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SPECTRAL PROPERTIES OF LARGE FULLERENES: FROM CLUSTER TO CRYSTAL

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Electronic structure methods are used to explore fullerenes from C_{60} to C_{3840} . The appearance and development of electronic and vibrational bands is tracked from the discrete molecular levels of small clusters to the quasi-continuous state density functions of large fullerenes. The electronic state density of C_{2160} is very similar to monolayer graphite, while the vibrational spectrum differs from graphite, even for C_{3840} .

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A question of considerable interest is how the properties of matter evolve from cluster-like to bulk-like as cluster size increases and begins to approximate bulk behavior. To a large extent, researchers understand the properties of both clusters and the bulk, but the intermediate regime (very large clusters or bulk fragments) is poorly understood. In this paper we explore the structure, electronic properties and vibrational spectra of fullerenes from C_{60} to C_{3840} . The reference "crystal" or bulk in this paper is a single infinite monolayer of graphite. As the size of the fullerene increases, its structure locally approximates monolayer graphite: the surface breaks into nearly flat facets of graphite¹ the area of which increase as the ball size increases. There are *qualitative* differences between crystals and clusters. For example, the spectrum of clusters, either electronic or vibrational, is discrete since there is a finite number of atoms in the cluster. State densities for these clusters are therefore palisades of Dirac δ functions. The detailed fashion in which these discrete cluster energies become dense and form vibrational or electronic bands

is unknown. This work shows the emergence of bands explicitly and reveals size dependence of energy gaps and the local effects of disorder (pentagonal rings) on electronic and vibrational spectra. This paper also has independent interest as the first report of electronic and vibrational spectral information about any system with several thousand atoms.

Other workers have explored fullerene energetics and structure for smaller systems² with accurate, quantum mechanical methods, and for larger systems with more approximate classical methods, not directly based upon the electronic structure. We choose to use an electronic structure method because the size dependence of the electronic density of states is of interest, and of course because an electronic structure based approach is more basic in nature, and tends to be more reliable for energetics and force calculations (the latter are needed both for relaxation studies and vibrational properties). Here, we use a relatively simple electronic structure method (a minimal basis tight-binding scheme) which has met with success on small fullerene systems³.

To some degree, fullerenes are an ideal system to study for the cluster to bulk evolution, since the underlying symmetry of the crystal (hexagonal graphite) is substantially built even into the smallest C_{60} bucky ball structure. All the fullerenes considered here have the same basic structure: I_h symmetry with twelve pentagons (one on each extreme of each of the six 5-fold symmetry axes) and the rest of the structure being covered by hexagons. The hexagonal regions resemble the structure of graphite, especially for the larger clusters, but also for the small ones. The smallest cluster C_{60} is perfectly spherical, and there have been proposals that the larger clusters might also be quasi-spherical.⁴ Nevertheless, as we show elsewhere¹, the evolution of the geometry as a function of cluster size for isolated clusters is not trivial: the icosahedral fullerenes with more than 60 atoms do not possess spherical symmetry; rather they facet (see Figure 1, and Ref. 1). This faceting originates in the competition of energy cost of bending the edges to form facets against the energy cost of distorting the planes to build a spherical curvature.⁵ The balance of this competition yields structures with protruding pentagonal sites and flat facets between them but with softly curved edges between the flat facets.

Compactly stated, the method of this paper is the following: (1) Fullerenes C_N of perfect I_h symmetry are constructed for N ranging from 60 to 3840. (2) After a rough relaxation with a Stillinger-Weber potential⁶, the quantum “order- N ” method of Ordejón *et al.*⁷ is applied to fully relax the fullerenes. The two-center orthogonal Hamiltonian of Xu *et al.*³ is employed. (3) Using the coordinates obtained from step (2), the (sparse)

Hamiltonian matrix is computed, and the moments of the global density of states are acquired by the methods of Ref. 8. The maximum entropy method is used to reconstruct the state density from the moments. This has major advantages over conventional continued fraction Lanczos⁹/recursion¹⁰ representations (see for example Ref. 11), and is also carried to a far higher order here, using 150 or more moments, which yields excellent spectral resolution with a minimum of spurious Gibbs phenomena (ringing). (4) For vibrational spectra the sparse dynamical matrix is computed using the methods of Ref. 12 and the vibrational spectral calculations proceed as for the electronic case in (3). For all of these calculations, CPU demand scales in a rigorously linear fashion with system size. The work reported here was implemented on modest workstations.

