

01.1

Spectrum of a hybrid C₇₃H₉₀ molecule containing the Stone–Wallace defect

© M.S. Chekulaev, S.G. Yastrebov

Ioffe Institute, St. Petersburg, Russia
E-mail: mchs89@gmail.com

Received July 7, 2021

Revised September 5, 2021

Accepted September 17, 2021

The spectral characteristics of hybrid cluster C₇₃H₉₀ were calculated using the time-dependent Density Functional Theory method. The calculated spectrum demonstrates two maxima: at 5.7 and 3.8 eV, which are close to those in interstellar medium and laboratory experiments.

Keywords: interaction of light with matter, new forms of carbon, interstellar medium, Stone–Wales defect.

DOI: 10.21883/TPL.2022.15.54272.18951

An extensive family of carbon-based amorphous materials, known collectively as „amorphous carbon“, is widely used in various technical applications due to the possibility of changing their structure at atomic scales (see, for example, [1]). Such a change affects primarily the optical properties and therefore requires study, in particular, for the purpose of diagnosis. According to our model [2], proposed as a result of studying the infrared emission spectra of the space object Elias 1 [3] and the distribution of carbon nanoclusters in meteoritic matter by size [4], hybrid clusters constructed from fragments of graphene and diamond [2,5,6].

As it was shown in our recent papers [5,6], the optical properties of hybrid clusters turned out to be very remarkable. Using the *ab initio* method, we have shown that the maximum of the molar extinction coefficient of such objects falls on the wavelength of ~ 217.5 nm (5.7 eV), which allows us to associate the contribution of such clusters with the absorption band known in astrophysics, which reaches the maximum value at the same length waves (see, for example, [7]), and make an assumption about the widespread occurrence of hybrid clusters in the interstellar medium. At the same time, it is also impossible to exclude the presence of both hybrid clusters and massive carbon nanoparticles encapsulated in an amorphous carbon matrix, which are components of cosmic dust. The latter is confirmed by the noticeable similarity of the experimental optical absorption and extinction spectra of the interstellar medium and amorphous carbon layers synthesized under laboratory conditions and characterized mainly by the *sp*³-hybridization of matrix atoms [8].

We note that the optical absorption spectrum of hybrid clusters coincides with the extinction curve of the interstellar medium only in the maximum region and differs from the shoulder on the interstellar extinction spectrum in the ~ 2.0 eV.

The purpose of this work is to test the hypothesis that the modification of the cluster C₇₃H₉₀ by the Stone–Wales

defect (an example of the defect is presented, for example, in [9]) leads to the initiation of absorption in the spectral area close to the shoulder.

ab initio methods were used for calculations. We note that the selection of a basis and method for a specific task solved by *ab initio* methods seems to be a fairly common practice and requires sorting through a significant number of available combinations and combinations of methods and bases and comparing the calculation results with the experiment for as close systems as possible. However, although such a procedure seems to be very useful and therefore necessary, it is also very resource-intensive both from the point of view of machine time and from the point of view of the experimenter's time. Indeed, in addition to B3LYP, even within the framework of DFT (density functional theory), there are many methods: classical, hybrid, double hybrid, etc. Each of them has its own features. Therefore, in order to save resources, the researchers often use literature data that tell about the successful application of certain methods and bases to solve similar problems. The study [10] reported on the successful application of the B3LYP exchange-correlation hybrid functional with a small basis 3-21G(*) to optimize the geometry and simulate the spectral and electrochemical properties of complex carbon complexes. Therefore, in this paper, the mentioned exchange-correlation hybrid functional and basis are used to optimize the geometry of the cluster containing the Stone–Wales defect and calculate its optical properties. The time-dependent density functional theory (TD DFT) method was used (in the Russian literature „non-stationary“).

The Gaussian 09 [11] package was used for calculations. Optimization of the hybrid cluster geometry in our case was performed using the Berni algorithm [12] together with the GEDIIS (geometry optimization using energy-represented direct inversion in the iterative subspace) [13] method. The result is shown in Fig. 1. The numerical value of the total energy of the molecular hybrid achieved during optimization at the minimum point is given in the caption to Fig. 1. The

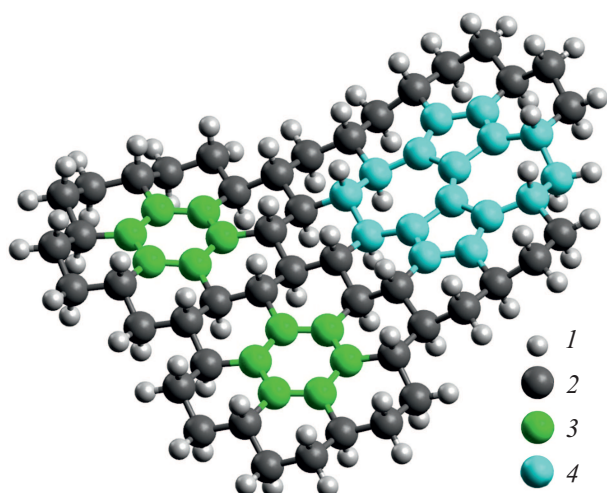


Figure 1. Hybrid cluster view $C_{73}H_{90}$ after geometry optimization. The balls 1 denote hydrogen atoms, balls 2 — carbon atoms sp^3 -hybridization, balls 3 — carbon atoms sp^2 -hybridization, balls 4 shows a fragment with a Stone defect—Wales. The total energy of the system after optimization is equal to -7385187 kJ/mol.

