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RESONANCE ENERGY TRANSFER FROM A DYE TO A CARBON NANOTUBE

O. Yu. Semchuk, A. A. Biliuk, O. O. Havryliuk

Chuiko Institute of Surface Chemistry NAS of Ukraine,
17 Oleh Mudrak Str., Kyiv-03164, Ukraine,
e-mail: semchuk1950@meta.ua

In this work, we have studied the process of energy transfer from a fluorophore to the electronic energy levels of a single-walled carbon nanotube. Recently, carbon nanotubes have attracted considerable attention due to a number of potential technological applications, such as optoelectronic devices, sensors, etc. Functionalization of nanotubes with fluorophores has led to interesting photophysical properties. Excitation energy transfer is an important photophysical process that experimentally shown to occur when dyes are functionalized on nanotubes. Motivated by these experiments, we have studied theoretically the process of resonance energy transfer from a fluorophore to a single-walled carbon nanotube. We used the dipole approximation for the dye, not the nanotube, when transferring energy from the dye to the nanotube. Resonance energy transfer is the process of non-radiative energy transfer from an excited donor to an acceptor. When the transfer involves electronic excitation energy and the donor is fluorescent, this is known as fluorescence resonance energy transfer (FRET). In FRET, the interaction between the donor and acceptor is Coulomb. The electron transition dipoles of the donor and acceptor interact electrostatically, resulting in a dependence of the transfer rate on the distance between the donor and acceptor. Förster investigated this process theoretically. In Förster's approach, this is approximated as the interaction between the corresponding transition dipoles. Metallic carbon nanotubes have an exponential dependence on distance when $\hbar\Omega < \varepsilon_g$ *and* d^{-5} *otherwise. There is no threshold on the amount of energy that can be transferred to metallic nanotubes. In contrast, for semiconductor nanotubes, energy transfer does not occur if* $\hbar\Omega \geq \varepsilon_g - \varepsilon_b$*. If* $\hbar\Omega \geq \varepsilon_b$*, then the rate has a dependence* d^{-5} *in the long-range limit. But if* $\varepsilon_g > \hbar\Omega \geq \varepsilon_g - \varepsilon_b$*, then the rate has an exponential dependence on distance. We also incorporate the possibility of energy transfer to excitons of semiconductor tubes into our analysis. Our calculations show that the energy transfer rate from pyrene to nanotube 5.5 is effective up to distances of the order of 16.5 nm.*

Key words: *graphene, surface plasmons, plasmonic, carbon, energy transfer, Forster theory, exciton, FRET, nanotube.*

INTRODUCTION

Semiconducting carbon nanotubes (CNTs) are one of the candidates for the next generation of semiconductor electronics [1], optoelectronics neighbor infrared range [2] and absorbers light or transparent conductors for solar elements [3]. In particular, with the use of semiconductors BHT from controlled forbidden zone, are being prepared now mesoscale networks with tight intertwined bundles (films) [4, 5]. These structures (films) can be used in photovoltaic installations and photodetectors, in which Semiconductor tubes are photoabsorbers, similar to electron-donating polymers in polymer solar elements [6]. Like polymers, CNTs have big optical absorption, which can be regulate, and them can process solution, but nanotubes demonstrate superfast charge and energy transfer to large distances and more stable in air [3]. Although photophysics individual nanotubes is a common topic of research [7, 8], the properties of these new mesoscale structures (films) mostly unknown. In addition, the possibility to control the composition of the prohibited substance zones films does their model system for studying various kinds of charge and energy transfer processes. The task of studying the features of energy transfer in such structures is interesting and relevant. The energy transfer from a dye molecule to a carbon nanotube can be considered as the process of nonradiative energy transfer from an excited donor this an acceptor. It is known as Forster resonance energy transfer (FRET) [9]. In FRET, the interaction between the donor and the acceptor are Coulombic. The electronic transition dipoles of the donor and the acceptor interact electrostatically leading to an R^{-6} dependence of the rate of transfer on the distance $\gamma(R)$ between the donor and the acceptor. Förster studied this process theoretically and obtained the analytical expression for the distance dependence of the rate of energy transfer [9]. The rate of FRET from a dipole to the bulk electronic excitation modes of a metal has a d^{-3} dependence (*d* is the distance from the dipole to the metal) [10, 11]. Recently, we have shown that the process of energy transfer from a fluorophore to graphene has a d^{-4} dependence and is very efficient [12, 13]. Experiments have shown that graphene can quench the fluorescence of the fluorophores and the process can be used to visualize graphene on surfaces [14] and graphene flakes in solution [15] and to suppress fluorescence in resonance Raman Spectroscopy [16]. In this work, we studied the features of the process of Förster resonance energy transfer from excited dye molecules (fluorophores) to semiconducting single-walled carbon nanotubes, in particular, the dependence of the energy transfer rate on the distance between the dye molecule and the carbon nanotube itself.

ENERGY TRANSFER RATE MODEL

Let us consider the process of resonant energy transfer from a dye molecule (fluorophore) to a single-walled carbon nanotube of radius R_0 and length L (see Fig. 1). In this case, we will consider the single-walled carbon nanotube as a rolled-up sheet of graphene [17, 18].

