INDUCTIVE-RESONANCE ENERGY TRANSFER IN HYBRID CARBON NANOSTRUCTURES

O.Yu.Semchuk[1,2], Silvio Osella[1], O.O.Havryliuk[2], A.A.Biliuk[2]

[1]Centre of New Technologies University of Warsaw, Stefana Banacha 2c, 02-097 Warszawa, Poland
[2]Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17 General Naumov Str., Kyiv 03164, Ukraine, philosoph.tb@gmail.com

Abstract In recent years, carbon-based hybrid nanostructures have become increasingly common. Such materials are already widely used in highly efficient photovoltaic devices and for biomedical imaging and sensing. The first experiments on similar systems were recently implemented, which illustrates the extremely efficient transfer of excitation energy from an adsorbed molecule to a carbon substrate (graphene). Until now, there was no microscopically justified explanation of how energy is transferred in such systems. Here, we present a microscopic view of the substrate–molecule interaction in a hybrid material consisting of graphene functionalized with a fluorophore molecule. Based on the first principles, we showed that the decisive role in energy transfer from the fluorophore molecule to the carbon substrate (graphene) is played by the Förster-type inductive-resonance energy transfer mechanism. We investigated its dependence on the substrate–molecule distance R and constructed graphical dependences of the energy transfer rate on the distance R for several materials. The obtained results can be applied to various hybrids based on carbon nanostructures.

1.Introduction

In recent years, many different materials based on hybridized carbon in its low dimensional forms (such as functionalized graphene, carbon nanotubes, graphene, graphene quantum dots, graphene nanoribbons, etc.) and these systems are widely used in optoelectronics, especially when interfaces with molecules are created [1,2]. They consist of small-sized nanostructures functionalized with the help of a separate molecule, which combines the excellent properties of both subsystems. thus, carbon nanostructures are excellent substrates, after which they show high sensitivity to changes in their environment [3,4]. At the same time, interaction with combined molecules induces additional properties, supplemented for specific technological. The observed energy transfer can be explained on the basis of two mechanisms of nonradiative energy transfer: inductive-resonant (Förster type) [5] and exchange-resonant (also called Dexter) [6] energy transfer mechanisms. Forster's) mechanism describes the direct non-radiative energy transfer from the optically excited dye molecule to the carbon substrate. The Förster and Dexter energy transfer rates can be calculated analytically via Fermi's golden rule with the momentum-dependent initial and final states of the graphene substrate and the HOMO and LUMO states of the molecule. Having characterized the hybrid material within the limits of DFT calculations, including the fully geometrical relaxation of the structure, its electronic band structure, optical properties and charge rearrangement, we will focus on energy transfer, which was measured recently experimentally. The obtained results will be applied to other carbon hybrid nanostructures and, in general, to the description of energy transfer processes when the molecular transition dipole moment and the substrate–molecule separation are known.

2. Materials and methods

In our paper, we will apply it to the study of energy transfer processes in new hybrid nanostructure – graphene functionalized by dye molecule (Fig.1). Our task is to calculate the rate of energy trans-fer from the dye molecule to graphene depending on the distance between them. There are two main mechanisms of energy transfer from dye molecule to graphene (as depicted in Fig. 2a): (i) For-ster coupling [6] describes a direct nonradiative transfer of energy from the optically excited dye molecule to graphene. (ii) Dexter coupling [7] is based on a charge transfer between the dye mole-cule and graphene states (Fig. 2b).For our research, we used the cell shown in Fig. 1
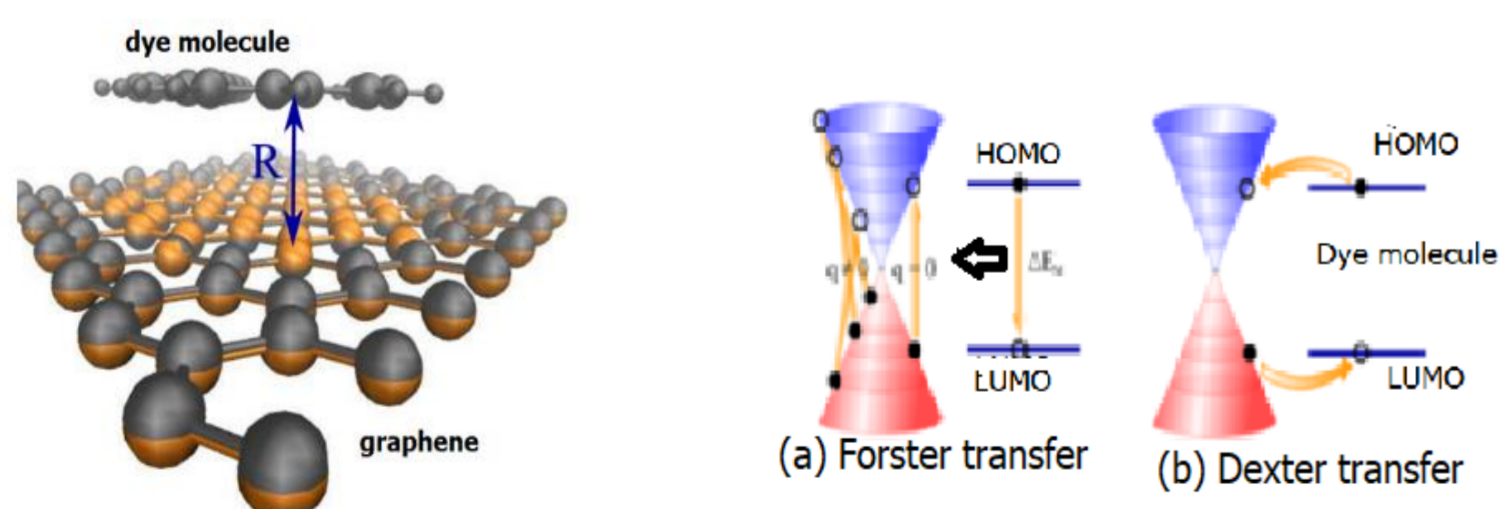