To test the tight-binding Hamiltonian, we also did some calculations with the *ab initio* tight-binding method of Sankey and coworkers¹³. The agreement is impressive for these molecules. Subsequent discussion in this paper will be based upon the simpler tight-binding scheme³. The graphite-fullerene energy difference is 0.37eV/atom for a C_{60} bucky ball, and is reduced to 0.008eV/atom for the huge C_{3840} fullerene. The latter is a tiny energy difference and is one indication of the similarity of graphite and large fullerenes.

Near linearity of the logarithm of relative energy versus $\ln(N)$ suggests that the energy difference between large fullerenes and graphite decays as a power-law with N . A least squares fit to the six energies yields: $E_{rel} \approx 9.1N^{-0.78}$ eV/atom. This is in good agreement with the theory of Witten and Li⁵, who predict an

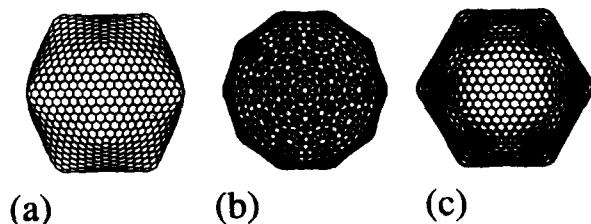


FIG. 1. Example of a large relaxed fullerene: C_{2160} . The three images represent the same cluster, viewed from different directions corresponding to symmetry axes of the cluster: (a) a two-fold axis, (b) a five-fold axis and (c) a three-fold axis. The shape is markedly polyhedral, with flat facets between pentagonal sites (this is especially clear in (a) and (c)), but with soft edges joining the facets.

asymptotic power law dependence of the form $N^{-5/6}$. Further discussion of energetics may be found in Ref. 1.

For a cluster, the number of energy eigenvalues is strictly discrete. However, as $N \rightarrow \infty$, the electronic energies are conveniently represented by a continuous function (the density of states or DOS) indicating the density of admissible energy states per unit energy range. In Figure 2, we illustrate the evolution of the DOS of C_N for N ranging between 60 and 3840. It is easy to see the evolution of discrete molecular orbital energies into the energy bands of the crystal. As with any method for reconstructing state density functions, some artifacts are evident stemming from the use of a finite number of moments (or recursion coefficients in a recursion method). These artifacts can be eliminated at the expense of reducing the spectral resolution, but are quite tolerable in the present work, so no artificial broadening was introduced.

The larger fullerenes C_{2160} and C_{3840} show features approximating the Van Hove singularities¹⁴ associated

with the crystal. For C_{2160} , it is apparent that the graphite and cluster electronic state density differ only in some small wiggles for occupied states (eg, states with energy $E < E_f$, for E_f the Fermi energy). In the highest energy band ($E > 0$ with all states unoccupied), there is more discrepancy between the cluster and graphite, though the overall agreement is still remarkable. The highest energy electronic states are more sensitive to the global curvature and facet edges than are the lower energy states. At least where occupied states are concerned, we can conclude that C_{2160} is electronically very similar to a crystalline monolayer of graphite.

