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# Iron–hydrocarbon cluster $Fe_{13}(C_2H_2)_6$

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**Abstract**

The stability of the iron–hydrocarbon cluster $Fe_{13}(C_2H_2)_6$ is studied within a metallic-bond-type theory. The theoretical model for the cluster structure indicates a centered $Fe_{13}$-icosahedron with $C_2H_2$-radicals arranged symmetrically on the icosahedron sides. © 2001 Elsevier Science B.V. All rights reserved.

Recently, an iron–hydrocarbon cluster $Fe_{13}(C_2H_2)_6$ has been synthesized by $CO_2$ laser pyrolysis of a gaseous mixture of iron pentacarbonyl and ethylene in a flow reactor [1]. It seems to be a 'magic' cluster with respect to both the number of iron atoms and $C_2H_2$-radicals. In view of the complexity of such an organo-metallic cluster we adopt a simplified model in order to test its stability and structural properties. Two hydrogen atoms are lost by ethylene during the synthesis reaction (in principle, either one from each carbon, giving thus rise to acetylene, or both from the same carbon, as corresponding to vinylidene), and the resulting $C_2H_2$ radical attaches itself to two iron atoms, like a clasp, yielding $Fe_2(C_2H_2)$. Very likely, by energetic arguments, the $C_2H_2$-radical is acetylenic, and the $Fe_2(C_2H_2)$-structure may be viewed as consisting of two $Fe(CH)$ radicals, denoted by R, which participate in the metallic bond of the cluster. Therefore, the cluster $Fe_{13}(C_2H_2)_6$ may be thought as consisting of 12 radicals $R = Fe(CH)$ and one Fe ion. The aim of this Letter is to investigate the stability and the structural properties of such a cluster model by means of a recently introduced theory of metallic bond [2–4]. The structural frame of the cluster is shown to be a perfect icosahedron, with the Fe ion at the centre, in agreement with the same magic structure obtained for homo-atomic metallic clusters [2–4]; the inter-atomic distances are estimated, as well as the contribution of the metallic bond to the binding energy, the vibration spectrum and the distribution of the electron density.

The metallic binding 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 (see, for instance, [5] as well as [6]). Such an approach is a version of the density-functional theory [7,8], suitable for a slightly inhomogeneous electron liquid moving in a background of point-like cations of effective valence $z_i^*$, where $i$ is the cation label. This effective valence charge may be determined from the atomic screening by means of the Thomas–Fermi theory for atoms; it is given [2–4] 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 $z_{Fe}^* = 0.57$, while for the Fe-ion in the R-radical introduced above we get $z_{Fe}^*/2 = 0.28$,

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since one of the two valence electrons of this Fe-ion is taken in the FeCH bond; therefore, we assign this effective valence $z_{\mathrm{R}}^{*} = 0.28$ to the R-radical, as originating in the Fe-ion in the Fe(CH)-radical. According to [2] the electron density $n$ is related to the self-consistent potential $\varphi$ through $n = (q^2/4\pi)\varphi$, where $q$ is the Thomas–Fermi screening wave vector. The energy is expressed in atomic units $e^2/a_{\mathrm{H}} = 27.2$ eV, where $-e$ is the electron charge, $a_{\mathrm{H}} = \hbar^2/me^2 = 0.53$ Å is the Bohr radius, $\hbar$ is Planck's constant and $m$ is the electron mass. The solution of Poisson's equation is then

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

i.e. a superposition of screened Coulomb potentials, as expected; $N$ denotes the total number of atoms in the cluster and $\mathbf{r}_{\mathrm{i}}$ denote the ionic positions. The potential energy is given by