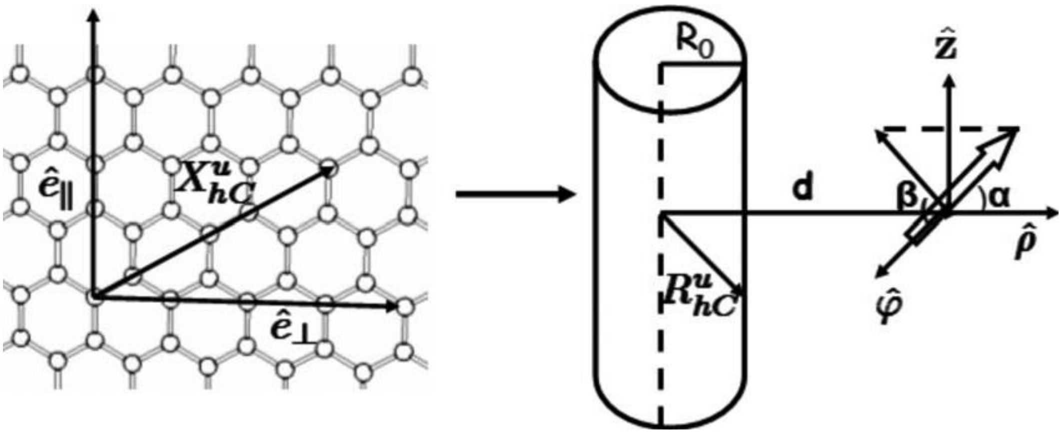
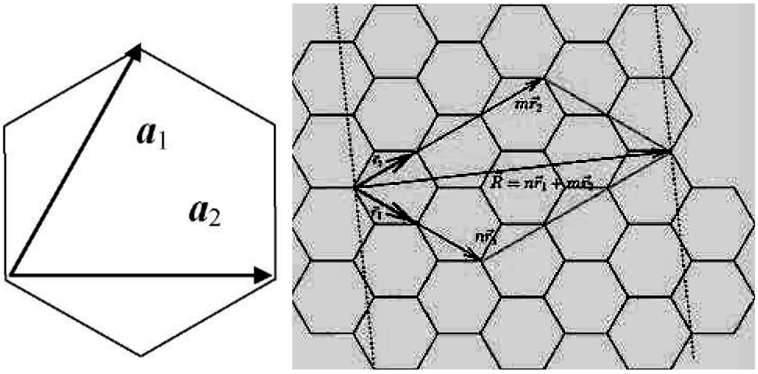


Fig. 1. Schematic representation of a single-walled carbon nanotube, which is formed by folding a graphene sheet. On the right, the transition dipole of the dye molecule (fluorophore) is shown, along with the angles it makes with the coordinate axes (*d* – distance from the nanotube to the dye molecule)

Next, manually enter the three-dimensional position vector for atoms on the nanotube, which we denote as R^u_{hC}, where *u* denotes the unit cells of the nanotube and takes values from 1 to U (U is the total number of unit cells in the tube), *h* denotes the unit cells of graphene inside the unit cell of the nanotube and varies from 1 to N (N is the number of hexagons per unit cell of the nanotube).

To describe the structure of nanotubes, the vector C is used, which connects two equivalent points on the graphene sheet (Fig. 2*a*). This vector is expressed by the formula:

$\vec{C} = n\vec{a}_1 + m\vec{a}_2$ where $\vec{a}_1$ and $\vec{a}_2$, the basis vectors of the unit cell of the graphene sheet, n and m, are the so-called hyral indices (integers, n > m). Vector $\vec{a}_1$ and $\vec{a}_2$ are the basis vectors of the graphene sheet's unit cell. [19].



a *b*

Fig. 2. Graphene plane (*a*) and basis vectors of the unit cell of a graphene sheet (*b*)

The indices n and m are related to the nanotube radius and the chiral angle θ by the following relations [20]:

$$R_0 = \frac{a}{2\pi}\sqrt{3(n^2 + nm + m^2)}, \quad \sin\theta = \frac{3m}{2\sqrt{n^2 + nm + m^2}},$$

where $|\vec{a}| = |\vec{a}_1| = |\vec{a}_2| = 0.246$ nm.

The nanotube is obtained by folding a graphene sheet and the two-dimensional position vector of the atom that occupies the position R_{hC}^{u} during folding will be denoted as X_{hC}^{u} (Fig. 1). The wave functions of the electron system of a nanotube can be written as

$$\psi_{\vec{k}}^{\pm}(\vec{r}) = \frac{1}{\sqrt{U}}\frac{1}{\sqrt{N}}\sum_{u=1}^{N}\sum_{h=1}^{N}\left[c_A^{\pm}(\vec{k})e^{i\vec{k}X_{hA}^{u}}\varphi(\vec{r} - R_{hA}^{u}) + c_B^{\pm}(\vec{k})e^{i\vec{k}X_{hB}^{u}}\varphi(\vec{r} - R_{hB}^{u})\right], \tag{1}$$

