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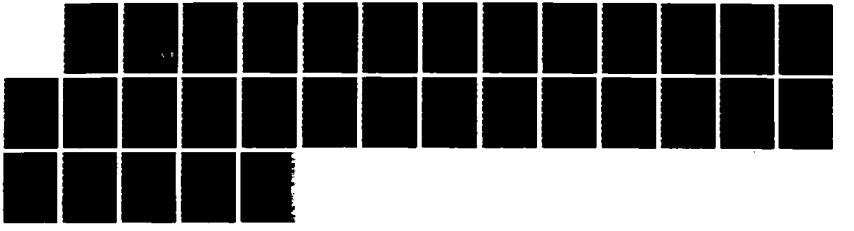

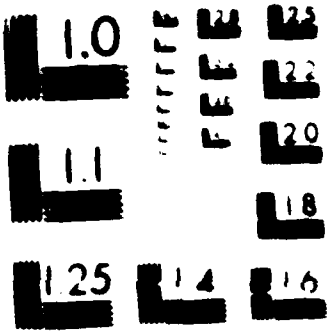
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The Huckel Model for Small Metal Clusters. III. Anion Structures and HMO Electron Affinities

by

D. M. Lindsay, Lin Chu, Youqi Wang and Thomas F. George

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State University of New York at Buffalo
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The most stable structures for the alkali-like clusters M_3^--M_9^- are calculated within the framework of the simple Hückel model. The Hückel geometries are, on average, slightly "less compact" than those of the neutral and cation clusters, a phenomenon which may be related to the additional electronic kinetic energy of the anions. Cluster compactness is quantified by an estimation of "soft sphere" volumes, which also allows for a comparison of classical and experimental polarizabilities. The Hückel model gives electron affinities which compare favorably with the experimental results for Cu_2^--Cu_9^-. To our knowledge, the Hückel results in this paper represent the first systematic search for the stable structures of small alkali-like anion clusters.

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THE HÜCKEL MODEL FOR SMALL METAL CLUSTERS. III. ANION STRUCTURES AND HMO ELECTRON AFFINITIES.

D. M. Lindsay and Lin Chu
Department of Chemistry
City University of New York, The City College
New York, New York 10031

Youqi Wang
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Thomas F. George
Departments of Chemistry and Physics & Astronomy
State University of New York at Buffalo
Buffalo, New York 14260

ABSTRACT

The *most stable* structures for the alkali-like clusters, M_3^- - M_8^-, are calculated within the framework of the simple Hückel model. The Hückel geometries are, on average, slightly "less compact" than those of the neutral and cation clusters, a phenomenon which may be related to the additional electronic kinetic energy of the anions. Cluster compactness is quantified by an estimation of "soft sphere" volumes, which also allows for a comparison of classical and experimental polarizabilities. The Hückel model gives electron affinities which compare favorably with the experimental results for Cu_2 - Cu_8. To our knowledge, the Hückel results in this paper represent the first *systematic* search for the stable structures of small alkali-like *anion* clusters.

I. INTRODUCTION

In previous work,[1,2] we reported Hückel molecular orbital (HMO) structures for alkali-like clusters M_n and M_n^+ with $2 \leq n \leq 9$. The *most stable* Hückel geometries were found to be the same (except for M_5^+ and M_6^+) as those predicted by local spin density (LSD)[3,4] and configuration interaction (CI)[5,6] calculations for the alkali metals. The Hückel results are also in accord with the experimentally determined structures of the ground state Group IA[7,8] and Group IB[9-11] trimer and heptamer molecules. Moreover, when specialized to neutral Na clusters, the relative agreement between HMO and LSD[3] atomization energies was less than 4%. For cation clusters, the discrepency between LSD atomization energies and the Hückel values, modified by the addition of a classical charge term, was (on average) only 2%. Hückel ionization potentials (IP's) give a good fit to the measured IP's for both Na_n and K_n, reproducing both the observed odd < even alternation in this parameter and the average, or classical, decrease towards the bulk work function.

Recently, two groups have made extensive electron affinity (EA) measurements on copper clusters.[16,17] These data show an odd > even alternation superimposed on a gradual increase towards the bulk work function. In this paper, we present simple Hückel calculations for alkali-like anion clusters M_n^-. As in the earlier analysis of M_n and M_n^+, we determine the most stable anion structures amongst *all possible* Hückel bonding arrangements. Cluster atomization energies are computed by combining HMO binding energies with a classical charge-correlation term similar to that introduced in Ref. 2. Using these energies plus the neutral cluster results of Ref. 3, the Hückel model gives electron affinities which reproduce quite well the experimental data for Cu_2-Cu_8.