Fig.1. Schematic representation of functionalized graphene. R – distance between dye molecule and graphene.

Fig.2. Schematic illustrate of the (a) Forster and (b) Dexter energy transfer in functionalized graphene. The Dirac cone represent the electronic band structure of graphene, while the electronic states of the dye molecules are described by a two level (HOMO-LOMO) momentum independent system

The crystal lattice of graphene is a combination of two interpenetrating lattices of Brave A and B with an elementary cell in the form of a regular rhombus (Fig. 3, 4). The period of these lattices is equal to Å (the length of the CC bond).
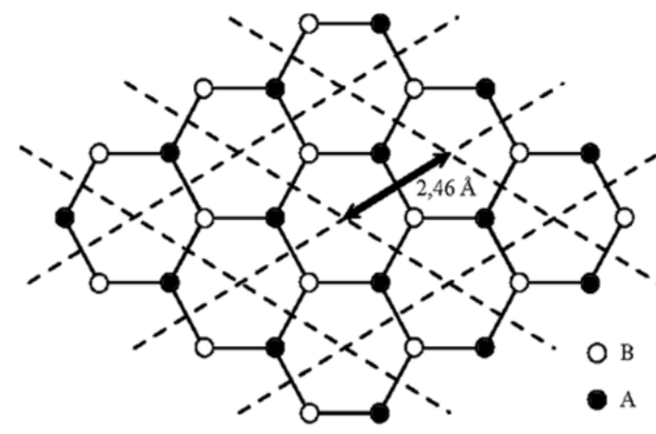

Fig.3. The unit cell of graphene and the vector of translation of Brave lattices A and B
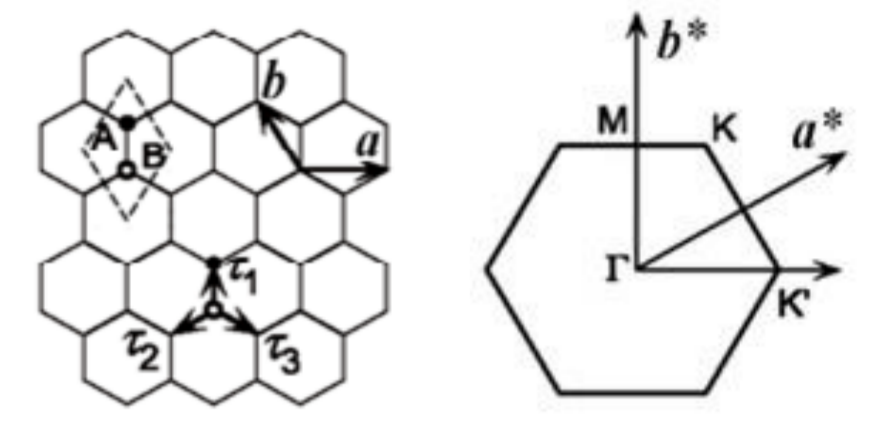