where the sign (-) denotes the valence band of graphene and the sign (+) denotes the conduction band of graphene, φ are the 2p$_z$ atomic orbital wavefunctions of the carbon atoms in the nanotube and are assumed to be perpendicular to the local surface of the nanotube . This is the simplest wavefunction that can be written and is good enough to analyze the dependence of the energy transfer rate on the distance from the dye molecule to the nanotube. d, k denotes the wave vector of an electron in graphene and is given as $\vec{k} = k_x\vec{i} + k_y\vec{j}$, $C_A^{\pm}(k) = 1/\sqrt{2}$ i $C_B^{\pm}(k) = \left(\pm 1/\sqrt{2}\right)e^{-i\delta_{\vec{k}}}$, where $\delta_{\vec{k}}$ is determined by the following expression [12]

$$\delta_{\vec{k}} = -\frac{H_{AB}(\vec{k})}{\left|H_{AB}(\vec{k})\right|}, \tag{2}$$

where

$$H_{AB}(\vec{k}) = -t\left[e^{ik_x a/\sqrt{3}} + 2e^{-ik_x a/2\sqrt{3}}\cos(k_y a/2)\right]. \tag{3}$$

In the above, t is the jump integral and $a = l_{C-C}\sqrt{3}.$

Our procedure for calculating the energy transfer rate, as in [12, 13], is to work with the transition density. The matrix element for the transfer is simply the electrostatic interaction between the transition density of the involved orbitals on the donor and on the acceptor. For a donor-acceptor pair separated by a distance much larger than their sizes, this can be approximated as the interaction between two transition dipoles, leading to a dependence of the energy transfer rate on the distance R^{-6}. This approximation breaks down at smaller distances and in such cases, discretized approaches to the matrix element estimation were developed in [21]. For energy transfer to a nanotube of large length, the dipole approximation will obviously not be applicable. If the size of the donor is small compared to the distance *d* to the nanotube, then the dipole approximation can still be used for the donor, but the transition density of the nanotube must be considered more carefully. Here we use an approach developed in [12, 13] that avoids the dipolar approximation for the transition density of the nanotube. This allows us to obtain analytical results for the behavior of the energy transfer rate at a large distance from the nanotube. The details of this approach are given below.

When the energy donor (fluorophore or dye molecule) is excited, an electron from an occupied orbital is excited and moves to an unoccupied orbital. Associated with this process is the transition dipole of the fluorophore μ_{eg} interacts with the electrons of the nanotube. As a result of the energy transfer, the fluorophore (donor) returns back to its place and the electron of the nanotube , which was in the state described by the wave function $\psi^{-}_{\vec{k}_i}(\vec{r})$, passes into the state described by the wave function $\psi^{+}_{\vec{k}_i+\vec{q}}(\vec{r})$. Electronic excitation leads to the appearance of a transient charge in $\rho(\vec{r})$ the nanotube , the density of which is given by the following expression

$$\rho(\vec{r}) = -e\psi^{*+}_{\vec{k}_i+\vec{q}}(\vec{r})\psi^{-}_{\vec{k}}(\vec{r}) \simeq -\frac{e}{UN}\sum_{u=1}^{U}\sum_{h=1}^{N}\begin{bmatrix} c_A^{+*}\left(\vec{k}_i+\vec{q}\right)c_A^{-}\left(\vec{k}_i\right)e^{-i\vec{q}X^U_{hA}}\varphi^*\left(\vec{r}-R^u_{hA}\right)\varphi\left(\vec{r}-R^u_{hA}\right)+ \\ c_B^{+*}\left(\vec{k}_i+\vec{q}\right)c_B^{-}\left(\vec{k}_i\right)e^{-i\vec{q}X^U_{hB}}\varphi^*\left(\vec{r}-R^u_{hB}\right)\varphi\left(\vec{r}-R^u_{hB}\right)\end{bmatrix}. \quad (4)$$

We have neglected the products belonging to other atoms of the nanotube , since their contribution to the density is insignificant. The electrostatic potential at point *r*, due to such a charge density, is

$$\Phi(\vec{r}) = \frac{1}{4\pi\varepsilon}\int d\vec{r}_2\,\frac{\rho(\vec{r}_2)}{\left|\vec{r}-\vec{r}_2\right|}, \quad (5)$$

where ε is the dielectric constant of the medium between the donor and acceptor. The density $\varphi^*\left(\vec{r}_2-R^u_{hC}\right)\varphi\left(\vec{r}_2-R^u_{hC}\right)$ is localized in the vicinity of the *C-th* atom nanotubes. Size $\left|\vec{r}-\vec{r}_2\right|$ changes very little in the region in which $\varphi^*\left(\vec{r}_2-R^u_{hC}\right)\varphi\left(\vec{r}_2-R^u_{hC}\right)$ and the value $\Phi(\vec{r})$ can be approximated by the following expression

$$\Phi(\vec{r}) = -\frac{e\chi\left(\vec{k}_i,\vec{q}\right)}{4\pi\varepsilon UN}\sum_{u,h}\frac{e^{-i\vec{q}X^u_{hc}}}{\left|\vec{r}-R^u_{hC}\right|}. \quad (6)$$