II. CLUSTER ANIONS

The HMO stability of an n atom (neutral or ionic) metal cluster is determined by the eigenvalues (ε_i) of the Hückel matrix whose elements are given by ($1 \leq i \neq j \leq n$):

$$H_{ii} = \alpha$$

$$H_{ij} = \begin{cases} -\beta, \text{ if i is bonded to j} \\ 0, \text{ otherwise} \end{cases} \qquad (1)$$

In Eq. (1), α and β denote the empirical Hückel Coulomb and resonance integrals, respectively.

For the anionic clusters of interest here, the binding energy of a particular bonding arrangement is

$$E^-(n) = (n+1)\alpha + \sum_i n_i \varepsilon_i^-$$

$$n + 1 = \sum_i n_i \qquad (2)$$

where the summations extend over all occupied ($n_i = 2$) or partially occupied ($n_i = 1$) molecular orbitals. It is most convenient to choose energy units for which $\alpha = 0$ and $\beta = 1$. As in two previous studies,[1,2] we term these "Hückel units", abbreviated to hu.

In order to determine relative HMO stabilities, it is necessary to diagonalize the Hückel matrices for all the ***physically realizable*** bonding arrangements of a particular sized cluster. As described in detail in Ref.1, this procedure is facilitated by using certain concepts from Graph Theory. Briefly, there is a 1-1 correspondence between the Hückel matrix of an n atom cluster containing q bonds and the adjacency matrix of a simple (n,q) graph. It is relatively straightforward to generate all (n,q) graphs and then to eliminate those that are isomorphic by making comparisons with "standard graphs" stored in the form of their incidence matrices. The validity of this procedure can be checked by Polya's

Enumeration Theorem, which can predict the number of distinct and also connected (n,q) graphs. The graphs may be arranged in order of decreasing stability, as defined by Eq.(2), eliminating those for which no hard sphere packing arrangement exists. In order to accomplish this last step, it was mathematically convenient (and physically plausible) to require a maximum separation between all non-bonded atoms.

Figure 1 shows the structures found for the most stable anions, M_3^- - M_8^-. The corresponding binding energies are given in column 3 of Table 1. While the geometries of M_4^- and M_7^- are the same as those found for the neutral (and cation) tetramer and heptamer,[1] this is not the case for the remaining anions. Thus, linear M_3^- is 0.8 hu more stable than the D_{3h} arrangement favoured by the neutral and cationic species. It is interesting to note that SCF–CI calculations on Li_3[18] and Ag_3[19] also find that the anion geometry is $D_{\infty h}$. Two isoergic structures were found for M_5^-. One of these, the square pyramid as shown in Fig.1c, is (by 0.2 hu) the second most stable HMO neutral.[1] While the "less compact" [20] D_{5h} structure is as stable as the square pyramid for M_5^-, it is 0.6 hu less stable for neutral M_5. The most stable M_6^- structure, Fig.1d, has very low symmetry and is best described as a capped, distorted square pyramid. The second (by only 0.02 hu) most stable M_6^- is much more compact. The structure shown in Fig.1e may be derived from M_7^- (Fig.1f) by removing one ring atom. The most stable M_8^- cluster is very similar to that found for neutral M_8.[1] The Fig.1g structure differs from that of Ref.1 by the breaking of a single bond, which lowers the anion energy by 0.1 hu but raises that of the neutral octamer by 0.4 hu.

Aside from M_3^- (we exclude the dimer), there have been no *ab–initio* calculations on the Group IA and IB cluster anions. The stabilities of a few *selected structures* for silver cluster anions up to about Ag_{20}^- have been explored by semi–empirical methods, mainly as an aid to interpreting electron affinity and ionization potential data.[21,22] To our knowledge, the HMO results presented here represent the first comprehensive attempt to understand the structures of small anion clusters.

