

**Iron-ethylene cluster  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$** 

L. C. Cune and M. Apostol

 Department of Theoretical Physics,  
 Institute of Atomic Physics,  
 Magurele-Bucharest MG-6,  
 POBox MG-35, Romania  
 email:cune@theory.nipne.ro
**Abstract**

The stability of the iron-ethylene cluster  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  is studied within a metallic-bond-type theory. The cluster is a centered Fe icosahedron with  $\text{C}_2\text{H}_2$  radicals arranged symmetrically on the icosahedron sides.

Recently, an iron-ethylene cluster  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  has been synthesized[1] by a laser-pulse reaction in vapour-mixture flow; it seems to be a rather "magic" cluster with respect to the number of both iron and ethylene radicals. Two hydrogen atoms (one from each carbon) are lost by ethylene during this reaction, and the resulting  $\text{C}_2\text{H}_2$  radical attaches itself to two iron atoms, like a clasp, yielding  $\text{Fe}_2(\text{C}_2\text{H}_2)$ ; this structure may be viewed as consisting of two  $\text{Fe}(\text{CH})$  radicals, denoted by R, which participate in the metallic bond of the cluster; therefore, the  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  cluster may be thought as consisting of 12 radicals  $\text{R}=\text{Fe}(\text{CH})$  and one Fe ion. The aim of this letter is to investigate the stability of this cluster by means of a recently introduced theory of metallic bond.[2]

According to this theory the metallic bond of large clusters consisting of heavy atoms (high atomic numbers  $Z$ ) is treated within the quasi-classical description, by a variational approach to the linearized Thomas-Fermi model;[3] it is a density-functional theory,[4] suitable for a slightly inhomogeneous electron gas moving in a background of point-like cations of effective valence  $z_i^*$ , where  $i$  is the cation label. This effective valence charge is determined usually from the atomic screening by means of the Thomas-Fermi model for atoms; it is given[2] by  $z^* = z(1 + 0.84Z^{1/3})e^{-0.84Z^{1/3}}$ , where  $z$  is the nominal valence of the atom.

For Fe ( $Z = 26, z = 2$ ) we obtain  $z_{\text{Fe}}^* = 0.57$ , while for the Fe ion in the R radical introduced above we get  $z_{\text{Fe}}^*/2 = 0.28$ , since one of the two valence electrons of this Fe ion is taken in the  $\text{Fe}(\text{CH})$  bond; we take this effective valence  $z_{\text{R}}^* = 0.28$  as that of the R radical. According to Ref.2 the shape of the cluster is obtained by minimizing the potential energy

$$\begin{aligned}
 E_{pot} = & -\frac{1}{4}q[3\sum_{i=1}^N z_i^{*2} + \\
 & + \sum_{i \neq j=1}^N z_i^* z_j^* (1 - 2/q|\mathbf{r}_i - \mathbf{r}_j|) e^{-q|\mathbf{r}_i - \mathbf{r}_j|}]
 \end{aligned}
 \tag{1}$$

with respect to the dimensionless parameters  $\mathbf{x}_i = q\mathbf{r}_i$ , where  $q$  is a variational Thomas-Fermi screening wavevector; this parameter is derived from the minimum value of the quasi-classical energy  $E_q = E_{kin} + E_{pot}$ , where the kinetic energy is given by  $E_{kin} = (27\pi^2/640)q^4 \sum_{i=1}^N z_i^*$ ; in eq. (1) above  $N$  represents the number of atoms in the cluster. The total energy  $E = E_q + E_{ex}$