Here we used the relation $\int d\vec{r}_2\varphi^*\left(\vec{r}_2-R^u_{hC}\right)\varphi\left(\vec{r}_2-R^u_{hC}\right)=1$. In the above equation

$$\chi\left(\vec{k}_i\;,\vec{q}\right) = c_A^{-}\left(\vec{k}_i\right)c_A^{+*}\left(\vec{k}_i+\vec{q}\right)+c_B^{-}\left(\vec{k}_i\right)c_B^{+*}\left(\vec{k}_i+\vec{q}\right) = \frac{1}{2}\left[1-e^{i\left(\delta_{\vec{k}_i}-\delta_{\vec{k}i+\vec{q}}\right)}\right]. \quad (7)$$

For small values of the transmitted momentum *q*, we can replace the sum in equation (6) by an integral and obtain

$$\Phi = -\frac{e\chi\left(\vec{k}_i,\vec{q}\right)}{4\pi\varepsilon UNA_u}\int d\vec{X}\,\frac{e^{-i\vec{q}\vec{X}}}{\left|\vec{r}-\vec{R}\right|}. \tag{8}$$

Here A_u is the area of the graphene unit cell.

The integral in the given case (8) $d\vec{X}$ is two-dimensional as is the entire area of the ribbon, which makes up the nanotube; $\vec{R}$ is the point on which is projected $\vec{X}$, during the folding of the nanoribbon . UN is the total number of hexagons. Therefore, $UNA_u = A$, where A is the total surface area of the carbon nanotube. We will use the Dirac cone approximation for the energy levels of graphene [12]. Furthermore, from now on we will denote by *k* the wave vector measured from the point *K*. So in this case [12]

$$\delta_k = \tan^{-1}\left(\frac{k_y}{k_x}\right). \tag{9}$$

The wave vector of an electron in a nanotube can be decomposed into a component parallel to the tube axis and a component perpendicular to the tube axis. The circumferential component *is* quantized due to the periodic boundary condition. Therefore, k and q can be written as

$$\vec{k}_i = k_{i,\|}\hat{e}_{\|} + k_{i,\perp}\hat{e}_{\perp}, \tag{10}$$

$$\vec{q} = q_{\|}\hat{e}_{\|} + q_{\perp}\hat{e}_{\perp}. \tag{11}$$

Here where $\hat{e}_{\|}$ and $\hat{e}_{\perp}$ are unit vectors along the pipe axis and perpendicular to the pipe axis, respectively. $k_{i,\perp} = 1/R_0\left(p_i + (m-n)/3\right), q_{\perp} = l/R_0$ [24]. p_i and l which can take the values 0, 1, 2..., are quantum numbers associated with the boundary condition of perpendicularity to the tube axes. $p_f = p_i + l$ quantum number corresponding to the electron energy level in the conduction band of the nanotube, to which the excitation energy falls. Therefore, from now on we will denote the excitations of the nanotube, which arise as a result of energy transfer as $p_i \to p_f$, as depicted in Fig. 3.

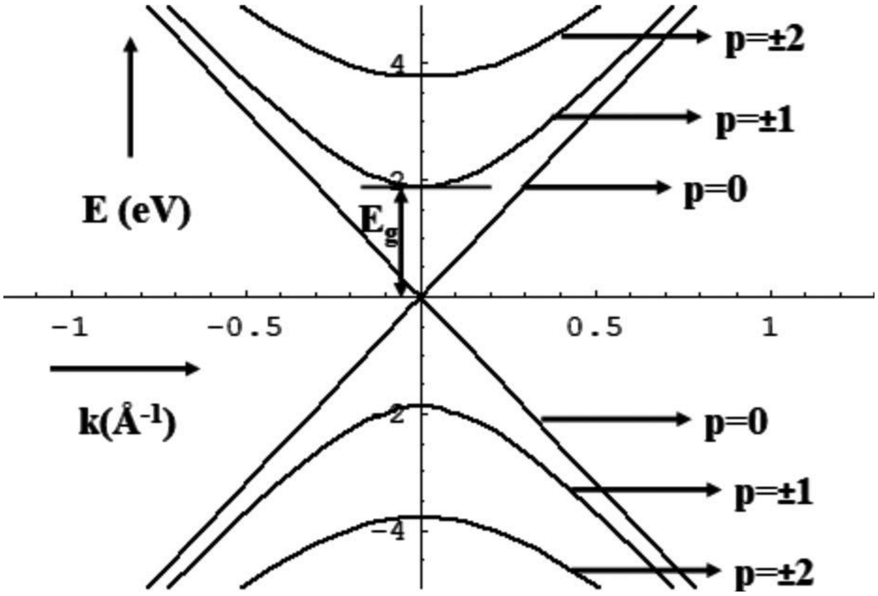


Fig. 3. Band structure of a 5.5 carbon nanotube. Note that the nanotube is metallic and that the electron-hole bands are symmetric about zero energy