III. ELECTRON AFFINITIES

The thermodynamic EA of a cluster is given by

$$EA(n) = EA(1) + \Delta E^{-}(n) - \Delta E^{0}(n) \qquad (3)$$

where $\Delta E^{0}(n)$ and $\Delta E^{-}(n)$ are the atomization energies of the neutral and anion cluster, respectively. The neutral cluster atomization energy is the endoergicity for

$$M_n = nM \qquad (4)$$

and, in the HMO model, is numerically equal to the neutral cluster binding energy, $E^{0}(n)$ in hu. Table I gives $E^{0}(n)$ obtained from Ref. 1. Table I also gives $\Delta E^{0}(n)$ for copper clusters. These data pertain to $\langle\beta\rangle = 1.06 \pm 0.07$ eV, which is an average obtained [23] from the experimental cohesive energy of the bulk[24] plus the dimer and trimer atomization energies. [25]

The anion atomization energy is the energy change for the process

$$M_n^{-} = (n-1)M + M^{-} \qquad (5)$$

and this is composed of a bond breaking term, numerically equal to $E^{-}(n)$ expressed in hu, plus an electrostatic term, $\xi^{-}(n)$. The latter represents the change in self-energy arising from the relocalization of negative charge implied in Eq. (5). Similarily to the previously discussed cation example,[2] we write $\xi^{-}(n)$ as

$$\xi^{-}(n) = {}^{5}/_{8}\, e^{2}\{1/r_1 - 1/r_n\} \qquad (6)$$

where e is the electron charge and r_n is the radius of an n atom anion cluster. In terms of an atomic radius, here taken to be the Wigner–Seitz radius (r_s),

$$r_n = r_s(n^{1/3} + \epsilon^{-}) \qquad (7)$$

where ε^- is a "charge spillout" parameter [2,17] for *anions*. We adopt $\varepsilon^- \sim 1$, which is in agreement with the atom–bulk interpolation discussed in the next paragraph. The choice $\varepsilon^- \sim 1$ is also in accord with the expected relative (compared to the neutral and cation) diffusiveness of an anion cluster, but is somewhat larger than that used in Ref.17.

The numerical factor of 5/8 in Eq. (6) is chosen to give agreement with the expression for the EA of a classical, conducting drop [26,27]

$$EA(n) = W(\infty) - {}^{5}/_{8}\, e^2/r_n \qquad (8)$$

where $W(\infty)$ is the work function of the bulk metal.[28] The correspondence between these two viewpoints may be seen as follows. For a "classical cluster", the bond energies of the neutral and anion species are identical, so that

$$EA(n) = EA(1) + \xi^-(n) \qquad (9)$$

For this situation, Eq. (6) together with the identity $EA(\infty) \equiv W(\infty)$, leads directly to Eq.(8). For $\varepsilon^- = 1$, Eqs. (7) and (8) imply

$$W(\infty) - EA(1) = 5e^2/16r_s \qquad (10)$$

Table II makes a comparison between $W(\infty) - EA(1)$ and $5e^2/16r_s$ for both the Group IA and Group IB elements.[29] Except for Li, the average deviation between these two parameters is less than 5%.

As in the case of M_n^+, we use *modified* simple Hückel atomization energies for the anions. These employ the HMO energies, column 2 of Table I, plus the charge-correlation term, Eq. (6) with $r_n = r_s(n^{1/3} + 1)$. Column 5 of Table I gives $\Delta E^-(n)/n$ for Cu_n^- assuming $\beta = 1.06$ eV and $r_s = 1.41$ Å.[24] The HMO results for Cu_2^- and Cu_3^- (0.72 eV and 1.20 eV, respectively) are about 10-15% smaller than the corresponding experimental data, namely

0.79 (3) eV and 1.4 (12) eV, from Ref.17. Table I also gives Hückel electron affinities obtained from Eq.(1) using EA(1) = 1.24 eV. The HMO electron affinities are compared with the corresponding experimental values[16,17] in Figure 2. The agreement between the two data sets is quite good. Both show an odd > even alternation in EA, superimposed on a smoothly increasing classical result.[31] The occurence of an odd-even alternation, which also appears in IP data, has a straightforward explanation.[16,17,21,22] Roughly speaking, an *even* numbered neutral cluster possesses a set of filled bonding orbitals plus an equal number of empty antibonding (AB) orbitals. The IP of such a cluster is (again, roughly speaking) the energy of the highest bonding orbital. *Odd* n clusters possess an additional, half filled nonbonding (NB) orbital, lying in between the bonding and AB manifolds. The lower energy of this orbital gives rise to the low IP of an odd atom neutral cluster. For anions, the lowest energy AB orbital is partially filled for n even, but is empty for n odd. As a consequence, the anion IP's are, in general, lower for even numbered cluster sizes. That there is a reasonable correspondence between this simple orbital picture and the more realistic HMO results is evident from the orbital diagram, Fig. 2 of Ref. 2.