$$\begin{aligned} E_{\mathrm{pot}} &= \int \mathrm{d}\mathbf{r} \cdot \left( -n\varphi + \frac{1}{2} n\varphi_{\mathrm{e}} \right) + \frac{1}{2}\sum_{i \neq j} z_i^{*} z_j^{*}/|\mathbf{r}_i - \mathbf{r}_j| \\ &= -\frac{1}{2}\int \mathrm{d}\mathbf{r} \cdot n(\varphi + \varphi_{\mathrm{ion}}) + \frac{1}{2}\sum_{i \neq j} z_i^{*} z_j^{*}/|\mathbf{r}_i - \mathbf{r}_j| \\ &= -\frac{q^2}{8\pi}\int \mathrm{d}\mathbf{r} \cdot \varphi(\varphi + \varphi_{\mathrm{ion}}) + \frac{1}{2}\sum_{i \neq j} z_i^{*} z_j^{*}/|\mathbf{r}_i - \mathbf{r}_j|, \end{aligned} \tag{2}$$

where $\varphi_{\mathrm{e}}$ is the electron contribution to the self-consistent potential, $\varphi_{\mathrm{ion}} = \sum_i z_i^{*}/|\mathbf{r} - \mathbf{r}_i|$ is the ionic contribution to the self-consistent potential, and $\varphi = \varphi_{\mathrm{e}} + \varphi_{\mathrm{ion}}$. Noteworthy, the Coulomb repulsion between the ionic cores is included in the potential energy above (last term in (2)). Making use of the self-consistent potential $\varphi$ given by (1) the calculations in (2) are straightforward; they involve standard two-centre integrals, which may be performed by means of the usual prolate–ellipsoidal coordinates [9]. Doing so, one obtains the potential energy

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

The geometric form of the cluster is obtained by minimizing this potential energy with respect to the dimensionless parameters $\mathbf{x}_i = q\mathbf{r}_i$. The position coordinates $\mathbf{r}_i$ in (3) correspond to one Fe-ion and to the 12 Fe-ions in the R-radicals; they represent the coordinates of those points where the charges participating in the metallic bond are localized. By minimizing the potential energy given by (3) we obtain for our cluster a perfect, inscriptible icosahedron with one Fe at the center and 12 R-radicals at the vertices, whose faces are all equal equilateral triangles; the side length is $x_{\mathrm{R-R}} = 2.63$, and the radius of the circumscribed sphere is $x_{\mathrm{Fe-R}} = 2.50$. The minimization of the potential energy given by (3) with respect to the position parameters $\mathbf{x}_i$ is carried out by the usual gradient method. One Fe-ion with effective charge $z_{\mathrm{Fe}}^{*} = 0.57$ and 12 R-ions with effective charge $z_{\mathrm{R}}^{*} = 0.28$ are randomly distributed in space, and their positions are allowed to move in successive steps along the forces computed from (3). The potential energy given by (3) indicates effective inter-atomic potentials

$$\Phi_{ij} = -\frac{1}{2} q z_i^{*} z_j^{*} \big(1 - 2/qr_{ij}\big) e^{-qr_{ij}}, \tag{4}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The equilibrium is reached, and the minimization process stops, for forces less than $10^{-4}$ eV/Å. The equilibrium means either the ground-state or isomers, and the stability of the geometric forms obtained by this way is further tested by computing the vibration spectra. This method has been applied to a large variety of homo-atomic metallic clusters ($N \leqslant 80$), and geometric magic forms and magic numbers have thereby been identified [2–4]. In particular, the centered icosahedron of 13 atoms has been obtained as an outstanding magic homo-atomic cluster, characterized by both a high stability and a high symmetry.