We also represent that $\vec{k}_f = \vec{k}_i + \vec{q} = k_{f,\|}\hat{e}_\| + k_{f,\perp}\hat{e}_\perp$. Now $\vec{X}$ we can express in terms of its components as $\vec{X} = Z\hat{e}_\| + R_0\phi\hat{e}_\perp$ where we wrote the component in the direction $\hat{e}_\perp$, $R_0\phi$, $\phi\epsilon(0.2\pi)$. Including the above definitions in equation (8), we obtain

$$\Phi(\vec{r}) = -\frac{eR_0\chi(\vec{k}_i,\vec{q})}{4\pi\varepsilon A}\int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dZ \frac{e^{-iq_\| - il\phi}}{|\vec{r}-\vec{R}|}. \tag{12}$$

Now we will use the following multipole expansion for $1/|\vec{r}-\vec{R}|$ in cylindrical coordinates [23]:

$$\frac{1}{|\vec{r}-\vec{R}|} = \frac{1}{\pi}\sum_{m'=-\infty}^{\infty} e^{im'(\varphi-\varphi)} \int_{-\infty}^{\infty} dk' e^{ik'(z-Z)} I_m(|k'|R_0) K_{m'}(|k'|d). \tag{13}$$

Here $\vec{r} = d\cos\varphi\hat{\vec{i}} + d\sin\varphi\hat{\vec{j}} + z\vec{k}$, $\vec{R} = R_0\cos\phi\hat{\vec{i}} + R_0\sin\phi\hat{\vec{j}} + Z\vec{k}$,

Substituting the above expression of the multipole expansion into equation (12) and evaluating the integrals, we obtain

$$\Phi(\vec{r}) = -\frac{eR_0\chi(\vec{k}_i,\vec{q})}{\varepsilon A} e^{iq_\| z - il\varphi} I_{|l|}(|q_\||R_0) K_{|l|}(|q_\||d). \tag{14}$$

Let us note that $l\hbar$ denotes the angular momentum of the excitation produced in the nanotube. The matrix element for energy transfer between the donor and acceptor can be is estimated using the following relation $U = \vec{\mu}_{eg}\nabla\Phi$ [5] and can be written as follows:

$$U(\vec{k}_i,\vec{q}) = -\frac{eR_0\chi(\vec{k}_i,\vec{q})}{\varepsilon A} e^{-iq_\| z - il\varphi} I_{|l|}(|q_\||R_0)\left[\mu_p \frac{\partial K_{|l|}(|q_\||d)}{\partial d} - i\left(\frac{l}{d}\mu_\varphi + q_\|\mu_z\right) K_{|l|}(|q_\||R_0)\right], \tag{15}$$

where we used the following expression to decompose $\vec{\mu}_{eg}$ into components as $\vec{\mu}_{eg} = \mu_p\hat{\vec{p}} + \mu_\varphi\hat{\vec{e}} + \mu_z\hat{\vec{z}}$ (see Fig. 1 for orientation of $\hat{\vec{p}}$, $\hat{\vec{e}}$ and $\hat{\vec{z}}$). Using Fermi's golden rule, the rate of energy transfer from the fluorophore (dye molecule) to a specific excitation of the nanotube is $p_i \to p_f$ (see Fig. 2 and 3) is given by the following expression:

$$\gamma_{p_i\to p_f}(\hbar\Omega) = \frac{L^2}{2\pi\hbar}\int dq_{i,\|}\int dk_{i,\|} \left|U(\vec{k}_i,\vec{q})\right|^2 \delta\left(E^+_{\vec{k}_i+\vec{q}} - E^-_{\vec{k}_i} - \hbar\Omega\right), \tag{16}$$

where $\hbar\Omega$ is the emission energy of the fluorophore (dye molecule). We use the linearization approximation for the energy levels of graphene in the following form $E^\pm_k = \pm\hbar v_f k$, where v_f is the Fermi velocity of electrons in graphene. We now substitute equation (16) into the expression for the energy transfer rate (16) and using equations. (8) and (10) we obtain [12]:

$$\gamma_{p_i\to p_f}(\hbar\Omega) = \frac{e_0^2}{16\pi^3\varepsilon_0^2\hbar v_f}\int dq_\| I^2_{|l|}(|q_\||R_0)\left|\begin{matrix}\mu_\rho \dfrac{\partial K_{|l|}(|q_\||R_0)d}{\partial d} - \\ -i\left(\dfrac{l}{d}\mu_\varphi + q_\|\mu_z\right)K_{|l|}(|q_\||d)\end{matrix}\right|^2 F(\vec{q}), \tag{18}$$

where $F(\vec{q})$ is an even function of q.

$$F\left(\vec{q}\right)=\int dk_{i,\|}\left[1-\frac{\vec{k}_i\cdot\left(\vec{k}_i+\vec{q}\right)}{\left|\vec{k}\right|\left|\vec{k}_i+\vec{q}\right|}\right]\delta\left(\left|\vec{k}_i+\vec{q}\right|+\left|\vec{k}_i\right|-\frac{\Omega}{v_f}\right). \tag{19}$$

