0
0	0	0	0	0	0	1	0	1	0
1	0	0	0	0	0	0	1	0	1
0	0	0	1	1	0	0	0	1	0

TABLE 2. The adjacency matrix for naphthalene shown in Fig. 2. Note that the matrix is symmetric around the main diagonal. Renumbering the molecule will lead to a different matrix, but the Hückel results will be the same.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y
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x
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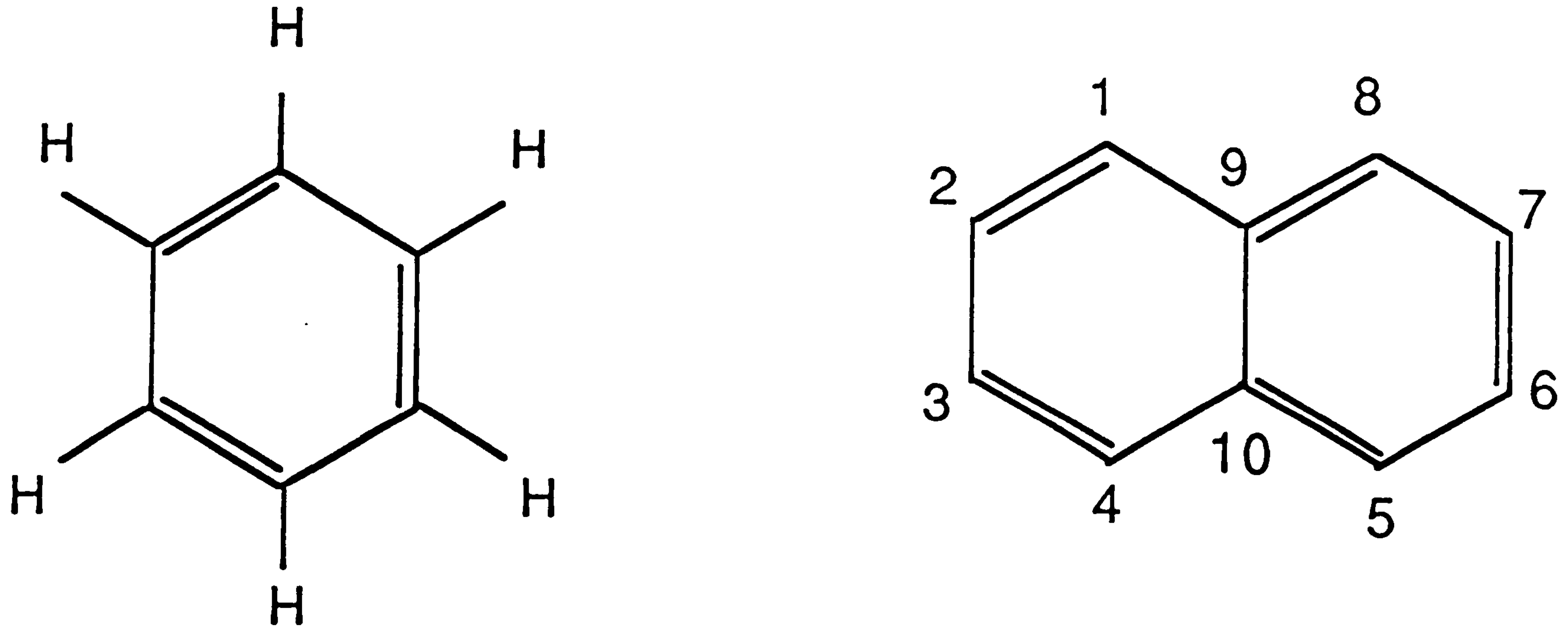


