Editors

V. E. Borisenko
S. V. Gaponenko
V. S. Gurin
C. H. Kam

20
YEARS WITH NANO
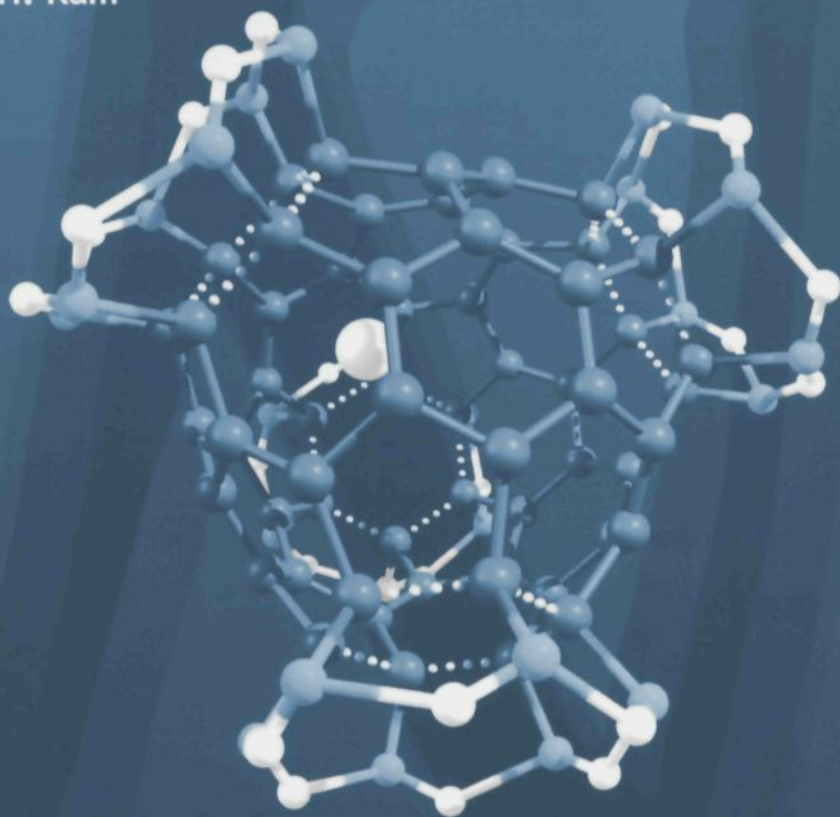
PROCEEDINGS OF INTERNATIONAL CONFERENCE
NANOMEETING - 2015

REVIEWS AND SHORT NOTES

PHYSICS, CHEMISTRY AND
APPLICATIONS OF NANOSTRUCTURES

PHYSICS, CHEMISTRY AND APPLICATIONS OF NANOSTRUCTURES

PHYSICS, CHEMISTRY AND APPLICATIONS OF NANOSTRUCTURES

REVIEWS AND SHORT NOTES

Minsk, Belarus,   26 – 29 May 2015

editors

V E Borisenko
Belarusian State University of Informatics and Radioelectronics, Belarus

S V Gaponenko
B I Stepanov Institute of Physics,
National Academy of Sciences of Belarus, Belarus

V S Gurin
Belarusian State University, Belarus

C H Kam
Nanyang Technological University, Singapore

PHYSICS, CHEMISTRY AND APPLICATION OF NANOSTRUCTURES
Proceedings of International Conference Nanomeeting — 2015

DENSITY FUNCTIONAL CALCULATIONS OF CHARGE AND MAGNETIC STATES OF CARBODODECAHEDRON

N. A. POKLONSKI[1], S. V. RATKEVICH[1], S. A. VYRKO[1],
E. F. KISLYAKOV[1], ANH D. PHAN[2], NGUYEN AI VIET[2]

[1]Belarusian State University, Nezavisimosti Ave. 4, 220030 Minsk, Belarus
[2]Institute of Physics, Dao Tan 10, Ba Dinh, 10000 Hanoi, Vietnam
poklonski@bsu.by

Magnetic moments of the carbododecahedron (C_{20} fullerene) with charges from (–5) to (+4) (in units of the elementary charge e) were calculated by linear combination of atomic orbitals method at the density functional level. It is established that the C_{20} in the charge state (–1) and the multiplicity 2 has the lowest total energy, while for charge states (–4), (–2) and (+4) the magnetic moment of $\mu = 2\mu_B$ (μ_B is the Bohr magneton) is found. Depending on the charge state and the multiplicity, carbon bonds and the I_h symmetry of the starting structure of the C_{20} can change substantially. Neutral C_{20} may have $\mu = 2\mu_B$.

