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Modeling of the interstellar medium Optical absorption spectrum by primitive hybrid molecules $C_{24}H_{30}$, $C_{32}H_{36}$ and $C_{73}H_{74}$

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Accounting for the different contributions of the aromatic rings, separated with sp^3 bonds, with ab initio method we constructed the hybrid cluster $C_{73}H_{74}$ which UV spectrum matches the most noticeable absorption band of 217.5 nm, known from astrophysical observations

Keywords: interaction of light with matter, new forms of carbon, interstellar medium.

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The interest in theoretical carbon material science, which has recently emerged and is still undiminished, is associated with the prospects of wide application of new allotropic forms of carbon, as well as fundamental research purposes, e.g., interpretation of astrophysical data.

We have previously shown that nanoclusters based on bound carbon atoms coupled by mixed sp^2- and sp^3-hybridization can emulate absorption spectra of interstellar medium [1]. Study [1] used the density functional theory to optimize geometry and calculate the molar extinction spectrum of molecular clusters constructed from a hybrid of diamondene and graphene fragments: $C_{32}H_{24}$, $C_{32}H_{36}$. Their broken bonds are passivated by hydrogen. The calculated spectra are compared with the results of astrophysical observations. It is shown that the considered hybrid molecular clusters can contribute to the formation of the known spectrum of light extinction by interstellar medium. It is also clear from the published results that the most intense band of the extinction spectrum of the molecular hybrid $C_{32}H_{36}$, whose center consists of two aromatic rings surrounded by sp^3-hybridized carbon atoms, is directly adjacent to the 217.5 nm absorption band known from astrophysics. The cluster band maximum, however, is in the low-frequency wing area of observational data. Therefore, the goal of the present study is to correct the number of atoms in the cluster $C_{32}H_{36}$ to achieve a better correspondence with the observational data. It is known from general considerations that when the number of aromatic rings in a molecular structure based on carbon atoms decreases, its absorption spectrum shifts to the high-frequency range. Therefore, we constructed a cluster $C_{24}H_{30}$ with only one aromatic ring in the center.

The Gaussian software package [2] was used in combination with the density functional theory (DFT) and time-dependent density functional theory (TD DFT) methods as a technique to optimize geometry and calculate the molar extinction spectrum. A 3-21G set of basis functions was used for the calculation. The hybrid B3LYP functional was used to account for the exchange-correlation interaction.

The final optimization of geometry of the hybrid cluster with one aromatic ring was performed using the Bernie algorithm [3] together with the GEDIIS (geometry optimization using energy-represented direct inversion in the iterative subspace) [4]. The result is shown in Fig. 1, *a*. The numerical value of total energy of the molecular hybrid achieved during optimization at the minimum point is given in the caption to Fig. 1, *a*. The sign and order of magnitude of that energy correspond to the values obtained by applying a similar calculation method to known hydrocarbons (see [5], for example). After confirming the stability of the geometry of the fragment with one aromatic ring by the TD DFT method, the molar extinction spectrum was calculated.

Fig. 1, *b* shows the calculated molar extinction spectrum together with the averaged interstellar medium light extinction curve from [6]. The spectrum of the cluster with two aromatic rings, taken from the paper [1] is also shown there for comparison purposes. It can be seen that the maximum of the spectrum of the hybrid with one ring is to the right of the maximum of the extinction band of interstellar medium, while the maximum of the absorption band of the cluster containing two rings is to the left of it. The suggestion is to take the sum of the bands with their weights to get the best fit with observational data. The result is presented in Fig. 2, which shows that the best match with the observation maximum is achieved when two clusters containing each one aromatic ring in the base are taken per one cluster containing two rings.

