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Possibility of stable spheroid molecules of ZnO

E. C. Behrman, R. K. Foehrweiser, J. R. Myers, and B. R. French
Physics Department, Wichita State University, Wichita, Kansas 67260-0032

M. E. Zandler
Chemistry Department, Wichita State University, Wichita, Kansas 67260-0051

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We present results of molecular-dynamics simulations of ZnO clusters. At certain magic numbers of atoms, the clusters spontaneously form into spheroids reminiscent of fullerenes. Molecular-orbital calculations confirm that the spheroids are stable. We suggest some experiments that might be profitable.

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Since their discovery [1] over seven years ago, fullerenes or "buckyballs" have intrigued a number of researchers [2]. Exciting new possibilities have opened up in many areas, from diamond manufacture to lubrication to electronics [2,3]. Though all spheroid cages so far observed have been constructed of carbon, this kind of structure may not be limited to that system. Recently, boron nitride has been found [4] to form tubular structures analogous to those previously observed [5] for carbon. Though zinc oxide is not, of course, isoelectronic with carbon as is BN, it does crystallize in the wurtzite structure, a hexagonal structure in which both species are tetrahedrally coordinated [see Fig. 1(a)]. In this paper we report the results of theoretical calculations of ZnO clusters. Our results suggest that ZnO may also be made in spheroid form.

Zinc and oxygen atoms were initially placed at their equilibrium (macroscopic crystal) positions [6] and given zero initial velocities. They were then moved according to the velocity form of the Verlet algorithm in a standard molecular-dynamics (MD) simulation [7], using a time step of 1 fs and a standard literature pair potential [8] of the Born-Mayer form: $V_{ij}(r_{ij})=q_iq_j/r_{ij}+A_{ij}\exp\{-r_{ij}/\rho_{ij}\}-C_{ij}/r_{ij}^6$. The clusters were equilibrated to a heat bath at 300 K [9] for 80% of the total time in each run. This is equivalent to a simulated annealing process. In

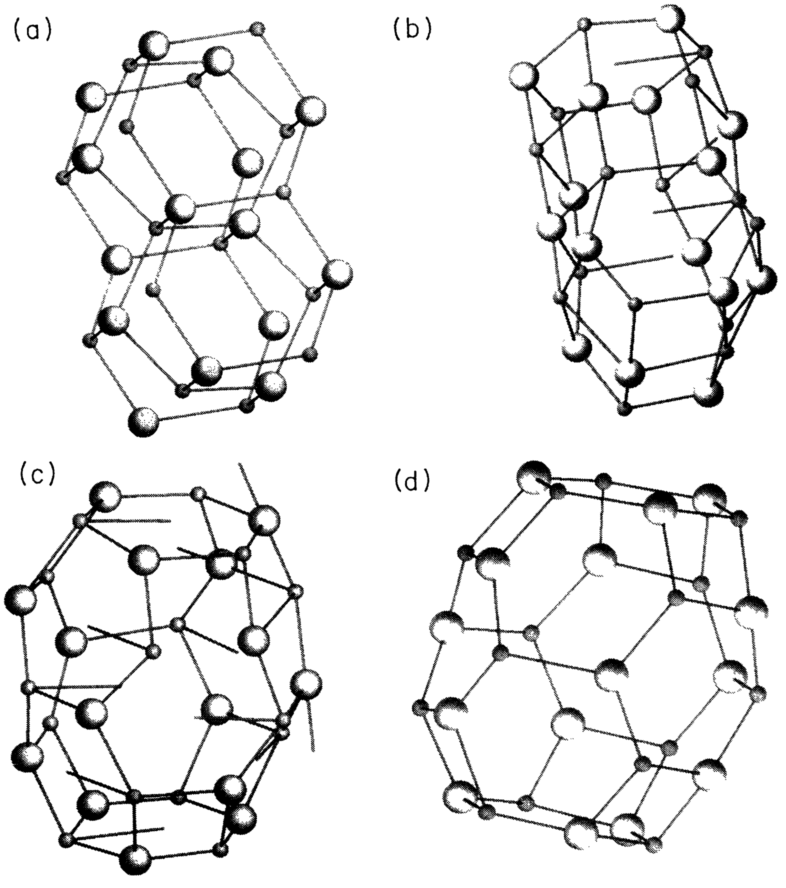

FIG. 1. Time evolution of the $(ZnO)_{15}$ fullerene. The small circles are zinc atoms and the large ones are oxygen atoms. (a) shows the initial configuration, a piece of the equilibrium structure for the bulk crystal. (b), (c), and (d) are snapshots at 10^4, 10^5 and 10^7 time steps, corresponding to 0.01, 0.1, and 10 ns, respectively.