For many important physical processes like transport and superconductivity, one is concerned with the details of the electronic state density in the vicinity of the Fermi energy. Graphite is well known to be a rather poor conductor: this is a consequence of the band structure of the material and its property that the valence (π) and conduction (π^*) bands barely overlap at E_f as in Figure 2. For the clusters, there is an appreciable "highest occupied molecular orbital - lowest unoccupied molecular orbital" (HOMO-LUMO) energy gap which decreases markedly with cluster size (Figure 3). These calculations were made by nearly "exact" calculations of the energy levels near E_f using a shifted Lanczos method¹⁵. The gap closes in a very asymmetri-

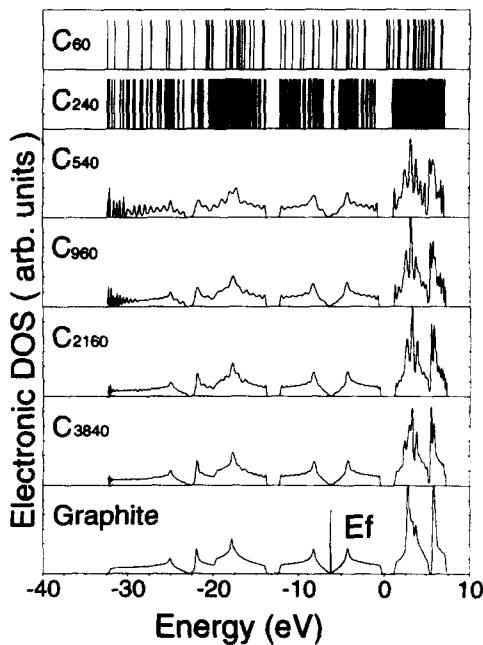


FIG. 2. Electronic state densities for clusters C_{60} - C_{3840} , computed exactly for C_{60} and C_{240} and with the methods of Ref. 8 for larger clusters. Of order 150 moments were used in constructing these densities. Convergence is nearly reached, at least for occupied states for $N = 2160$. The Fermi level is near -7eV for each fullerene, and is indicated by a vertical line for C_{3840} .

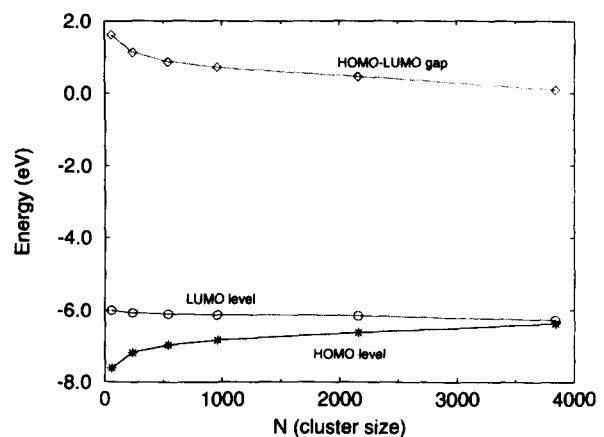


FIG. 3. HOMO-LUMO gap for clusters. The highest occupied molecular orbital (HOMO) energy level and the lowest unoccupied molecular orbital (LUMO) are plotted (lower curves, star and circle respectively). The top curve (diamonds) is the HOMO-LUMO gap, eg. the energy difference between the LUMO and HOMO levels. In each case the lines are only a guide to the eye.

cal fashion: the LUMO level changes by a tiny amount over all of the fullerenes studied, whereas the HOMO level changes dramatically, and nearly closes the gap at $N = 3840$ (where the HOMO-LUMO gap is 0.10 eV, versus 1.62 eV for C_{60}). The near pinning of the LUMO level stems from the pentagonal sites, and therefore its position is quite invariant with the size of the cluster, since the pentagonal sites are always present. As Figure 2 reveals, even for the C_{2160} , the DOS is very similar to graphite near the Fermi level: there are very few energy levels near E_f . Thus, a small number of energy levels appear to close the gap primarily from below as the cluster size increases.