Fig 7

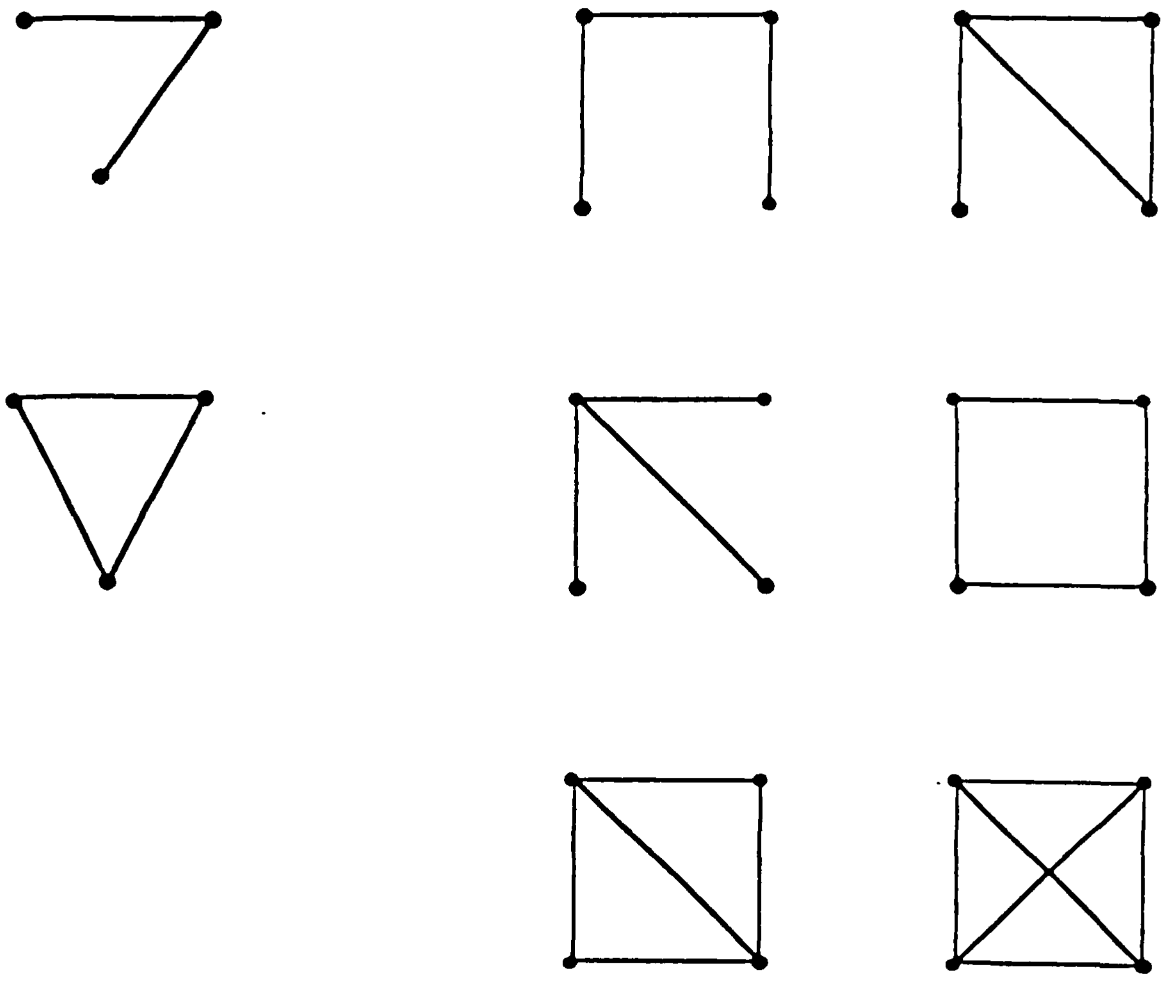
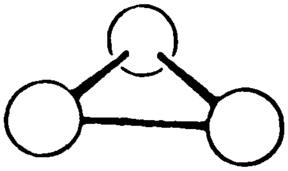
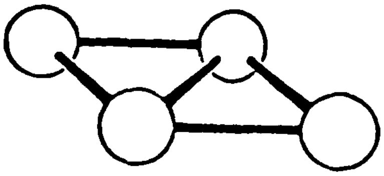