Therefore, expression (19) simplifies to

$$\gamma_{p_i\to p_f}\left(\hbar\Omega\right)=\frac{e_0^2}{16\pi^3\varepsilon_0^2\hbar v_f}\int_{-\infty}^{\infty}dq_{\|}I_{|l|}^2\left(\left|q_{\|}\right|R_0\right)\left[\begin{matrix}\mu_\rho^2\left(\dfrac{\partial K_{|l|}\left(\left|q_{\|}\right|d\right)}{\partial d}\right)^2+\\+\left(q_{\|}^2+\dfrac{l^2\mu_\varphi^2}{d^2}\right)K_{|l|}^2\left(\left|q_{\|}\right|d\right)\end{matrix}\right]^2F\left(\vec{q}\right).(20)$$

Now let us investigate the explicit orientational dependence of the energy transfer rate. Let us assume that the transition dipole $\vec{\mu}_{eg}$ in the dye, for example, forms angles α and β with respect to the directions $\hat{\vec{\rho}}$ and , $\hat{\vec{\varphi}}$ respectively (Fig. 1). Therefore, we have

$$\mu_\rho=\mu_{eg}\cos\alpha,\quad \mu_z=\mu_{eg}\sin\alpha\sin\beta,\quad \mu_\varphi=\mu_{eg}\sin\alpha\cos\beta,$$

where we defined $\mu_{eg}=\left|\vec{\mu}_{eg}\right|$. Using the definitions above, we can now write relation (20) as

$$\gamma_{p_i\to p_f}\left(\hbar\Omega\right)=\frac{e_0^2\mu_{eg}^2}{16\pi^3\varepsilon_0^2\hbar v_f}\int_{-\infty}^{\infty}dq_{\|}I_{|l|}^2\left(\left|q_{\|}\right|R_0\right)\left[\begin{matrix}\cos^2\alpha\left(\dfrac{\partial K_{|l|}\left(\left|q_{\|}\right|d\right)}{\partial d}\right)^2+\\+\sin^2\alpha\left(\begin{matrix}q_{\|}^2\sin^2\beta+\\ \dfrac{l^2\cos^2\beta}{d^2}\end{matrix}\right)K_{|l|}^2\left(\left|q_{\|\|}\right|d\right)\end{matrix}\right]F\left(\vec{q}\right).(21)$$

Now, averaging over all possible orientations of the transition dipole of the dye, we obtain:

$$\gamma_{p_i\to p_f}\left(\hbar\Omega\right)=\frac{e_0^2\mu_{eg}^2}{48\pi^3\varepsilon_0^2\hbar v_f}\int_{-\infty}^{\infty}dq_{\|}I_{|l|}^2\left(\left|q_{\|}\right|R_0\right)\left[\left(\frac{\partial K_{|l|}\left(\left|q_{\|}\right|d\right)}{\partial d}\right)^2+\left(\begin{matrix}q_{\|}^2+\\ \dfrac{l^2}{d^2}\end{matrix}\right)K_{|l|}^2\left(\left|q_{\|}\right|d\right)\right]F\left(\vec{q}\right). \tag{22}$$

First, let us consider the case where the wave vectors k_i and k_f have components only along the axial direction of the nanotube , which means that $k_{i,\perp}=0$ and $k_{f,\perp}=0$. Therefore, $l=0, q_\perp=0$ and $F\left(q\right)$ depends only on $q_{\|}$. Using (11) and (12) and we obtain for $F\left(q\right)$ next expression

$$F\left(q\right)=\int_{-\infty}^{\infty}dk_{i,\|}\left[1-\frac{k_{i,\|}\left(k_{i,\|}+q_{\|}\right)}{\left|k_{i,\|}\right|\left|k_{i,\|}+q_{\|}\right|}\right]\delta\left(\left|k_{i,\|}\right|+\left|k_{i,\|}+q_{\|}\right|+\frac{\Omega}{v_f}\right). \tag{23}$$

The above integral can be calculated exactly and the following relation can be obtained for $F\left(\vec{q}\right)$

$$F\left(q\right)=2\left|q_{\parallel}\right|\delta\left(\left|q_{\parallel}\right|-\frac{\Omega}{v_f}\right). \tag{24}$$

Using the above expression for *F (q)* together with *l* = 0 from equation (22) we obtain:

$$\gamma_{p_i\to p_f}=\frac{e_0^2\hbar^2\mu_{eg}^2\Omega^3}{12\pi^3\varepsilon_0^2\left(\hbar v_f\right)^4}I_0^2\left(\frac{\Omega R_0}{v_f}\right)\left[K_1\left(\frac{\Omega d}{v_f}\right)+K_0\left(\frac{\Omega d}{v_f}\right)\right]. \tag{25}$$

In the approximation large distance limit $\left(\Omega d/v_f\right)$>>1 we use the following asymptotic form of the Bessel function $K_n\left(\Omega d/v_f\right)\simeq\sqrt{\frac{\pi v_f}{2\Omega d}}\exp\left[-\frac{\Omega d}{v_f}\right]$ [29] from (25) we can obtain the following simplified expression for the energy transfer rate:

$$\gamma_{p_i\to p_f}=\frac{e^2\hbar\Omega^2\mu_{eg}^2}{12\varepsilon_0^2\pi^2\left(\hbar v_f\right)^3}I_0^2\left(\frac{\Omega R_0}{v_f}\right)\left(\frac{e^{-\frac{2\Omega d}{v_f}}}{d}\right). \tag{26}$$