1. Introduction

Following the discovery of the smallest fullerene C_{20} [1], the models of different fullerene formation involving C_{20} become more reasonable. Experimentally observed nanotubes (5,0) have the same diameter as the C_{20} [2]. Calculations [3] show anomalous thermal stability of carbododecahedron cage. The path of C_{20} fullerene formation in the plasma-arc discharge proposed in [4] is consistent with the kinetic models [5,6]. Note, that small fullerenes as electron acceptors are promising for applications in organic photovoltaics [7,8] and medicine [9].

The analysis of the survey [10] on the prospects of molecular magnetism and data from [11] on features of magnetism of nanoparticles and their experimental production leads to the question of magnetic states of a charged C_{20}. By *ab initio* calculations [12] it have been shown that carbododecahedron in the ground state with different spin configurations can have a magnetic moment, while there is a distortion of the starting symmetry due to the Coulomb distortion and the Jahn–Teller effect. Changes in symmetry of the carbododecahedron are also discussed [13]. The purpose of the paper is to investigate theoretically stability of C_{20} fullerene in different charge and magnetic states.

2. Calculation details

For quantum chemical calculations the linear combination of atomic orbitals (LCAO) method realized in software package Gaussian 09 [14] was chosen as the most suitable and widely used for calculating the properties of molecules or

clusters. The calculations were performed within the hybrid functional exchange-correlation UB3LYP (unrestricted Becke, Lee, Yang, and Parr) potential and basis wave functions 6-31G (d, p) for open electron shells. In the calculations a full optimization of C_{20} molecule structure with the given charge state Q and multiplicity M was performed (with an accuracy in energy of 0.01 eV per molecule). For the purpose of optimization we used a quasi-Newton ion relaxation implemented in the Broyden–Fletcher–Goldfarb–Shanno method. The calculations were carried out for the charge states of carbododecahedron from

(–5) to (+4) with the I_h icosahedral (dodecahedral) starting point group symmetry. For the charge state (+5) we could not find stable configurations.

3. Results and discussion

The magnetic moment μ is defined as $\mu = (M - 1)\mu_B$, where μ_B is Bohr magneton and M is the multiplicity. For each charge state the calculations of the C_{20} with multiplicity corresponding to the minimum total energy of molecule is present in Figs. 1 and 2. The charge states (–3, –2, –1, 0, +2, +4) shown in Figs. 1 and 2 are stable (which were confirmed by the absence of imaginary frequencies in IR-spectrum), while the charge states (–5, –4, +1, +3) are metastable. Figs. 1a and 1b show the calculation results of the magnetic moments and the corresponding total energy difference with respect to the minimum energy ($E_{UB3LYP} = -20.722$ keV), which belongs to the charge state (–1) of the C_{20} molecule. This fact may be attributed to the acceptor properties of all carbon fullerenes and nanotubes [7]. The neutral carbododecahedron in the triplet state has almost the same total energy with respect to the singlet state, and the difference between these energies is about 0.07 eV. Therefore, the C_{20} molecule could probably have a magnetic moment of 2 μ_B (see, *e.g.*, [12]). It is shown in [12] that Coulomb interactions may cause the magnetic moment formation in the neutral C_{20}. Fig. 1 shows that for the charge states (–4), (–2) and (+4) the magnetic moment $\mu = 2\mu_B$. Note, that the energy difference between HOMO-LUMO for the neutral singlet state C_{20} is 1.948 eV, which agrees with the results of calculations given in [15] (1.93 eV for C_{20} isomer in the form of "cage").

The dependence of the optimized average C–C bond lengths (a total of 30 bonds in the molecule) with respect to the charge state is shown in Fig. 2. Note, that for $Q \neq +2e$ the C_{20} has different bond lengths that break its starting I_h
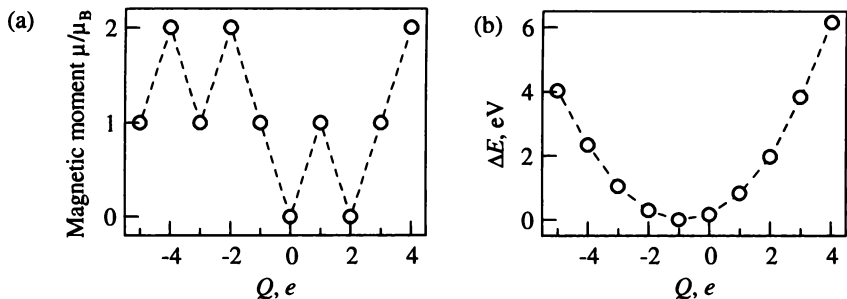
Figure 1. (a) The dependence of the magnetic moments μ (in units of the Bohr magneton μ_B) of C_{20} molecule with respect to the charge Q (in units of the elementary charge e); (b) the dependence of the energy difference $\Delta E = E(Q) - E(-1e)$ on the charge Q.
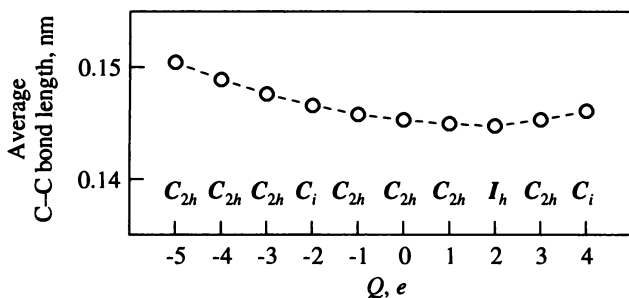