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TABLE I. Characteristics of ZnO fullerenes. Bond lengths are averages over the entire cluster. Potential energies are calculated per (ZnO) pair, and are given by the average repulsion energy minus the average attraction energy.

Fullerene	Number of hexagons	MD calc. bond length (Å)	MO calc. bond length (Å)	MD calc. potential energy (eV)	MO calc. potential energy (eV)
$(ZnO)_{11}$	7	1.803(7)	1.80	−38.592(5)	−321.174
$(ZnO)_{12}$	8	1.798(5)	1.96	−38.901(4)	−321.276
$(ZnO)_{15}$	11	1.798(6)	2.00	−38.889(5)	−321.247

Fig. 1 is shown the time evolution of a 30-atom configuration, $(ZnO)_{15}$. For short runs, 1 ns or less, the system is not equilibrated: cessation of Maxwell rescaling leads to the system's heating up. This is graphically illustrated in Figs. 1(b) and 1(c): the dangling bonds for each cation point to where that atom's bond partner had been at the end of the equilibration part of the run. One can thus see the cluster's evolution towards the spheroid. By 10 ns in real time, the spheroid is formed. It appears to be stable on this time scale; further runs starting from this configuration do not isomerize. Other stable spheroids found are $(ZnO)_{11}$ and $(ZnO)_{12}$. Note that all the stable spheroids are made up of six rhombuses and some number of hexagons; compare the carbon fullerenes, which have 12 pentagons and some number of hexagons. (Of course, ZnO spheroids could not be expected to form pentagons, since the presence of any odd polygon would force an atom to bond with a like atom.) One can thus imagine a whole family of $(ZnO)_n$ clusters, beginning with $(ZnO)_4$ (a cube) and $(ZnO)_6$ (a hexagonal prism); for larger n the form begins to resemble that of a hollow spheroid, though for $n < 11$ the MD calculations predict that the spheroids are not stable.

It has not escaped us that this is a very surprising result, that atoms interacting with only a simple central force potential would spontaneously fall into a hollow spherical shape. (A great deal of heat is generated during the calculation; the system has quite a lot of energy to explore phase space.) Energy minimization calculations of alkali halide clusters [10] show that, as one would expect, more compact structures, in which not all atoms lie on the surface, are preferred. As a check on our calculations we did a simulation of NaCl with our MD code, using the same Born-Mayer potential form, and the parameters of Ref. [10]. This cluster did not form a spheroid, and, in fact, reproduced the structure predicted by Martin's energy minimization calculations.

As a further, independent check on our results, we also performed quantum molecular-orbital (MO) calculations on our spheroids. We used the semiempirical molecular-orbital code MOPAC, with the PM3 Hamiltonian (third parametrized model of MNDO, modified neglect of differential overlap), which uses four basis orbitals per atom plus a core. The core terms are optimized [11] for a total of 28 elements, including zinc (and, of course, oxygen). The optimization is done so that the code reproduces successfully the heats of formation, geometry, dipole moment, and ionization potentials of a number of molecules containing each of the elements. This particular code has also been used successfully [12] for calculations on C_{60} and C_{70}. We used as a starting configuration the data from our MD calculation; MOPAC then uses a gradient descent to minimize the heat of formation. [It is important to note that the code need not maintain the starting configuration, but moves the atoms around to find the lowest possible energy available. To ensure that this was so, we tried also starting configurations that did not have the symmetry (C_2, T_h, and C_{3h}, respectively) of the spheroids.] The spheroids are predicted to be vibrationally stable, with all real frequencies. Heats of formation (from the elements in standard states) are about −129.33 kcal/mole for $(ZnO)_{11}$, −169.38 kcal/mole for $(ZnO)_{12}$, and −201.84 kcal/mole for $(ZnO)_{15}$. These numbers correspond to approximately −0.5102, −0.6125, and −0.5839 eV per ZnO, respectively. For comparison, the heat of formation of macroscopic crystalline ZnO is −3.632 71 eV per ZnO pair [13]. Thus $(ZnO)_{12}$, for example, is thermodynamically unstable with respect to the macroscopic crystal by 3.020 eV per ZnO pair; compare C_{60}, which is unstable with respect to graphite by about 1 eV per pair of C atoms [14]. However, the $(ZnO)_{12}$ spheroid, like the C_{60}, is at least a stable local minimum.