IV. DISCUSSION

Within the framework of the HMO model, at least, there is a tendency for anion clusters to adopt structures which are somewhat less compact[20] than those found for the neutrals. One possible cause for this behaviour is the additional kinetic energy (KE) associated with the extra electron of the anions. A close packing arrangement minimizes the potential energy (PE) of a cluster by maximizing the number of bonds between atoms. For *rare gas* clusters, in which the electrons are confined to the atomic cores, this interaction is dominant and so the most compact arrangement of atoms is generally predicted to be the most stable one.[32] The stability of a *metal* cluster is determined not only by the pairwise potential interaction between nearest neighbor atoms, but also by the KE of the valence electrons which are delocalized over the molecular framework. In the HMO model, there is a strong correspondence between the energy (E_{1S}, in hu) of the lowest

1s-molecular orbital and <q>, the average number of bonds (i.e. nearest neighbours) per atom in the cluster. Table III shows some representative examples. Included in this Table are the most stable neutral cluster structures found by HMO calculations in Ref.1, plus some additional geometries ($D_{\infty h}$, T_d for n = 3 and 4; C_{4v} and D_{5h} for n = 5) which compare differing packing arrangements and dimensionalities. For the data of Table II the average difference between E_{1s} and <q> is only 2%.

A similar correspondence pertains to macroscopic samples.[2,24] The 1s level in HMO theory correlates with the k = 0 position (k = wavevector) of a metal in the bulk limit.[2] In the tight binding model, which is the macroscopic counterpart of Hückel theory, the electronic energy of a metal may be expanded near k = 0 to give a PE term plus a KE term.[2,24] The latter is the same as the energy expression obtained from the Fermi gas model for free electrons. The PE (in hu) is numerically identical to the number (6, 8 or 12) of nearest neighbours in a (simple, body centered or face centered) cubic lattice.

Thus for an HMO cluster, the total energy may be considered to be approximately partitioned into two competing components: a negative potential contribution, nearly equal in magnitude to the energy of the 1s level, and a positive KE associated with the delocalized valence electrons. This implies that any stabilization of less compact structures originates in a reduction of the electronic KE, suggesting that more compact structures confine the valence electrons to a smaller volume. This should give rise to larger KE's which would be of relatively greater importance for negatively charged clusters. A similar competition might explain why, for the neutral tetramer and pentamer, the less compact planar structures are predicted [2-6] to be more stable than the three-dimensional arrangments favored by rare gas clusters.

It is straightforward to compute packing fractions for differing, but regular, arrangements of atoms in a macroscopic sample.[24] For a cluster composed of *hard* sphere (eg. argon) atoms, then the volume occupied by the electrons is independent of structure. For the case of alkali-like atoms, however, the valence electrons presumably occupy a

volume defined by the shape and bonding arrangement of the individual cluster. This volume was estimated using a *soft* sphere model. Each atom was assigned a unit charge occupying a spherical volume *larger* than the hard sphere volume which determines nearest neighbour distances. The soft sphere radius was chosen as the distance where the electron density for an atomic (for example Na) Slater orbital has fallen to about 90% (say) of its maximum value.[33] The total size of a particular arrangement of n atoms is the volume enclosed by n overlapping soft spheres, and this may be estimated by Monte Carlo integration.[34]

Some pertinent soft sphere cluster volumes are given in column 5 of Table III. The data pertain to neutral Na clusters, with estimated errors (1 standard deviation uncertainty) given in parentheses and a total of 50,000 integration points except for n = 2-5 for which 10^6 points were employed. Cluster volumes are displayed as total volumes, V(n), divided by the volume of n individual atoms. For n = 6 - 9, the data correspond to the most stable HMO neutral structures (point group given in column 2) as discussed in Ref. 1. The data for n = 3, 4 and 5 compare the soft sphere volumes of clusters having different degrees of compactness. Thus the D_{3h} trimer has an approximately 4% smaller volume than the linear $D_{\infty h}$ arrangement. Similarily, the three-dimensional tetrahedral cluster is approximately 2.5% smaller in total volume than the planar (but more stable [2-6]) rhombus. The variation amongst pentamer structures is somewhat greater. The pentagonal arrangement is 5% larger than the most stable [2-6] neutral (C_{2v} point group), and 7.5% larger than the three-dimensional square pyramid (C_{4v} point group).