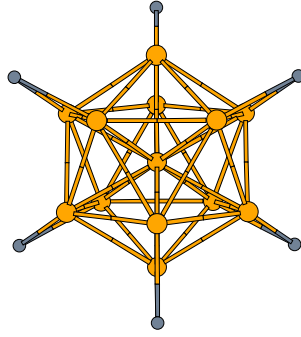


Figure 1:  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  with  $\text{Fe}_{13}$  in the icosahedron vertices and  $(\text{C}_2\text{H}_2)_6$  on sides

is obtained by adding the exchange contribution  $E_{ex} = -(9/32)q^2 \sum_{i=1}^N z_i^*$  to the quasi-classical energy. It is shown in Ref.2 that the total energy  $E$  obtained in this way coincides in fact with the cluster binding energy. The equilibrium shape of the cluster is obtained from the minimum value of the potential energy (1) by the usual gradient-method; this way, one gets[2] a  $\text{Fe}_{13}$ -centered icosahedron, with a quite stable ground-state of energy  $E = 68.9\text{eV}$  and a radial inter-atomic distance  $r \simeq 2\text{\AA}$ , in agreement with other calculations;[5] in addition,  $N = 13$  is an outstanding geometric magic number, in the sequence[2]  $N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61$ . It is also shown in Ref.2 that these magic numbers are universal for homo-atomic metallic clusters, in the sense that they do not depend on the effective valence  $z^*$  (in a physically reasonable range like, for instance,  $0 < z^* < 3$ ), or the atomic species.

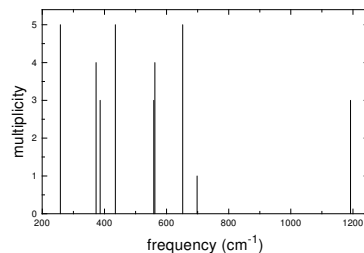


Figure 2: Vibration spectrum for  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  as estimated from the present theory

The above theory is applied to the  $\text{R}_{12}\text{Fe}$  cluster, according to the discussion made above, and the results are assigned to the iron-ethylene cluster  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$ . By minimizing the potential energy given by (1) one obtains a centered icosahedron shown in Fig.1, where the  $\text{C}_2\text{H}_2$  radicals are located on the icosahedron sides in a highly symmetric manner; this symmetry of the  $\text{C}_2\text{H}_2$ -radicals distribution and the magic number 13 indicate that the corresponding  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  cluster is itself a "magic" cluster with respect to the variation of both the Fe and the  $\text{C}_2\text{H}_2$  content, in agreement with the experimental mass-spectrum.[1] The radial inter-atomic distance of the  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$  icosahedron is  $2.47\text{\AA}$ , and the "binding" energy obtained here is  $\simeq 19.92\text{eV}$ ; noteworthy, this is

only the metallic contribution to the total binding energy of the cluster, and the binding energy involved by the reaction  $2\text{Fe} + \text{C}_2\text{H}_2 \rightarrow \text{Fe}_2(\text{C}_2\text{H}_2)$  must be added (as well as the dissociation energy implied by forming up the  $(\text{C}_2\text{H}_2)$  radical); however, the evaluation of the latter is beyond the range of applicability of the present theory. It is also noteworthy that the above results do not change qualitatively for reasonable changes in the effective valence charges  $z_{\text{Fe}}^*$  and  $z_{\text{R}}^*$ .

The vibration spectrum of the  $\text{R}_{12}\text{Fe}$  cluster can be estimated by assuming a  $\text{Fe}(\text{CH})$  mass for the R radical; this is a qualitative approximation to the low- and middle-frequency range of the spectrum of the  $\text{Fe}_{13}(\text{C}_2\text{H}_2)_6$ . The vibration spectrum obtained in this way is given in Fig.2, and one can see that indeed it agrees qualitatively with other calculations of the vibration spectra for Fe-based icosahedra.[6]

Finally, one may note that similar calculation can be carried out for other inclusions in metallic clusters, like, for instance, hydrogenated- or oxygenated- iron clusters.[6],[7] In addition, according to Ref.2 the electrons in a cluster move in a self-consistent potential

$$\varphi = \sum_{i=1}^N (z_i^* / |\mathbf{r} - \mathbf{r}_i|) e^{-q|\mathbf{r} - \mathbf{r}_i|} \quad , \quad (2)$$

which is a superposition of screened Coulomb potentials; for highly-symmetric clusters, or for statistical ensembles of cluster isomers, the well-known (quadrupole-) deformed potential[8] can be derived from (2); the lowest-energy electronic-excitation spectrum can then be computed, including the cluster chemical potential, as well as the various cluster response functions; these computations, related to the electronic properties of such clusters, are left for a forthcoming investigation.

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