Fig.4. Graphene lattice and its first Brillouin zone

3. Results and discussion

Now let's apply the theoretical results, obtained above, for the analysis of energy transport in hybrid carbon nanostructures. Let's enter the values

$$\alpha_1 = \frac{e_0^2\left(d_x^2 + d_y^2 + 2d_z^2\right)\left(\Delta E_M\right)^3}{128\pi\hbar\varepsilon_0^2\left(\hbar v_F\right)^4}, \; \alpha_2 = \frac{2\Delta E_M}{\hbar v_F}, \; \alpha_3 = \frac{3}{1024\pi}\frac{\Delta E_M}{\hbar}, \; R_0 = \sqrt{\frac{e\sqrt{d_x^2 + d_y^2 + 2d_z^2}}{\varepsilon_0 \Delta E_M}}$$

we can write down the formulas for $\gamma_F(R)$, obtained above, in the following form, which is convenient for numerical integration and graphical analysis:

$$\gamma_F(R) = \begin{cases} \alpha_1 \int_0^1 \frac{\exp\{-\alpha_2 Rx\}x^3 dx}{\sqrt{1-x^2}}, & \text{exact formula,} \\ \alpha_3\left(\frac{R_0}{R}\right)^4, & \text{...long-range approximatin.} \end{cases}$$

For the graphene, functionalized by the dye molecule IPCA [22], we can received: $\alpha_1 = 1.061\cdot10^{16}$ s⁻¹ $\alpha_2 = 1,7847\cdot10^{-10}$ m, $\alpha_3 = 0,933\cdot10^{13}$ s⁻¹, $R_0 = 5,57\cdot10^{-10}$ m

At the Fig.5 presented the ratio of energy transfer from fluorophore IPCA to graphene as function of the distance R between molecule of fluorophore and graphene.

Fig.5. Comparison between curves, built for exact (21) and approximation (23) formulas. a) – for the small distance R; b) - for long range approximation.

One can see from Fig. 5 and 6 for small distances $R < 3.1$ A⁰ there is a difference in the results given by the exact and approximate formulas. Therefore, in this range, it is most likely necessary to use the exact formula (21) for calculation. In the range $R > 3.1$ A⁰, both formulas can be used.

The efficient Forster energy transfer rate take place at the $R=R_0=R_{min}$ (R_{min} is the short substrate−molecule distance). For example, for the perylene-functionalized graphene $R_0 = 3.25$, we obtain a very efficient Forster energy transfer of $\gamma_F(R_0) = 0.277$ fs⁻¹ For the system IPCA functionalized graphene this distance may be $R_0 = 3.25$ [22] and, therefore, $\gamma_F(R_0) \approx 0,298$ fs⁻¹

4. Conclusion

Using tight-binding-based consideration of graphene wave functions allows us to obtain an analytic expression for the Förster energy transfer rate. Our calculations reveal strongly efficient Förster coupling with rates in the range of fs-1. In contrast, the Dexter energy transfer mechanism is found to be negligibly small due to small overlap between the involved strongly localized substrate and dye molecule orbital functions. The obtained results can be applied to other carbon-based hy-brid nanostructures and in general to the description of energy transfer processes in molecular func-tionalized nanostructures, once the molecular dipole moment and the substrate−molecule separation are known.

References

1. S. Osella, M. Wang, E. Menna, and T. Gatti, Lighting-up nanocarbons through hybridization, Optoelectronic properties and perspectives, Optical Materials X 12, 100100 (2021).
2. O. Semchuk, T. Gatti, and S. Osella, Carbon based hybrid nanomaterials: overview and challenges ahead, Surface 14(29), 78-94 (2022).
3. Reich S., Thomsen C., Maultzsch J. Carbon Nanotubes: Basic Concepts and Physical Properties (Willey-VCH: Berlin, 2004).
4. Jorio A., Dresselhaus M., Dresselhaus G. Carbon nanotubes: Advanced Topics in the Syntheses, Properties, and Application (Springer: Berlin, 2008).
5.Forster T. Zwischenmolekulare Energiewanderung und Fluoreszenz. Ann. Phys. 1948. 437: 55.
6.Dexter D. L. A Theory of Sensitized Luminescence in Solids. J.Chem. Phys. 1953. 21: 836.
7. Malic E, Appel H., Hoffman O.T., Rubio A. Forster -Induced energy transfer in Functionalized Graphene. J.Chem.Phys. 2014. 118: 9283.