While small, these differences in soft sphere volumes are both statistically and physically significant. The volume of an n atom cluster is proportional to its classical polarizability, $\alpha(n)$, [35] implying

$$\frac{\alpha(n)}{n\alpha(1)} = \frac{V(n)}{nV(1)} \qquad (11)$$

Figure 3 compares soft sphere V(n)/nV(1) data from Table III with the experimental polarizabilities for Na_2 - Na_9.[36] The experimental polarizabilities decrease slowly to a bulk value of $\alpha(n)/n\alpha(1) \sim 0.4 - 0.5$, but oscillate about the soft sphere average particularily at small n. These oscillations arise from quantum effects and have been partially accounted for by jellium calculations.[4,37,38] The soft sphere model does not (of course) include quantum effects and the slight discontinuity at $n \sim 6$ is a manifestation of the transition from two-dimensional to three-dimensional geometries.

Also shown in Fig.3 is a cruder classical approximation:

$$\frac{\alpha(n)}{n\alpha(1)} = \frac{(n^{1/3} + \varepsilon^o)^3}{n(1 + \varepsilon^o)^3} \qquad (12)$$

Eq. (12) assumes that the cluster is a spherical classical drop whose radius is related to an atomic radius (r_o) by

$$r = r_o (n^{1/3} + \varepsilon^o) \qquad (13)$$

This expression is similar to Eq. (7), but here ε^o is the "charge spillout" parameter appropriate to a *neutral* cluster. The classical drop curve shown in Fig. 3 pertains to $\varepsilon^o = 0.23$, which was obtained by fitting all the polarizability data (n = 2 - 40) in Ref. 36. The agreement between the two classical results is surprisingly good, especially in view of the differing and independent parameterizations for each model and so lends additional authority to the classical drop model invoked in this work and elsewhere.[2,12,17,36]

In conclusion, we have determined the most stable HMO structures for the alkali-like metal cluster anions, M_3^- - M_8^-. The HMO geometries are somewhat less "compact" than those of the neutral and cation clusters, and it is suggested that this may be related to the additional electronic KE of the anions. The cluster compactness is quantified not only by bond enumeration, but also through an estimation of soft sphere volumes, the latter

being directly related to cluster polarizabilities. The Huckel model gives electron affinities which compare favorably with the experimental results for Cu_2 - Cu_8

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20. One measure of a structure's compactness is the total number of bonds (q). Thus, for example, the C_{4V} geometry for M_5 with q = 8 is significantly more compact than the D_{5h} arrangement for which q = 5. A three-dimensional model provides a less objective but more enlightening gauge of compactness. We have found a balloon containing ping-pong balls to be particularly helpful in visualizing cluster shapes. In Section IV, we relate cluster compactness to cluster volume.

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32. For example, see: M. R. Hoare and P. Pal, Adv. Phys. 20, 161 (1971); M. R. Hoare, Adv. Chem. Phys. 40, 49 (1979).

33. In practice we chose a soft sphere radius, $r_c = 0.75$ in units of the nearest- neighbour distance. If the latter is taken to be twice the Wigner-Seitz radius, then for Li → Cs the Slater orbital electron density at $r_c = 0.75$ is approximately 10 - 15% of its maximum value.

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TABLE I. Hückel binding energies, atomization energies and electron affinities. Data in eV pertain to Cu, using β = 1.06(7) eV (see text). Neutral cluster energies from Ref.1.

n	$E^{o}(n)$	$E^{-}(n)$	$\Delta E^{o}(n)/n$	$\Delta E^{-}(n)/n$	EA(n)
	hu			eV	
1	0.0000	0.0000	0.00	0.00	1.24
2	- 2.0000	- 1.0000	1.06	0.72	0.56
3	- 3.0000	- 2.8284	1.06	1.20	1.65
4	- 5.1231	- 4.1231	1.36	1.28	0.93
5	- 6.6443	- 6.4721	1.41	1.54	1.91
6	- 9.3711	- 8.2005	1.66	1.61	0.95
7	-11.1054	-11.1054	1.68	1.83	2.26
8	-14.1604	-12.7268	1.88	1.82	0.82

TABLE II. Atomic electron affinities, EA(1), bulk work functions, $W(\infty)$, and Wigner-Seitz radii (r_s, in Å) for the Group IA and IB metals. Columns 5 and 6 compare $W(\infty)$ - EA(1) with $5e^2/16r_s$. Energy units are eV.