In Table I we report average bond lengths and potential energies as calculated by both MD and MO, for each of the spheroids. Since the Hamiltonians used by the two methods are quite different, it is no surprise that the calculated energies are, also; however, the relative numbers are comparable, as are the bond lengths. Note that the bond lengths shown here are averages over the entire cluster, which in each case contains at least two different kinds of bonds: $(ZnO)_{15}$, for example, has six different kinds. In Fig. 2 are shown the equilibrium structures for $(ZnO)_{12}$ as calculated by MD and MO. The basic structures are the same, though the MD produces noticeably rounder structures: This is because the MD potential does not contain "valence forces"; that is, the molecular-orbital calculation takes the presence of the nonbonding electron pairs into account.

We would expect that the smaller ZnO fullerenes, like the smaller carbon fullerenes, become more strained as the smaller polygons are forced to share an edge: this is thought [2] to be why there are few stable fullerenes smaller than C_{60}, the smallest carbon fullerene in which it is possible for none of the pentagons to share an edge. $(ZnO)_{12}$ is analogous to C_{60} in this sense. This spheroid is also of much higher symmetry than either of the other two, and thus, as one would expect, is significantly more

TABLE II. Comparison of MD and MO results for $(ZnO)_{12}$.

	Bond length, rhombus (Å)	Bond length, hexagon (Å)	O—Zn—O bond angle in rhombus (deg)	Zn—O—Zn bond angle in rhombus (deg)	O—Zn—O bond angle in hexagon (deg)	Zn—O—Zn bond angle in hexagon (deg)
MD	1.833(3)	1.745(2)	88.2(1)	91.8(2)	119.8(1)	120.1(1)
MO	2.057	1.915	78.8	91.2	94.6	134

stable according to both the MD and the MO calculations: $(ZnO)_{11}$ is 0.102 eV less stable per ZnO pair, according to MO, and $(ZnO)_{15}$ is 0.029 eV less stable; by the MD calculations the numbers are 0.309 eV and 0.012 eV. Table II compares the individual bond lengths and angles for this most promising cluster as calculated by the two methods. We see that both predict the bond lengths to be larger in the rhombuses, as one would expect; also, that the more rounded shape of the MD spheroid is reflected in the bond angles.

It might be argued that the MD data are suspect, because the potential used is an empirical pseudopotential fitted to macroscopic data, that it might very easily not be appropriate for use in a cluster. Experience has shown [10] that the use of Coulomb plus Born-Mayer potentials works quite well for alkali halide clusters and microcrystals; this might not be true for ZnO. On the other hand zinc, like its fellows in group 2b, Cd and Hg, is not properly considered [15] a "transition element," since its compounds do not involve ionization of the *d* shell. In this sense zinc is more like an alkali metal (or, alkaline earth) than one might think. Experience in other applications like biomolecules has shown [16] that simple potentials of the sort used here are quite satisfactory, provided the zinc atoms are well separated (as they are here; the closest pair of zinc atoms is approximately 2.9 Å apart). Furthermore, preliminary results of *ab initio* Hartree-Fock calculations at the STO3G (Slater-type orbital) 3*G* level show that the spheroid $(ZnO)_{12}$ is a stationary point on the electronic potential-energy surface.