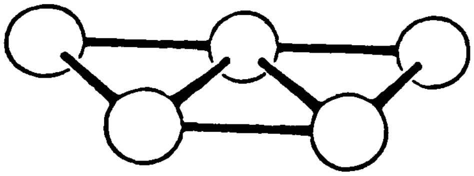
Fig A3



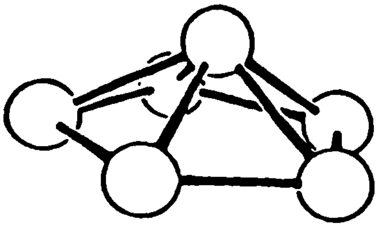
(a) M_3, D_{3h}



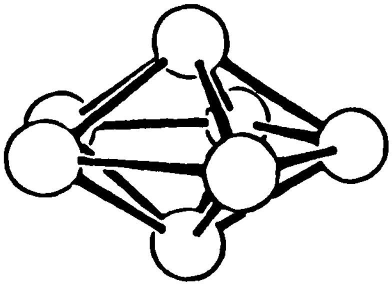
(b) M_4, D_{2h}



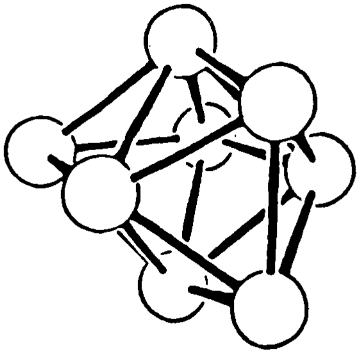