	EA(1) [a]	$W(\infty)$ [b]	r_s [c]	$W(\infty)$ -EA(1)	$4.5/r_s$
Li	0.62	2.32	1.72	1.70	2.62
Na	0.55	2.75	2.08	2.20	2.16
K	0.50	2.30	2.57	1.80	1.75
Rb	0.49	2.09	2.75	1.60	1.64
Cs	0.47	2.14	2.98	1.67	1.51
Cu	1.24	4.65	1.41	3.41	3.19
Ag	1.30	4.26	1.60	2.96	2.81
Au	2.31	5.1	1.59	2.8	2.83

[a] From Ref. 30.
[b] From Ref. 28.
[c] From Ref. 24.

TABLE III. Comparison of the average number of bonds/atom <q> with the lowest Hückel orbital energy (E_{1s} in hu), and of soft sphere volume polarizabilities V(n) with the experimental α(n) for Na_n.

n	Point Group	<q> [a]	$\lvert E_{1s} \rvert$	V(n)/nV(1) [b]	α(n)/nα(1) [c]
2	$D_{\infty h}$	1.00	1.00	0.920	0.800
3	D_{3h}	2.00	2.00	0.862	0.980
3	$D_{\infty h}$	1.33	1.41	0.896	
4	T_d	3.00	3.00	0.814	
4	D_{2h}	2.50	2.56	0.835	0.856
5	C_{4v}	3.20	3.24	0.798	
5	C_{2v}	2.80	2.94	0.819	0.907
5	D_{5h}	2.00	2.00	0.859	
6	C_{5v}	3.33	3.45	0.781	0.857
7	D_{5h}	4.29	4.32	0.742	0.723
8	D_{2d}	4.50	4.54	0.726	0.687
9	D_{3h}	4.67	4.70	0.717	0.738

[a] From Ref. 1.

[b] Estimated error ± 0.003 for n = 2 - 5; ± 0.013 for n = 6 - 9.

[c] From Ref. 36.

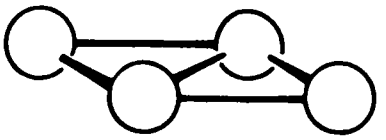
FIGURE CAPTIONS

Fig. 1. Geometries for the most stable HMO clusters, M_3^- - M_8^-.

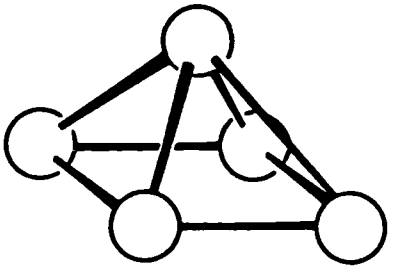
Fig. 2. Comparision of Hückel and experimental electron affinities for Cu^- - Cu_8^-. Open circles pertain to this work. Triangles and full circles are EA data from Refs.16 and 17, respectively.

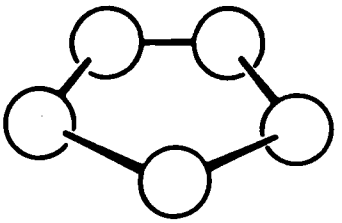
Fig. 3. Comparison of experimental polarizabilities (Na data from Ref. 36) with soft sphere (see text) and classical drop approximations.