To emphasize the difference between cluster and bulk behavior, we computed local densities of electronic states for a pentagon site and a midfacet site for the particular case of the C_{2160} fullerene. The former is maximally "cluster" like, the latter is locally as graphitic as possible in a given cluster. In Figure 4, the differ-

ences between the pentagonal and facet-center spectra are clearly exhibited. The facet-center site bears close resemblance to graphite and is nearly indistinguishable from the global state densities presented in Figure 2. The pentagonal site has asymmetrical π and π^* bands near the Fermi level, and the " sp^2 " band (near -20eV) is particularly different at the higher energies of that band. Observe also that the density of states at the $\pi-\pi^*$ gap energy is noticeably higher than for the facet-center site.

By using the methods of Ref. 12, one can readily compute the vibrational spectra of these enormous molecules. Figure 5 clearly shows how the DOS of the fullerenes evolves from the discrete spectrum of C_{60} to a continuum spectrum for the largest clusters that resembles the one of a graphite plane (also shown for comparison in Figure 5). This was expected, given the flat, graphite-like surfaces present in the larger clusters. This is particularly true for the low frequency acoustic modes, and also for the high frequency optical, out-of-

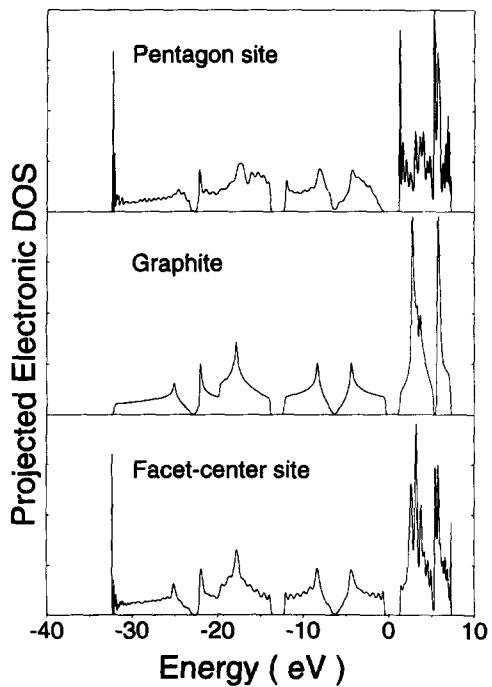


FIG. 4. Local electronic state densities for facet-center site and pentagonal site for C_{2160} . The DOS for monolayer graphite is shown in the middle panel. Note the asymmetry in the π and π^* bands for the pentagonal site, and the high degree of coincidence between the facet-center site and the result for graphite.

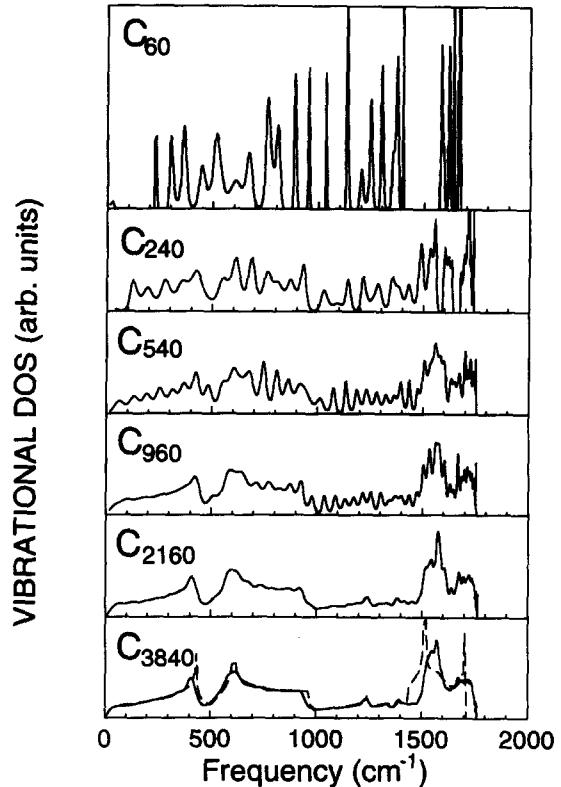


FIG. 5. Phonon DOS for several icosahedral carbon fullerenes, from C_{60} to C_{3840} . For comparison, superimposed to the C_{3840} spectrum, we also show (dashed line) the results for a perfect single graphite plane, computed exactly.