(c) M_5, C_{2v}



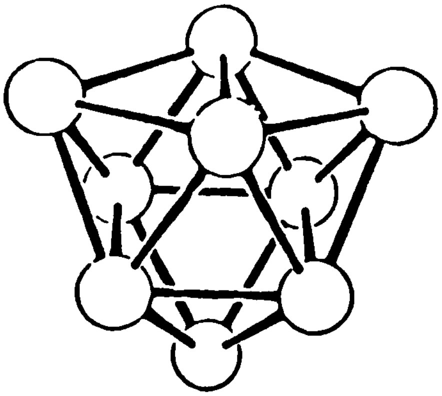
(d) M_6, C_{5v}



(e) M_7, D_{5h}



(f) M_8, D_{2d}



(g) M_9, D_{3h}

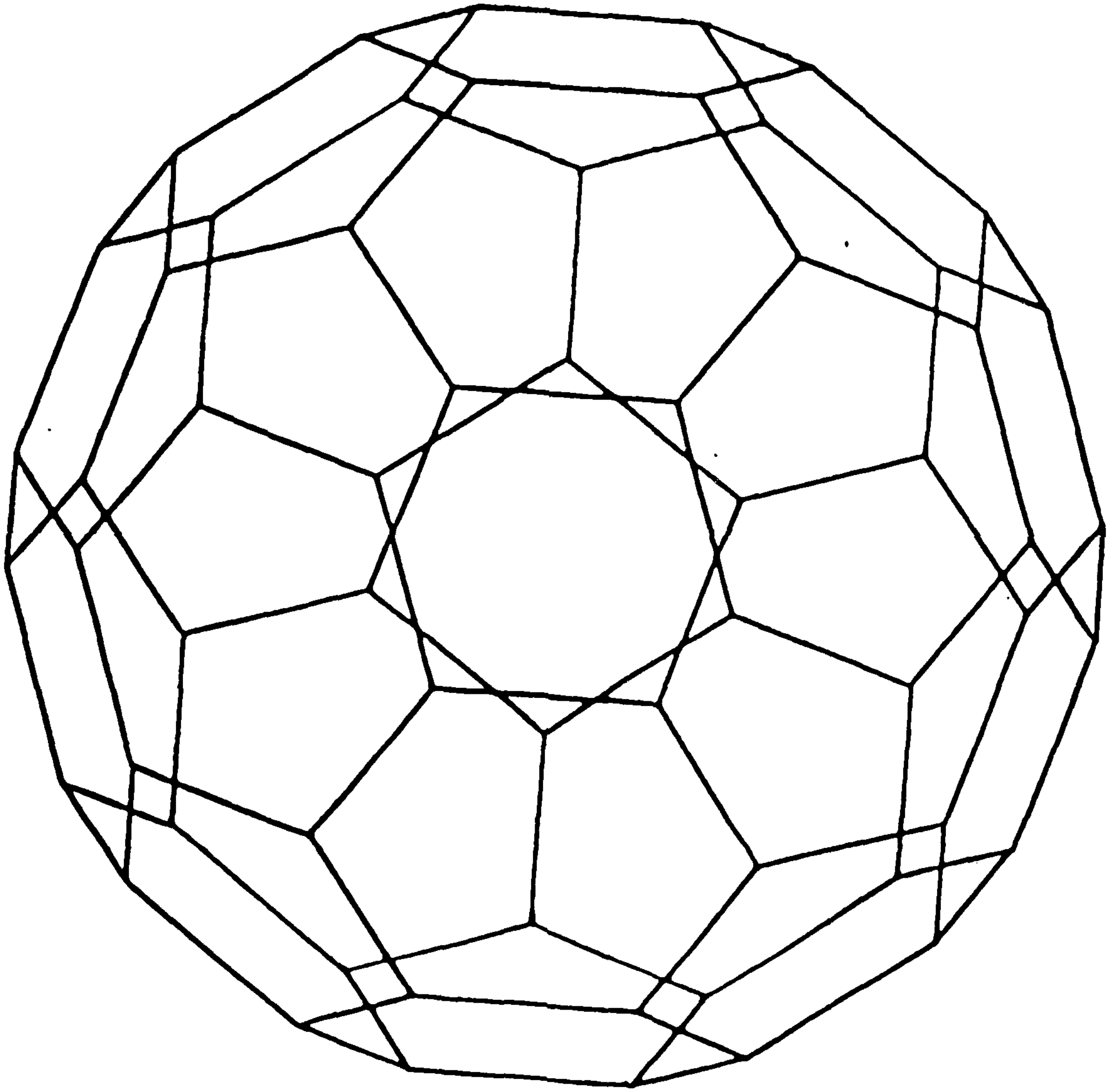
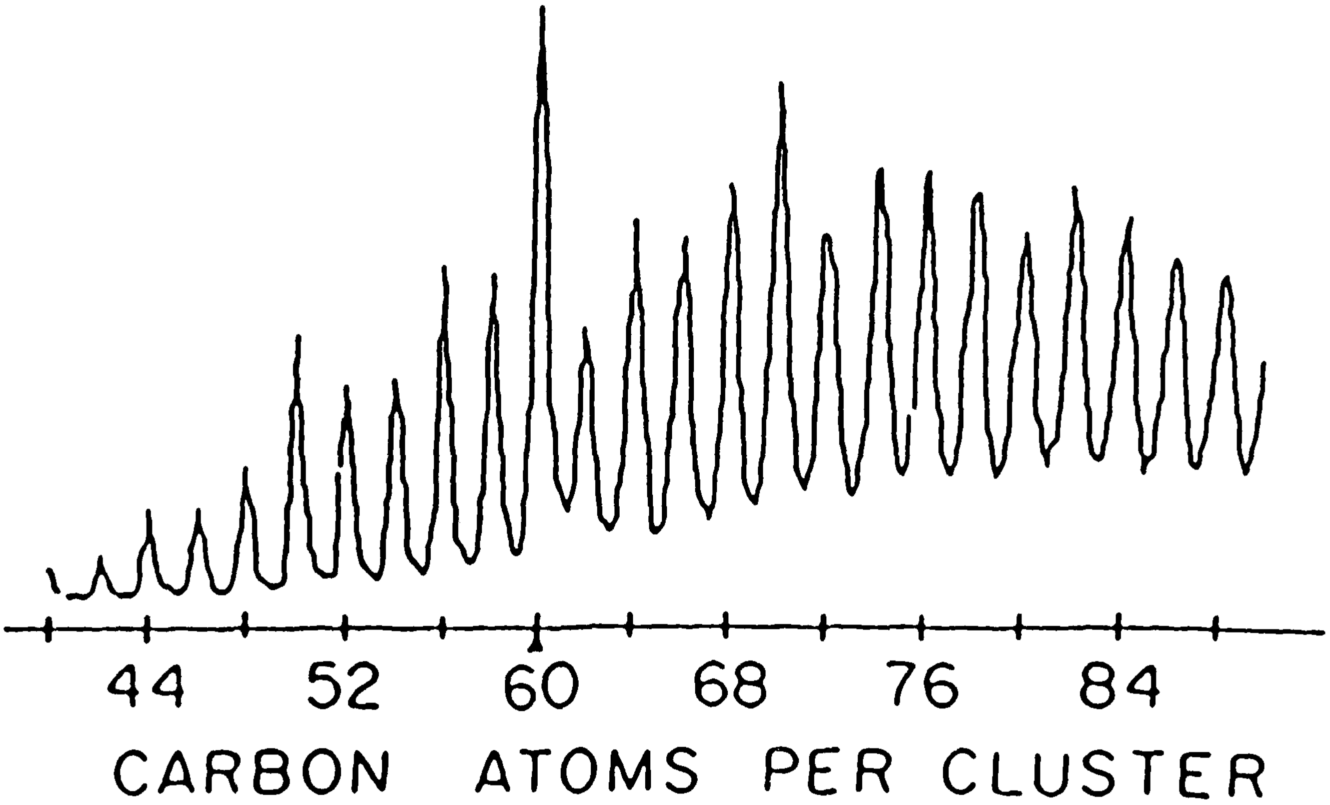