Beside the position parameters $\mathbf{x}_i$ (or $\mathbf{r}_i = \mathbf{x}_i/q$), the theory contains another variational parameter, which is the Thomas–Fermi screening wave vector $q$. This parameter is derived from the minimum value of the quasi-classical energy $E_{\mathrm{q}} = E_{\mathrm{kin}} + E_{\mathrm{pot}}$, where the kinetic energy is given by $E_{\mathrm{kin}} = (27\pi^2/640)q^4 \sum_{i=1}^{N} z_{i\,1}^{*}$ and $E_{\mathrm{pot}}$ is given by (3). One obtains $q = 1.01$ Å for the icosahedral ground-state determined above for our cluster; it follows that the inter-atomic distances are $r_{R-R} = x_{R-R}/q = 2.60$ Å for the side length, and $r_{Fe-R} = x_{Fe-R}/q = 2.47$ Å for the icosahedron radius. The total energy $E = E_q + E_{ex}$ 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 [2] that the total energy $E$ obtained in this way coincides in fact with the cluster binding energy within the quasi-classical description. The quasi-classical description of the metallic cohesion has been tested on various homo-atomic clusters [2–4]. One gets, for instance, [2–4] a perfect, centered icosahedron for the cluster $Fe_{13}$, with quite a stable ground-state of energy $E = -68.9$ eV and a radial inter-atomic distance $r \simeq 2$ Å, in agreement with other calculations, based on density-functional approaches (see, for instance, [10]). In addition, $N = 13$ is an outstanding geometric magic number in the sequence [2–4] $N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61$ of homo-atomic metallic clusters. It is also shown in [2] that, within the quasi-classical description and for point-like ionic cores, these magic numbers do not depend on the effective valence $z^*$ (in a physically reasonable range like, for instance, $0 < z^* < 3$), or the atomic species.

The above theory has been applied to the $R_{12}Fe$ cluster, according to the discussion made above, and the results are assigned to the iron–hydrocarbon cluster $Fe_{13}(C_2H_2)_6$. By minimizing the potential energy given by (3) one obtains the perfect, centered icosahedron shown in Fig. 1, where the $C_2H_2$ radicals are located on the icosahedron sides in a highly symmetric manner; the symmetry of the $C_2H_2$-radicals distribution and the magic number 13 suggests that the corresponding $Fe_{13}(C_2H_2)_6$ cluster may itself be a magic cluster with respect to the variation of both the Fe- and the $C_2H_2$-content, in agreement with the experimental mass-spectrum [1]. The structure shown in Fig. 1 coincides with the structure proposed in [1] as being the most probable structure, according to its high symmetry (symmetry group $T_h$); however, a distinct structure shown in Fig. 2, of lower symmetry, may also be accepted as a possible structure, within the present calculations. The difference in energy between the two structures arises solely from the interaction between the $C_2H_2$

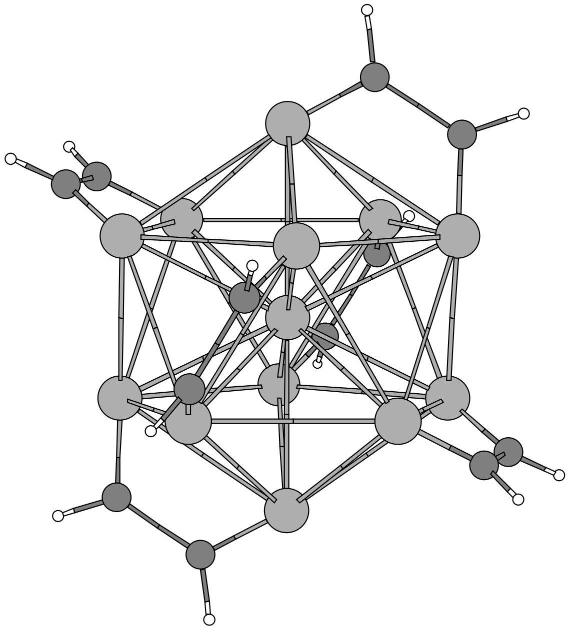

Fig. 1. $Fe_{13}(C_2H_2)_6$ with $Fe_{13}$ in the icosahedron vertices and $(C_2H_2)_6$ on sides (symmetry group $T_h$).