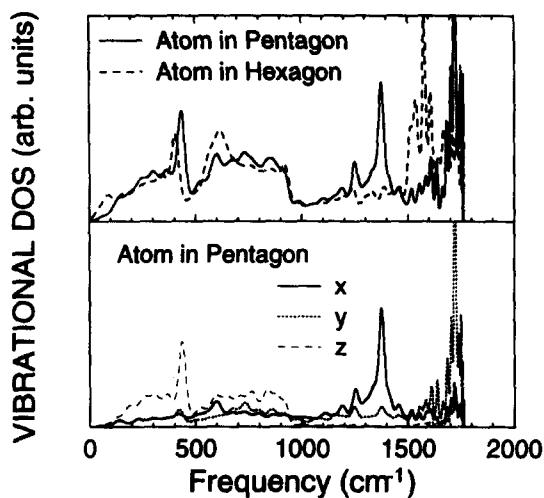


FIG. 6. Local vibrational DOS for different atoms and directions of space for the phonons of the C_{2160} fullerene. The top panel shows the density of vibrational states for an atom in a pentagon, and for an atom in a hexagon in the middle of a flat facet. The lower panel shows the DOS of the pentagon atom decomposed in x , y and z directions.

plane modes. However, the optical modes above 1500 cm^{-1} are significantly shifted toward higher frequencies in the fullerenes, compared to the graphite spectrum. This shift has its origin in the internal stress which is present in the fullerene structures, that originates from the spherical topology of the clusters.

The present method also allows us to compute the partial DOS for any atom of the system, and its decomposition into spatial directions. In Figure 6 we show an example for the C_{2160} fullerene, where we have computed the local DOS for two different atoms: one of them forms part of one of the twelve pentagons of the cluster, and the other is on a hexagon in the middle of a flat facet. The difference in the dynamics of these two atoms is

particularly apparent in the high frequency part of the spectrum. The atom in the pentagon shows a strong peak at about 1370 cm^{-1} , which is not present in the hexagon atom (nor in the graphite DOS), and which is a characteristic stretching mode of the pentagons. This mode is observed in all the fullerenes studied, since all of them contain twelve pentagons. On the other hand, the pentagon atoms do not support the strong optical band at about 1500 cm^{-1} which is present in the graphitic planes. We have also decomposed the local DOS for the pentagon atom into the three directions of space (z corresponding to the radial direction). We can see that the 1370 cm^{-1} peak corresponds to an in-plane vibration in the x direction, with a large stretching character. The z direction corresponds to out-of-plane vibrations, and therefore has a large DOS on small frequencies, up to 900 cm^{-1} .

In conclusion, we have shown that, using state of the art techniques very recently developed, it is possible to study the spectral properties of very large systems containing thousands of atoms, and that this opens the possibility of detailed studies on how the electronic and vibrational properties evolve from cluster-like to crystal-like with increasing cluster size. We have studied the case of large fullerenes, and found that, whereas the electronic properties approach very rapidly those of monolayer graphite, the vibrational spectrum differs significantly even for the larger clusters considered (C_{3840}). Therefore, the electronic structure depends essentially on the local environment, whereas the vibrational properties are more sensitive to the large scale structure, and in particular to the topology of the cluster.