(a). M_3^-

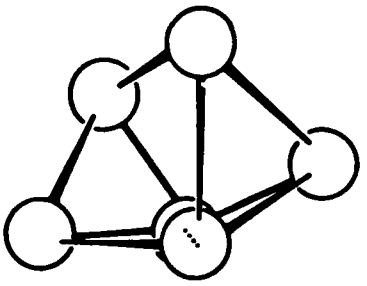


(b). M_4^-

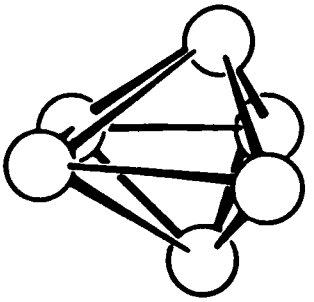




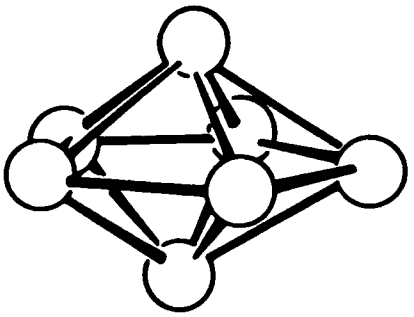
(c). ISOERGIC M_5^- STRUCTURES



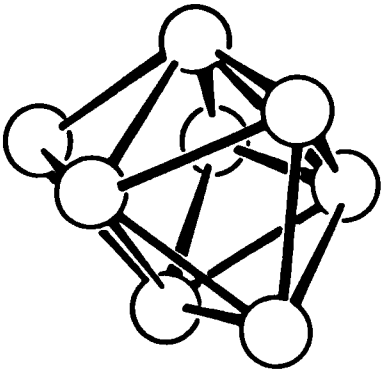
(d). M_6^- (FIRST)



(e). M_6^- (SECOND)