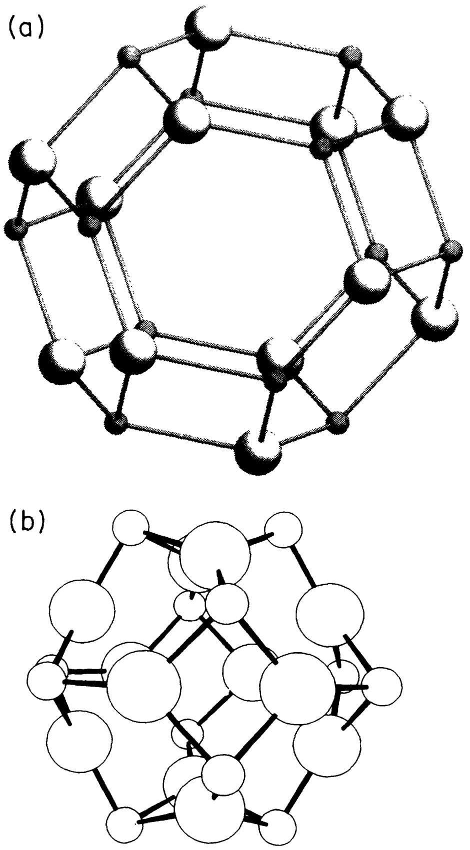

FIG. 2. Comparison of the MD results with the MO results. (a) and (b) show the equilibrium structures for $(ZnO)_{12}$ as calculated by MD and MO, respectively.

It is also of interest to compare other probable cluster configurations with the fullerene configuration. We therefore performed MOPAC calculations to determine the relative thermodynamic stability of several of the six stable configurations found for $(NaCl)_{12}$ from Ref. [10], Fig. 2, including stacked hexagonal rings, two rocksalt configurations, and a planar configuration. Two of these were optimized under the constraints of retaining the given cluster configuration. Results are shown in Table III. None represented a stationary point, and all were significantly higher in energy than the spheroid configuration, ranging from +124.87 kcal/mol (0.452 eV per ZnO pair) for the stacked hexagons, to +187.58 kcal/mole (0.678 eV per pair) for the 3×2×4 rocksalt.

TABLE III. Comparison of MO results for different configurations of $(ZnO)_{12}$. The last row shows data for the bulk equilibrium crystal, for comparison; data taken from Ref. [13]. Heats of formation are given from the elements in their standard states.

Configuration of $(ZnO)_{12}$	ΔH_f, in eV per ZnO pair	Bond length (Å)
Fullerene	−0.6125	2.057 (rhombus) 1.915 (hexagon)
Stacked hexagons	+0.4515	1.944 (rhombus) 1.866 (hexagon)
Stacked rectangles (3×2×4 rocksalt)	+0.6782	2.088
Stacked squares (2×2×6 rocksalt)	+0.4655	2.051
Planar (4×6 rocksalt)	+0.5461	1.977
Bulk equilibrium crystal	−3.63271	1.9915 (along *c* axis) 1.9760 (not along *c* axis)

Most significantly, the 3×2×4 rocksalt configuration, when further optimized, this time *without* any constraints, collapsed to the same spheroid cluster found earlier. This is a quantum-mechanical analogue of the MD annealing calculation, which was started from (a buckled form of) the stacked hexagon configuration, this being the equilibrium bulk crystal form.

While these results show that it might be possible to make the spheroids, they do not address the question of their stability with respect to each other; that is, would the spheroids tend to coalesce once cooled down? With that in mind, we have also performed some preliminary MOPAC calculations on clusters, in various starting orientations, of two and four $(ZnO)_{12}$ fullerenes. In none of these did the spheroids react with each other, an encouraging result. No preferred orientation or distance could be established, however, and further calculations need to be done.

In conclusion, we believe that we have shown that stable spheroid molecules of ZnO may exist. Our prediction is borne out by two extremely dissimilar calculations, which agree; of course, ultimately the real test is that of experiment. Laser ablation of a single crystal of ZnO followed by Fourier transform ion cyclotron resonance mass spectrometric detection might show that certain cluster numbers are particularly stable, as calculated here. It seems likely that $(ZnO)_n$ fullerences, if they exist, are most stable around some particularly magic numbers, as carbon ones are; symmetry arguments, and our calculations, suggest that these may be 12 and 16. In addition, it is difficult to believe that, if the ZnO fullerenes can be made, the situation is unique to this particular inorganic compound. We are therefore investigating other divalent metal oxides and sulfides, as well as other variations. For example, there is considerable evidence for metallocarbohedrenes of the stoichiometry M_8C_{12}; but a recent paper [17] showed an additional, large, peak, at $Fe_{12}C_{12}$, in the mass spectrum of the iron-carbon cations. It is possible that this species is of the type we here predict for $(ZnO)_{12}$.