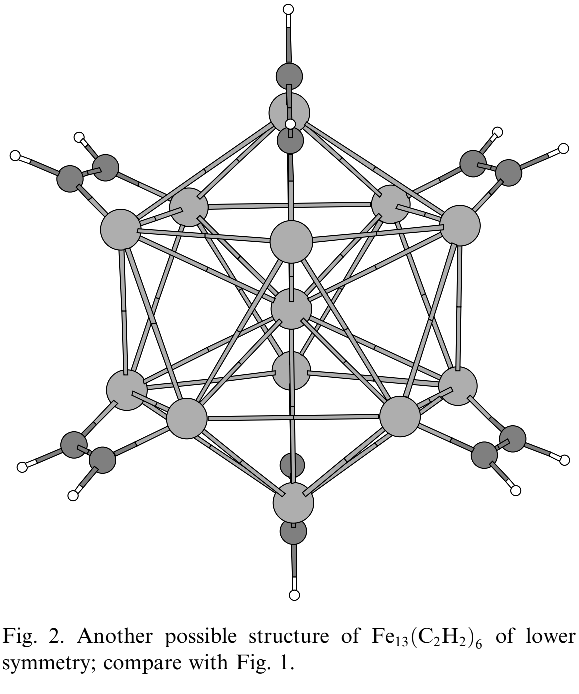

Fig. 2. Another possible structure of $Fe_{13}(C_2H_2)_6$ of lower symmetry; compare with Fig. 1.

radicals, and in order to minimize the energy these radicals must be arranged in the highest symmetric form given in Fig. 1. Indeed, the six $C_2H_2$ radicals in Fig. 1 form a perfect octahedron, which is another magic structure obtained for homo-atomic metallic clusters within this theory [2–4]. Consequently, with respect to the distribution of the $C_2H_2$ radicals, one may consider this structure as being the most probable structure for the ground-state of the cluster $Fe_{13}(C_2H_2)_6$, while the structure shown in Fig. 2 is an isomer. In both cases, the radial inter-atomic distance of the $Fe_{13}(C_2H_2)_6$ icosahedron is 2.47 Å, and the 'binding energy' is $\simeq -19.92$ eV; noteworthy, this is only the metallic contribution to the total binding energy of the cluster, and the binding energy involved by the reaction $2\ Fe + C_2H_2 \rightarrow Fe_2(C_2H_2)$ must be added (as well as the dissociation energy implied by forming up the $(C_2H_2)$-radical); however, the evaluation of the latter is beyond the range of applicability of the present model. It is also noteworthy that the above results do not change qualitatively for reasonable changes in the effective valence charges $z^*_{Fe}$ and $z^*_R$.

The vibration spectrum of the $R_{12}Fe$ cluster can be estimated by assuming a Fe(CH) mass for the R radical; this is a qualitative approximation to the low- and middle-frequency range of the spectrum of the $Fe_{13}(C_2H_2)_6$. The vibration spectrum obtained this way is given in Fig. 3, and one can see indeed that it agrees qualitatively with other density-functional calculations of the vibration spectra for Fe-based icosahedra [11]. Beside providing an additional test to the stability of the icosahedral structure obtained herein, the agreement of the vibration spectrum given in Fig. 3 with the vibration spectrum obtained in [11] may be viewed as another indication for the consistency of the present theoretical model.

In a more general treatment the quasi-classical description of the slightly inhomogeneous electron liquid may be employed for getting the equilibrium form, the inter-atomic distances, the binding energy, and other physical and chemical properties, including the quantum properties of the single-particle electron states, of a cluster consisting of 13 Fe atoms, 12 C atoms and 12 H atoms. However, in contrast to the $R_{12}Fe$-metallic model employed here, the calculations imply non-central potentials, as derived from the directional character of the atomic-like orbitals of the C-atoms. Instead of an effective point-like charge there appears several effective charge parameters in such a case, and the atomic-screening theory is not appropriate anymore for estimating them. A more general discussion of the theory of the slightly inhomogeneous electron liquid and its relevance for the chemical bond is given in [12,13].