(f). M_7^-



(g). M_8^-

FIG. 1

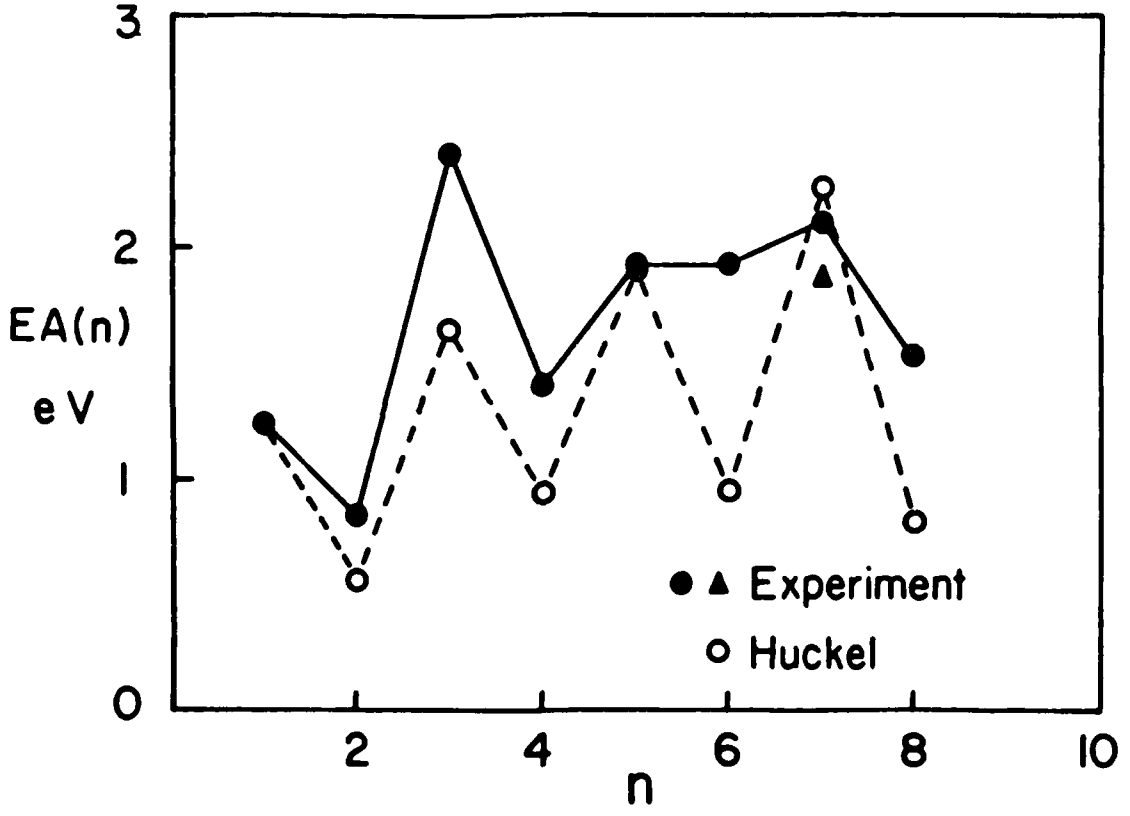


FIG. 2

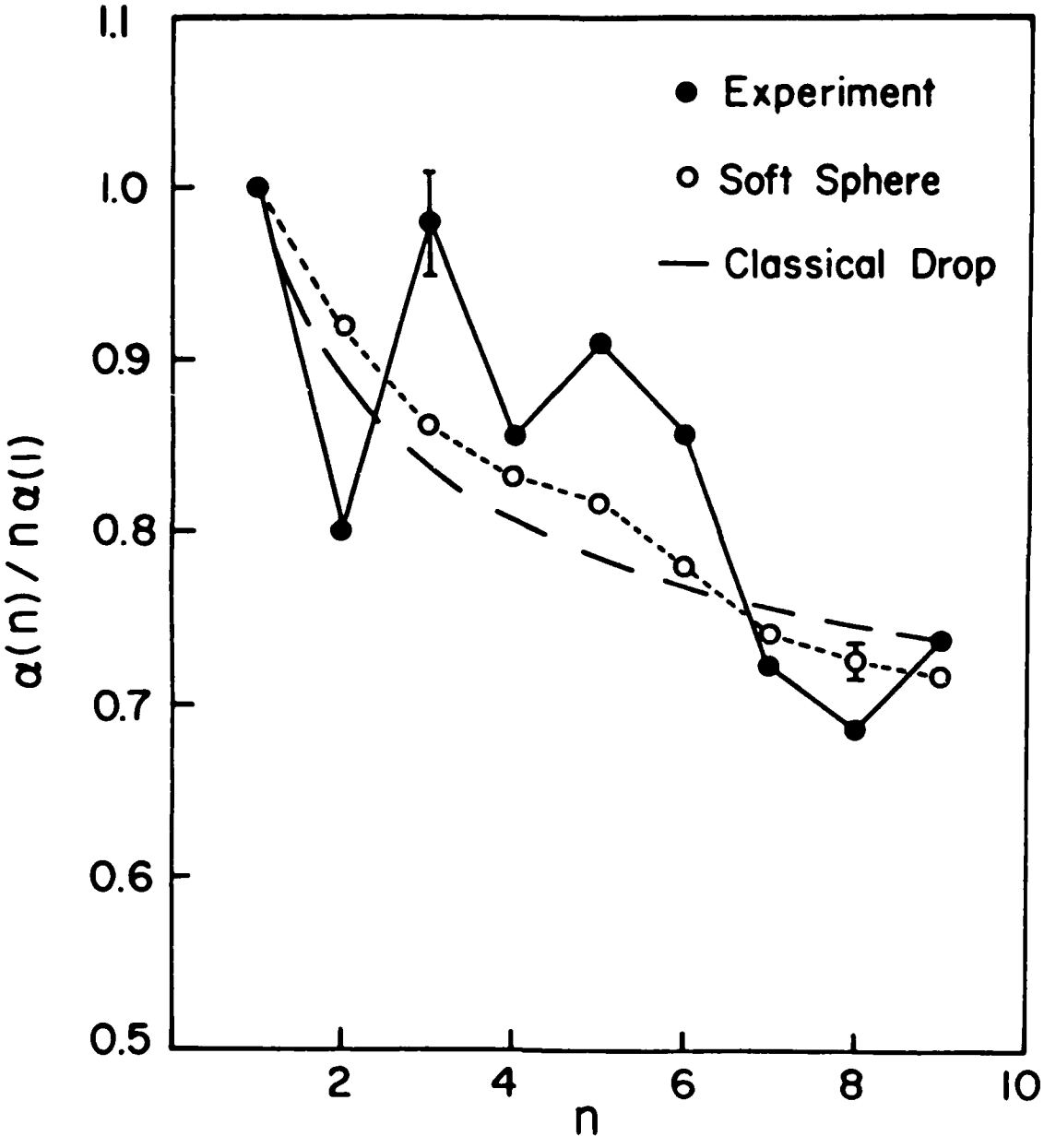

1.1
1.0
0.9
0.8
0.7
0.6
0.5
α(n) / n α(1)
2
4
6
8
10
n
Experiment
Soft Sphere
Classical Drop

FIG. 3

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