Recalling the condition of local interaction between electromagnetic radiation and matter, the above result suggests the existence of a single compound cluster, which is a hybrid of the molecules considered above. After combining these clusters into one and optimizing the geometry, a new

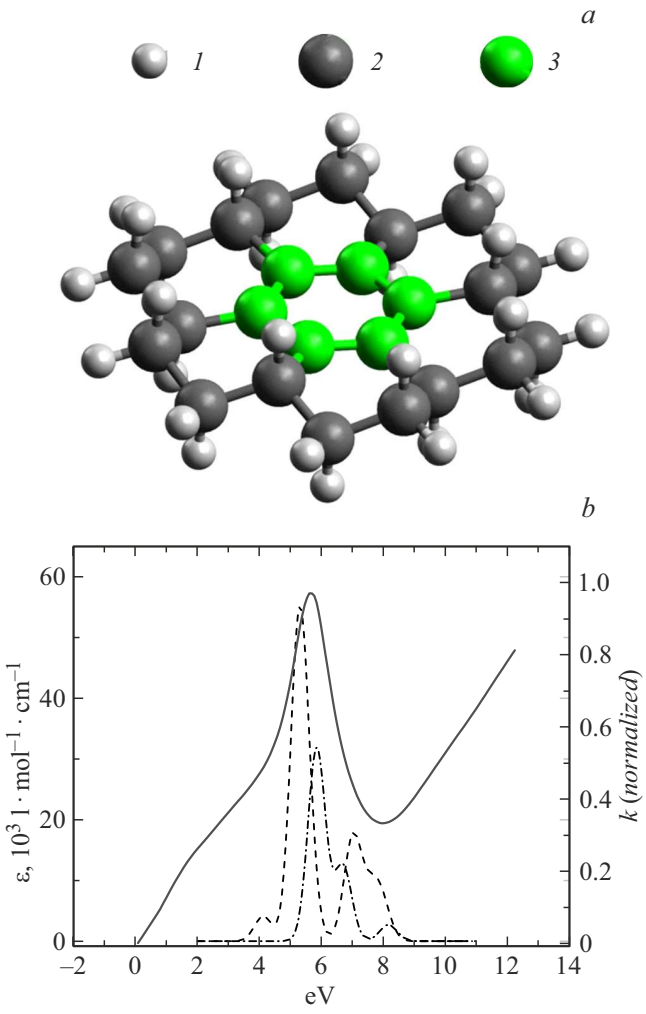

Figure 1. *a* is a $C_{24}H_{30}$ cluster (with one ring) after geometry optimization. *1* are hydrogen atoms, *2* are carbon atoms of sp^3-hybridization, *3* are carbon atoms of sp^2-hybridization. The total energy of the system after optimization is −2 437 069 kJ/mo. *b* is the calculated molar extinction spectrum of the fragment with one aromatic ring ($C_{24}H_{30}$) (dashed line) together with the averaged curve of light extinction by interstellar medium from [6] (solid line). For comparison, the absorption spectrum of a cluster with two aromatic rings taken from [1] (dashed line) is presented.

structure ($C_{73}H_{74}$) is formed, its general view shown in Fig. 3, *a* and the molar extinction spectrum in Fig. 3, *b*. The total energy of the system given in the caption to the figure and obtained after geometry optimization indicates its stability. Fig. 3, *b* shows that the most intense absorption band is also close to the observational data, resting a little away from them. In the analysis, however, one should take into account the peculiarities of modern quantum-chemical methods of modeling UV-absorption spectra. Taking them into account, we may consider that all the analyzed hybrids can act as candidates for the role of an absorber of optical radiation in the UV spectrum in interstellar medium.