Figure 2. Dependence of the optimized average length of C–C bonds of the C_{20} molecule on the charge Q; corresponding symmetry point group C_i, C_{2h} and I_h are indicated; magnetic moments and energies correspond to the states shown in Fig. 1.

symmetry. The symmetry of the carbododecahedron decreases to C_{2h} or C_i. The I_h symmetry for $Q = +2e$ is preserved contrary to the results obtained by semi-empirical PM3 method in [16], where the symmetry was lowered to D_3. The stability of the C_{20} in the charge state (+2) may be attributed to the closed π-electron shells and the number of π-electrons which is equal to 18 and satisfies the Hückel rule [17]: $4n + 2$, where $n = 0, 1, 2, ...$

4. Conclusion

On the basis of calculations by the LCAO method realized in Gaussian 09 the stable structures of carbododecahedron in different charge states from (–5) to (+4) have been revealed. It was established that in the charge state (–1) with multiplicity $M = 2$ and magnetic moment $1\mu_B$ the carbododecahedron has the lowest total energy. The neutral carbododecahedron has almost equal energies in

singlet and triplet states, so the C_{20} may have a magnetic moment ($\mu = 2\mu_B$) (see also [12]), or does not have any ($\mu = 0$).

The calculations show that the I_h symmetry of the carbododecahedron is reduced to C_{2h} or C_i for all charge states under consideration, except for the charge state (+2). Semi-empirical and *ab initio* methods give different results in calculations of stable states of the carbododecahedron with charge (+2): in the calculation by LCAO method the highest I_h symmetry is preserved, but in the calculation by PM3 method the highest symmetry is lowered to D_3 [16].

Acknowledgments

References

1. H. Prinzbach *et al.*, *Nature* **407**, 60 (2000).
2. Z. K. Tang *et al.*, *Science* **292**, 2462 (2001).
3. I. V. Davydov, A. I. Podlivaev, L. A. Openov, *Phys. Solid State* **47**, 778 (2005).
4. N. A. Poklonski, E. F. Kislyakov, O. N. Bubel', S. A. Vyrko, in: *Proc. of IV Int. Conf. Plasma Physics and Plasma Technology* (PPPT-4), (Trovant, Troitsk, 2003) Vol. II, pp. 999–1001.
5. N. I. Alekseev, G. A. Dyuzhev, *Tech. Phys.* **47**, 643 (2002).
6. G. N. Churilov, A. S. Fedorov, P. V. Novikov, *JETP Lett.* **76**, 522 (2002).
7. A. J. Ferguson, J. L. Blackburn, N. Kopidakis, *Mater. Lett.* **90**, 115 (2013).
8. T. Liu, A. Troisi, *Adv. Mater.* **25**, 1038 (2013).
9. A. Dellinger *et al.*, *Nanomedicine* **8**, 1191 (2013).
10. D. Gatteschi *et al.*, *Solid State Sci.* **10**, 1701 (2008).
11. S. P. Gubin *et al.*, *Russ. Chem. Rev.* **74**, 489 (2005).
12. M. J. Han, G. Kim, J. I. Lee, J. Yu, *J. Chem. Phys.* **130**, 184107 (2009).
13. V. M. Talanov, N. V. Fedorova, V. V. Gusarov, *Russ. J. Gen. Chem.* **79**, 274 (2009).
14. M. J. Frisch *et al.*, Gaussian 09 (Gaussian Inc., Wallingford CT, 2009) [http://www.gaussian.com].
15. T. Heaton-Burgess, W. Yang, *J. Chem. Phys.* **132**, 234113 (2010).
16. N. A. Poklonskii, E. F. Kislyakov, O. N. Bubel', S. A. Vyrko, *J. Appl. Spectr.* **69**, 323 (2002).
17. J. Burdett, *Chemical Bonds: A Dialog* (Wiley, Chichester, 1997).