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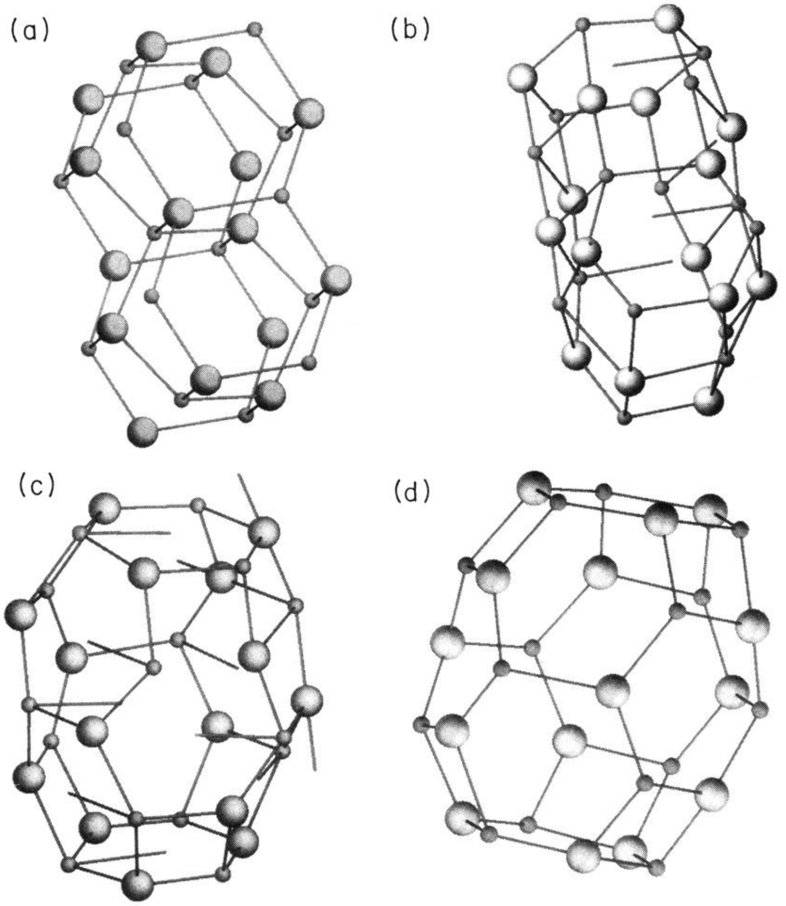

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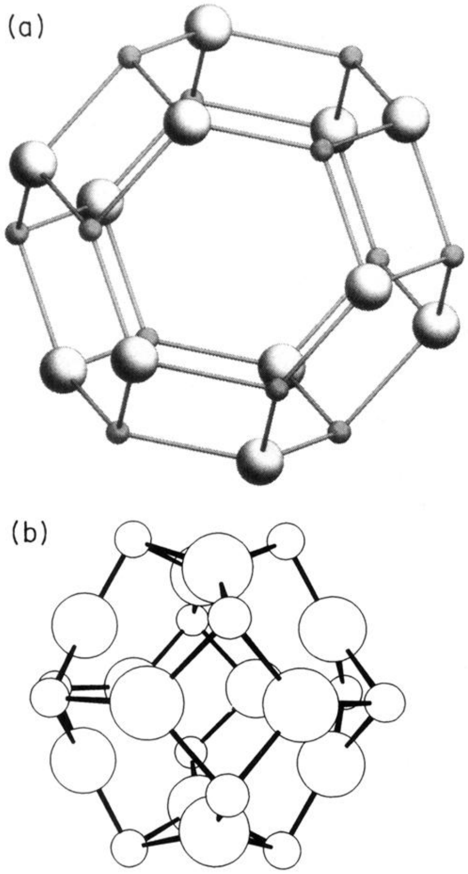

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