If we introduce a quantity $R_f=\frac{v_f}{\Omega}$, which has the dimension of length (meter) and is related to the Fermi velocity of electrons in graphene and depends on the energy $\hbar\Omega$ transferred from the dye (donor) to the carbon nanotube , then (26) can be written as follows:

$$\gamma_{p_i\to p_f}=\frac{e^2\hbar\Omega^2\mu_{eg}^2}{12\varepsilon_0^2\pi^2\left(\hbar v_f\right)^3}I_0^2\left(\frac{R_0}{R_f}\right)\left(\frac{e^{-\frac{2d}{R_f}}}{d}\right). \tag{27}$$

For the function $I_0^2\left(x\right)$ the following asymptotic approximation can be used

$$I_{\left|m_q\right|}\left(x\right)=\left(\frac{x}{2}\right)^{\left|m_q\right|}\frac{1}{\Gamma\left(\left|m_q\right|+1\right)}. \tag{28}$$

We have $\left|m_d\right|=0$ and from (28) it is not difficult to obtain

$$I_0^2\left(\frac{R_0}{R_f}\right)=\left[\left(\frac{R_0}{2R_f}\right)^0\frac{1}{\Gamma\left(0+1\right)}\right]^2=\left[\frac{1}{\Gamma\left(0+1\right)}\right]^2=\left[\frac{1}{\Gamma\left(1\right)}\right]^2=1. \tag{29}$$

And now (27) can be written as follows:

$$\gamma_{p_i\to p_f}=\frac{e^2\hbar\Omega^2\mu_{eg}^2}{12\varepsilon_0^2\pi^2\left(\hbar v_f\right)^3}\left(\frac{e^{-\frac{2d}{R_f}}}{d}\right)=\frac{e^2\hbar\Omega^2\mu_{eg}^2}{12\varepsilon_0^2\pi^2\left(\hbar v_f\right)^3R_f}\left(\frac{e^{-\frac{2d}{R_f}}}{\frac{d}{R_f}}\right). \tag{30}$$

Therefore, the rate of energy transfer from the fluorophore (dye molecule) to the nanotube has $\left(l = 0, k_{i,\perp} = 0\right)$ an exponential dependence on the distance between them.

For the estimation we choose $\hbar\Omega = 3.2$ eV, $\mu_{eg}^2 = 4.5D$, $v_f = 1.1\cdot 10^6$ m/s, $R_f = \frac{v_f}{\Omega}$. For purine $R_f = \frac{v_f}{\Omega} = 2.26\cdot 10^{-10} m = 0.226$ nm.

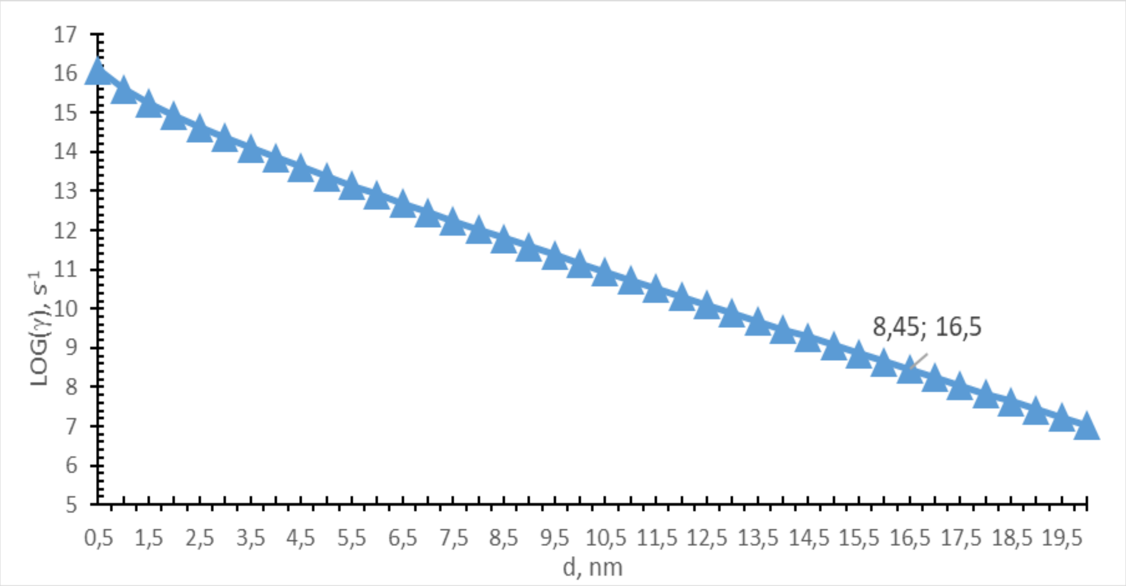


Fig. 4. Calculated from equation 30

We take $\hbar\Omega = 3.2$ eV, the emission maximum of pyrene [24] and use μ_{eg} = 4.5 Debye, obtained by performing *ab initio* calculations for pyrene B3LYP/6-311++G level of calculation [12].