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REFERENCES

1. S. Itoh, P. Ordejón, D. A. Drabold and R. M. Martin, Submitted to Phys. Rev. B. The calculations are based on an electronic structure based molecular dynamics relaxation (see Ref. 7) to obtain minimum energy structures of the clusters under consideration.
2. G. B. Adams, O. F. Sankey, M. O'Keefe, J. B. Page and D. A. Drabold, Science **256**, 1792 (1992).
3. C. H. Xu et al. J. Phys. Condens. Matt. **4**, 6047 (1992), O. F. Sankey and R. E. Allen, Phys. Rev. B **33**, 7164 (1986).
4. Spherical shapes have been observed experimentally by D. Ugarte, Nature (London) **359**, 707 (1992) for multishell fullerenes, in which several fullerene balls with different size are placed inside each other forming a nearly spherical onion struc-

- ture. No experimental information is available, however, on what is the most favorable shape for isolated large fullerenes.
5. T. A. Witten and H. Li, *Europhysics Lett.* **23**, 51 (1993).
 6. F. H. Stillinger and T. A. Weber, *Phys. Rev. B* **31**, 5262 (1985).
 7. P. Ordejón, D. A. Drabold, M. P. Grumbach, and R. M. Martin, *Phys. Rev. B* **48**, 14646 (1993); P. Ordejón, D. A. Drabold, R. M. Martin and M. P. Grumbach, *Phys. Rev. B* **51**, 1456 (1995), and references therein. The electronic problem is approached in a novel way: (i) a new energy functional which can be freely minimized (without orthogonality constraints) to yield the exact ground state band energy and a set of orthonormal orbitals spanning the occupied electronic subspace. (ii) a localized Wannier-like representation for the electronic states is introduced. Since these electronic orbitals decay rapidly (even for the small-gap fullerenes here), they may be truncated (set to zero) outside some spatial range with virtually no loss of accuracy for a sufficiently large range. We have found that the appropriate truncation radii for the fullerenes is $R_c^\sigma = 2.5 \text{ \AA}$ and $R_c^\pi = 5.0 \text{ \AA}$, for states with σ and π symmetry, respectively. When the electronic problem is cast in this form, the computational expense scales linearly with the system size, enabling the relaxations of the large molecules which we report here. An essentially identical computational method was proposed independently by F. Mauri, G. Galli and R. Car, *Phys. Rev. B* **47**, 9973 (1993).
 8. D. A. Drabold and O. F. Sankey, *Phys. Rev. Lett.* **70**, 3631 (1993), and references therein. The information theoretic principle of maximum entropy

- (E. T. Jaynes, *Papers on Probability, Statistics and Statistical Physics*, Kluwer, Dordrecht, 1983) was used to estimate the state densities from the moment data accumulated from the matrix-vector operations. Because (orthogonal polynomial) moments are used in the reconstructions, the edges are more resolved than the center, since the moments carry more information about the edges. It is worth noting that this scheme yields the *global* density of states order- N , whereas Lanczos methods are order- N for a *basis-projected* spectral function. Within our scheme, basis-projected spectral functions may be obtained from moments from the (sparse) vector selected to be the basis function of interest.
9. C. Lanczos, *Applied Analysis* (Prentice-Hall, Englewood Cliffs, 1956), Chapter II.
 10. See the collection of papers in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz, D. Turnbull and H. Ehrenreich (Academic Press, New York, 1980), Vol. 35. This work is also of interest for early attempts to understand the transition from short-range to long-range order in amorphous systems.
 11. S. Glanville, A. T. Paxton and M. W. Finnis, *J. Phys. F* **18**, 693 (1988).
 12. P. Ordejón, D. A. Drabold, S. Itoh, and R. M. Martin, *Phys. Rev. Lett.* **75**, 1324 (1995).
 13. O. F. Sankey and D. J. Niklewski, *Phys. Rev. B* **40**, 3979 (1989).
 14. J. Ziman, *Principles of the theory of solids* (Cambridge Univ. Press, Cambridge, 1964).
 15. G. Grossi, L. Martinelli and G. Pastori Parravicini, *Il Nuovo Cimento D* **15**, 269 (1993).