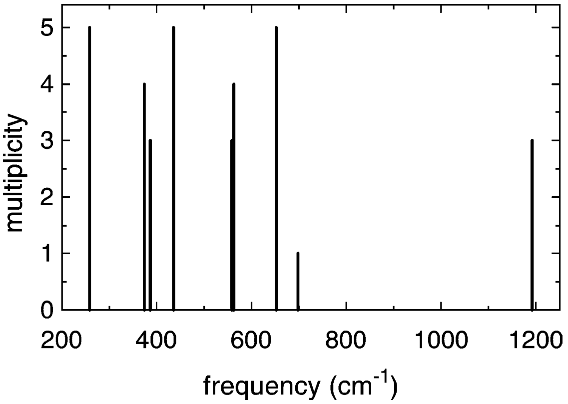

Fig. 3. Vibration spectrum for $Fe_{13}(C_2H_2)_6$ as estimated from the present theory.

Finally, one may note that similar calculations can be carried out for other inclusions in (or additions to) metallic clusters, like, for instance, hydrogenated- or oxygenated-iron clusters [11,14]. In addition, the single-electron quantum states can be obtained by solving the Schrodinger equation for the self-consistent potential $\varphi$ given by (1). Quantum corrections can thus be calculated to the quasi-classical description, as arising from the short-scale length variations of the self-consistent potential and the electron density. An overall estimate of these corrections indicates a 17%-contribution to the relevant quantities [2–4,12,13]. Subsequent iterations required for ensuring the self-consistency have to be checked against the effects of the finite lifetime of the single-electron states, in order to ensure the relevancy of the calculations. For large, highly symmetric clusters, or for statistical ensembles of cluster isomers, where the long-wavelength behavior is dominant, the well-known (quadrupole-) deformed potential [15]

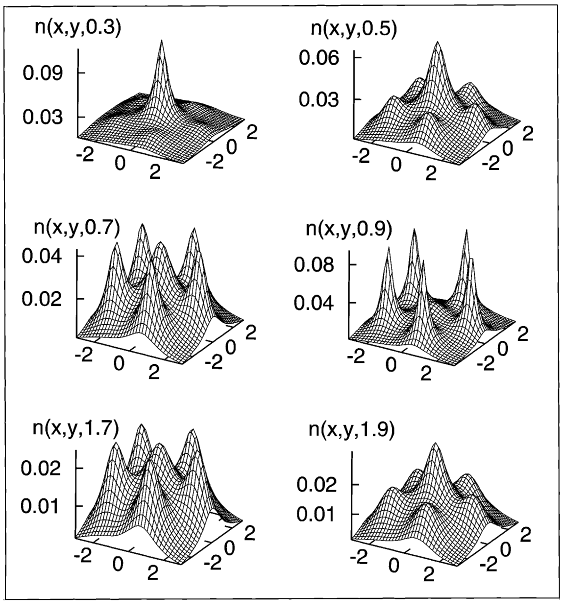

Fig. 4. Electron-density in $Fe_{13}(C_2H_2)_6$ at various $z$-distances with respect to the middle plane.

can be derived from (1), as the first relevant approximation; as usually, it may serve to determining the 'electronic' magic numbers of such clusters. The lowest-energy electronic-excitation spectrum, including the cluster chemical potential, as well as various cluster response functions related to the electronic properties, are left for a forthcoming investigation. We limit ourselves to note here that, by making use of the self-consistent potential $\varphi$ given by (1), the electron density $n = (q^2/4\pi)\varphi$ is plotted in Fig. 4 at various distances from the middle plane in the $Fe_{13}(C_2H_2)_6$ cluster. One can see in Fig. 4 the accumulation of the electron density on Fe-ions, as well as its slow spatial variation over the inter-ionic regions, in agreement with the quasi-classical prescriptions of the present theoretical approach.

In conclusion, beside its relevant results, it is also worth noting the limitations of the present model. First, the extension of the theory to include the directional character of the atomic-like orbitals of the C-atoms would allow the treatment of the cohesion and the structural properties of the $Fe_2(C_2H_2)$-ligands. Noteworthy, the point-like model employed here for the charges of the ionic cores needs also to be extended, such as to include the spatial dependence of the charge distribution of these ionic cores. Secondly, the quantum corrections must also be included, as discussed above; though such corrections affect only to a relatively little extent the main qualitative features derived here, they will serve to getting a complete overall picture of atomic clusters of such complexity.

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