Fig D5

Fig. 6



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University of Minnesota
Minneapolis, Minnesota 55455

Dr. A. Reisman
Microelectronics Center of North Carolina
Research Triangle Park, North Carolina
27709

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Laboratory for Surface Science and
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Orono, Maine 04469

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Chemistry Department
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Dr. Irvin Heard
Chemistry and Physics Department
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Lincoln University, Pennsylvania 19352

Dr. K.J. Klaubunde
Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

Dr. C. B. Harris
Department of Chemistry
University of California
Berkeley, California 94720

Dr. F. Kutzler
Department of Chemistry
Box 5055
Tennessee Technological University
Cookesville, Tennessee 38501

Dr. D. DiLella
Chemistry Department
George Washington University
Washington D.C. 20052

Dr. R. Reeves
Chemistry Department
Renssaeler Polytechnic Institute
Troy, New York 12181

Dr. Steven M. George
Stanford University
Department of Chemistry
Stanford, CA 94305

Dr. Mark Johnson
Yale University
Department of Chemistry
New Haven, CT 06511-8118

Dr. W. Knauer
Hughes Research Laboratory
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University of California
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Dr. J. B. Hudson
Materials Division
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. Theodore E. Madey
Surface Chemistry Section
Department of Commerce
National Bureau of Standards
Washington, D.C. 20234

Dr. J. E. Demuth
IBM Corporation
Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, New York 10598

Dr. M. G. Lagally
Department of Metallurgical
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University of Wisconsin
Madison, Wisconsin 53706

Dr. R. P. Van Duyne
Chemistry Department
Northwestern University
Evanston, Illinois 60637

Dr. J. M. White
Department of Chemistry
University of Texas
Austin, Texas 78712

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Department of Physics
Naval Postgraduate School
Monterey, California 93940

Dr. R. L. Park
Director, Center of Materials
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University of Maryland
College Park, Maryland 20742

Dr. W. T. Perla
Electrical Engineering Department
University of Minnesota
Minneapolis, Minnesota 55455

Dr. Keith H. Johnson
Department of Metallurgy and
Materials Science
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dr. S. Sibener
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Arnold Green
Quantum Surface Dynamics Branch
Code 3817
Naval Weapons Center
China Lake, California 93555

Dr. A. Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02912

Dr. S. L. Bernasek
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Department of Chemistry
University of California
Los Angeles, California 90024

Dr. R. P. Messmer
Materials Characterization Lab.
General Electric Company
Schenectady, New York 22217

Dr. Robert Gomer
Department of Chemistry
James Franck Institute
5640 Ellis Avenue
Chicago, Illinois 60637

Dr. Ronald Lee
R301
Naval Surface Weapons Center
White Oak
Silver Spring, Maryland 20910

Dr. Paul Schoen
Code 6190
Naval Research Laboratory
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Dr. John T. Yates
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Dr. Richard Greene
Code 5230
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Washington, D.C. 20375-5000

Dr. L. Kesmodel
Department of Physics
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Cornell University
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