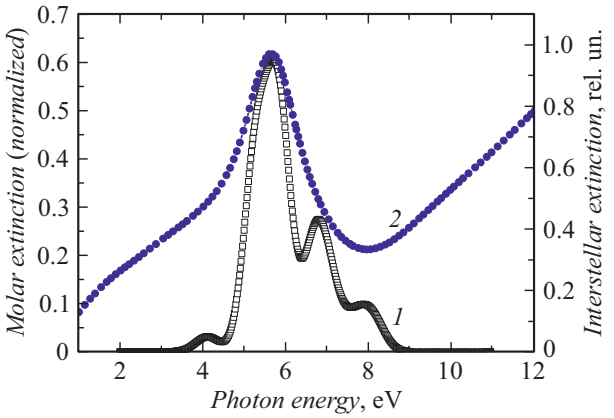

Figure 2. The sum of the absorption bands, taken with weights at which a single $C_{32}H_{36}$ cluster with two aromatic rings at the base has two $C_{24}H_{30}$ clusters containing one ring (*1*); the interstellar medium extinction spectrum (*2*) is shown for comparison purposes.

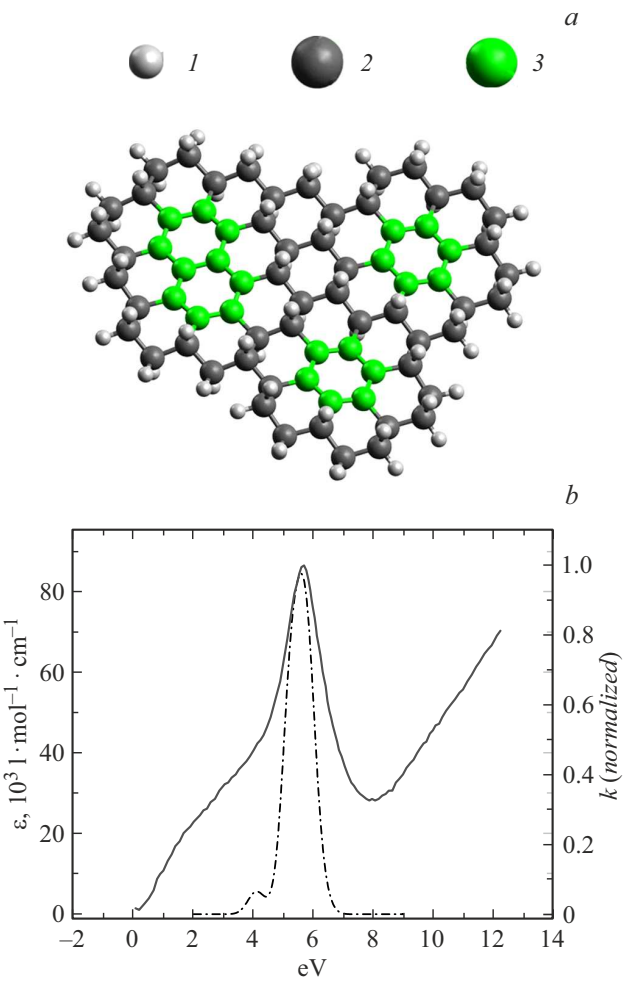

Figure 3. *a* is the appearance of the combined hybrid ($C_{73}H_{74}$) cluster after geometry optimization. *1* are hydrogen atoms, *2* are carbon atoms of sp^3-hybridization, *3* are carbon atoms of sp^2-hybridization. The total energy of the system after optimization is −7 385 608 kJ/mol. *b* is the molar extinction spectrum of the fragment shown in part *a* (dashed line), together with the averaged light extinction curve of the interstellar medium from [6] (solid line).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M.S. Chekulaev, S.G. Yastrebov, Letters to JTP, **47** (4), 19 (2021). DOI: 10.21883/PJTF.2021.04.50639.18413
[2] 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).
[3] H.B. Schlegel, Adv. Chem. Phys., **67**, 249 (2007). DOI: 10.1002/9780470142936.ch4
[4] X. Li, M.J. Frisch, J. Chem. Theory Comput., **2**, 835 (2006). DOI: 10.1021/ct050275a
[5] N.B. Hasan, Adv. Phys. Theor. Appl., **24**, 83 (2013).
[6] E.L. Fitzpatrick, D. Massa, Astrophys. J. Suppl. Ser., **72**, 163 (1990).