Therefore, the rate of energy transfer from the fluorophore to the nanotube at $\left(l = 0, k_{i,\perp} = 0\right)$ has an exponential dependence on the distance between them.

Now let us apply the formulas (27)–(30) we obtained to analyze the energy transfer from the purine molecule to the 5.5 carbon nanotube. Note that the nanotube is metallic and that the electron-hole bands are symmetric about zero energy. Fig. 2 shows the band structure of the 5.5 metallic carbon nanotube. Note that its electron-hole bands are symmetric about zero energy.

As an example, consider the case of energy transfer from a fluorophore to a 5.5 metal nanotube . The band structure of a 5.5 nanotube within the linear dispersion relation is shown in Fig. 2. The long-distance behavior of the energy transfer rate corresponding to this excitation has an exponential dependence on distance, see (27). For a metal chiral nanotube, energy transfer is possible even for very low fluorophore emission energies (see Fig. 2). Note that for other metal nanotubes, p=0 may not correspond to the linear band near the Fermi energy shown in Fig. 3. However, by appropriately redefining p, one can obtain p=0 for linear bands near the Fermi energy for such nanotubes.

CONCLUSIONS

We have studied the process of resonant energy transfer from a fluorophore to a single-walled carbon nanotube by developing a simple analytical model for the transfer rate as a function of the distance between the fluorophore and the nanotube. Metallic carbon nanotubes have an exponential dependence on distance when $\hbar\Omega < \varepsilon_g$ and d^{-5} otherwise. There is no threshold on the amount of energy that can be transferred to metallic nanotubes . In contrast, for semiconductor nanotubes, energy transfer does not occur if $\hbar\Omega \geq \varepsilon_g - \varepsilon_b$. If $\hbar\Omega \geq \varepsilon_b$, then the rate has a dependence d^{-5} in the long-range limit. But if $\varepsilon_g > \hbar\Omega \geq \varepsilon_g - \varepsilon_b$, then the rate has an exponential dependence on distance. We also incorporate the possibility of energy transfer to excitons of semiconductor tubes into our analysis. Our calculations show that the energy transfer rate from pyrene to nanotube 5.5 is effective up to distances of the order of 16.5 nm.

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ПЕРЕНЕСЕННЯ РЕЗОНАНСНОЇ ЕНЕРГІЇ ВІД БАРВНИКА ДО ВУГЛЕЦЕВОЇ НАНОТРУБКИ

О. Ю. Семчук, А. А. Білюк, О. О. Гаврилюк

[1]*Інститут хімії поверхні ім. О. О. Чуйка Національної академії наук України,*
вул. Олега Мудрака, 17, Київ, 03164,
е-пошта: semchuk1950@meta.ua

У цій роботі ми досліджували процес передачі енергії від флуорофора до електронних енергетичних рівнів одностінної вуглецевої нанотрубки. Останнім часом вуглецеві нанотрубки привернули значну увагу завдяки низці потенційних технологічних застосувань, таких як оптоелектронні пристрої, сенсори тощо. Функціоналізація нанотрубок флуорофорами призвела до цікавих фотофізичних властивостей. Передача енергії збудження є важливим фотофізичним процесом, який, як експериментально показано, відбувається, коли барвники функціоналізуються на нанотрубках. Натхненні цими експериментами, ми теоретично вивчили процес резонансної передачі енергії від флуорофора до одностінної вуглецевої нанотрубки. Ми використовували дипольне наближення для барвника, а не для нанотрубки, під час передачі енергії від барвника до нанотрубки. Резонансна передача енергії – це процес невипромінювальної передачі енергії від збудженого донора до акцептора. Коли передача включає енергію електронного збудження, а донор є флуоресцентним, це відомо як резонансна передача енергії флуоресценції (FRET). У FRET взаємодія між донором та акцептором є кулонівською. Диполі електронних переходів донора та акцептора взаємодіють електростатично, що призводить до залежності швидкості передачі від відстані між донором та акцептором. Ферстер досліджував цей процес теоретично. У підході Ферстера це апроксимується як взаємодія між відповідними диполями переходу. Металеві вуглецеві нанотрубки мають експоненціальну залежність від відстані, коли $\hbar\Omega < \varepsilon_g$ і коли d^{-5}.

Немає порогу для кількості енергії, яку можна передати металевим нанотрубкам. Навпаки, для напівпровідникових нанотрубок передача енергії не відбувається, якщо $\hbar\Omega \geq \varepsilon_g - \varepsilon_b$. *Якщо* $\hbar\Omega \geq \varepsilon_b$, *то швидкість має залежність у межах* d^{-5} *дальньої дії. Але якщо* $\varepsilon_g > \hbar\Omega \geq \varepsilon_g - \varepsilon_b$, *то швидкість має експоненціальну залежність від відстані. Ми також враховуємо можливість передачі енергії до екситонів напівпровідникових трубок у нашому аналізі. Наші розрахунки показують, що швидкість передачі енергії від пірену до нанотрубки 5.5 є ефективною до відстаней порядку 16.5 нм.*

Ключові слова: *графен, поверхневі плазмони, плазмонний, вуглець, передача енергії, теорія Форстера, екситон, FRET, нанотрубка.*