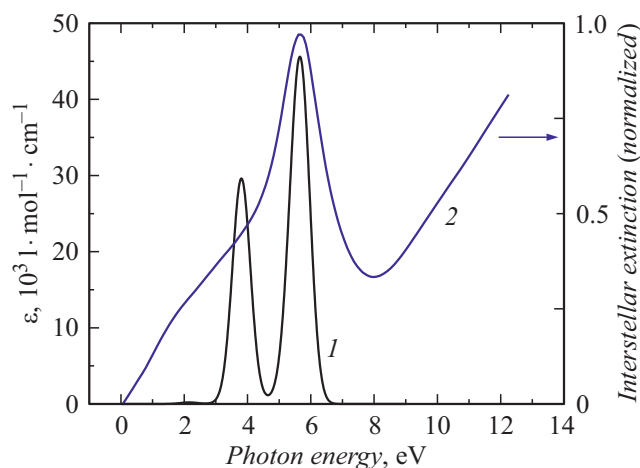


Figure 2. The molar extinction spectrum of the fragment shown in Fig. 1 (1), together with the averaged light extinction curve by the interstellar medium from the work [7] (2).

sign and order of magnitude of this energy correspond to those obtained with a similar calculation method for known hydrocarbons (see, for example, [14]). After optimizing the geometry, the molar extinction spectrum was calculated.

Fig. 2 shows the calculated molar extinction spectrum together with the averaged light extinction curve by the interstellar medium (see work [7] and references therein). It can be seen from the figure that the most intense absorption band is close to the observational data in the region of the band maximum of 217.5 nm (5.7 eV). Moreover, in the region close to the „arm“ of the astrophysical spectrum (at a wavelength of approximately 2 eV), an absorption band with a maximum at a photon energy of 3.8 eV is also visible

on the calculated spectrum. The last band is missing on the spectrum of the cluster calculated earlier with $C_{73}H_{74}$ and therefore may be related to the Stone—Wales defect, which changes the cluster topology from two-dimensional to three-dimensional [9].

So, unlike a cluster With ${}_{73}H_{74}$ on the molar extinction spectrum of a related object with ${}_{73}H_{90}$ two absorption bands are distinguished, close to the features observed on astrophysical spectra.

Acknowledgments

The authors thank E.Yu. Tupikin (St. Petersburg State University) for useful discussions and consultations on the Gaussian package and its application.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] T.C. Zhang, H. Lin, J. Mayorov, A. Wang, Y. Orofeo, C. Ferry, D. Andersen, H. Kakenov, N. Guo, Z. Abidi, I. Sims, H. Suenaga, K. Pantelides, B. Özyilmaz, *Nature*, **577**, 199 (2020). DOI: 10.1038/s41586-019-1871-2
- [2] M.S. Chekulaev, S.G. Yastrebov, *Pisma v ZhTF*, **45** (8), 47 (2019) (in Russian). DOI: 10.21883/PJTF.2019.08.47623.17516
- [3] T.R. Geballe, *ASP Conf. Ser.*, **122**, 119 (1997).
- [4] I.C. Lyon, *Meteorit. Planet. Sci.*, **40**, 981 (2005).
- [5] M.S. Chekulaev, S.G. Yastrebov, *Pisma v ZhTF*, **47** (4), 19 (2021) (in Russian). DOI: 10.21883/pjtf.2021.04.50639.18413
- [6] M.S. Chekulaev, S.G. Yastrebov, *Pisma v ZhTF*, **47** (19), 44 (2021) (in Russian). DOI: 10.21883/PJTF.2021.19.51514.18849
- [7] E.L. Fitzpatrick, D. Massa, *Astron. J.*, **130**, 1127 (2005).
- [8] J. Larraquert, L. Rodríguez-de Marcos, J. Méndez, P. Martin, A. Bendavid, *Opt. Express*, **21**, 27537 (2013). DOI: 10.1364/OE.21.027537
- [9] A.J. Stone, D.J. Wales, *Chem. Phys. Lett.*, **128**, 501 (1986). DOI: 10.1016/0009-2614(86)80661-3
- [10] M.E. Zandler, F. D’Souza, *C.R. Chim.*, **9**, 960 (2006). DOI: 10.1016/j.crci.2005.12.008
- [11] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A.J. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, *Gaussian 09* (2013).

- [12] H.B. Schlegel, *Adv. Chem. Phys.*, **67**, 249 (2007).
DOI: 10.1002/9780470142936.ch4
- [13] X. Li, M.J. Frisch, *J. Chem. Theory Comput.*, **2**, 835 (2006).
DOI: 10.1021/ct050275a
- [14] N.B. Hasan, *Adv. Phys. Theor. Appl.*, **24**, 83 (2013).