DIFFUSIVE SPECTRA OF ANTISTOKES WING OF PHOTOLUMINESCENCE OF CARBON NANOSTRUCTURES

Kumekov S.E., Saitova N.K.

Kazakh National Research Technical University named after K.I. Satpaev, Almaty, Kazakhstan,
skumekov@mail.ru

In paper the photoluminescence radiation with a wavelength shorter than the wavelength of the exciting light that usually have been called anti-Stokes, is studied. These features of photoluminescence were observed previously in such carbon-containing objects as amorphous hydrogenated carbon α-C: H and native biopolymer-collagen. The general structural property of these objects is the presence of carbon hexagons — the nuclei of the benzene ring. A dimer-excimer model of photoluminescence in carbon nanostructures was developed to explain the anti-Stokes wing of the spectra. The temperature dependence of the distribution function of thermally activated pre-excited states in carbon-containing objects is determined. The spectral dependence of the intensity of the anti-Stokes wing taking into account the density of states in the excimer well is calculated.

INTRODUCTION

Relatively recently [1–6], interesting features of the photoluminescence (PL) of carbon quantum dots (CQD) were discovered: the wide structureless band in the visible spectral region, the half width, the photon energy at the band maximum, and whose shortwave edge depend on the energy of the excitation quantum. Similar features of PL were observed previously in such carbon-containing objects as amorphous hydrogenated α-C: H carbon [7] and native biopolymer-collagen [8]. An additional feature of the PL spectra of α-C: H and collagen was the observation of anti-Stokes radiation (ASR) at temperatures above the temperature of liquid nitrogen. With an increase in the temperature of the samples, the spectral range of the ASR wing expanded to the short wavelength region. Measurements of attenuation kinetics showed the fluorescent character of ASR.

In [7], the observed ASR is explained by the recombination of carriers thermally excited by localized states above the excitation level (Fig. 1). In [8], a qualitative assumption was made about the excimer nature of PL in collagen (Fig. 2).

The general structural property of these objects [1–8] is the presence of carbon hexagons — the nuclei of the benzene ring. The structural feature of the above objects can lead to the formation of sandwich structures [9] representing physical dimers of carbon hexagons-aromatic rings, or their combination, while the term dimer means a physical dimer consisting of two monomers [9].

Dimers can be of different geometry. With a parallel arrangement of monomers, the dimer represents a sandwich structure. It is these dimers that are discussed in this article. In such dimers, monomers are considered as flat graphene-like clusters of different sizes, depending on the number of hexagons forming the cluster.

In the present work, a similar representation of the structure allowed us to develop a dimer-excimer model of radiative processes and explain the main features of the experimental ASR PL spectra in α-C: H and collagen.
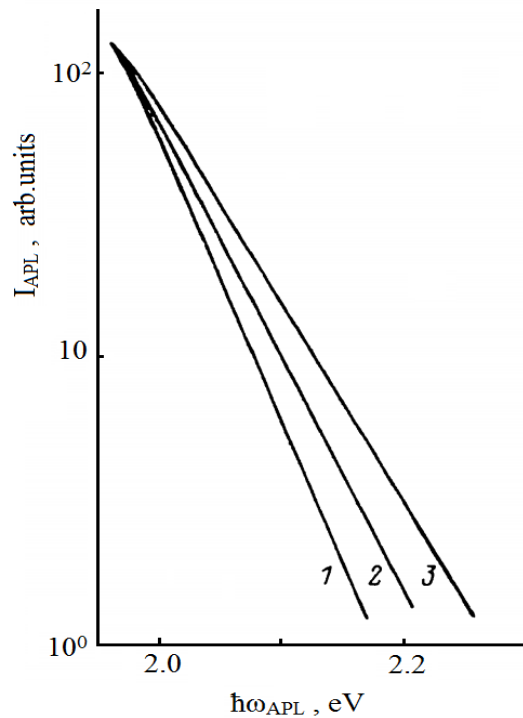
Fig.1. Experimental spectra of ASR in amorphous hydrogenated carbon α-C: H [7]
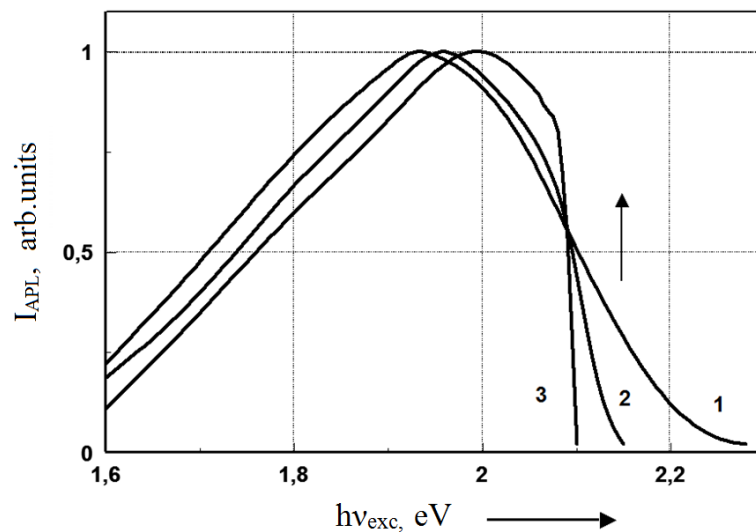
Fig.2. PL spectra of NC, measured at excitation $h\nu_{exc} = 2.14$ eV. (arrow) and three temperatures: 1-300 K, 2-78 K, 3-4.2 K [8].

1. Model

Figure 3 illustrates the pattern of the origin of the diffuse emission spectrum of an excimer [10]. E_1 and $E*$ are the electronic terms of the ground and excited states of an excimer; $\hbar\omega_e$ is the energy of a quantum of excitation and resonant fluorescence at transitions 1-1', $\hbar\omega_{APL}$ is the energy of a quantum of anti-Stokes radiation at transitions 2-2'. The energy interval between states 1 and 1'is ε, and states 2 and 2' is δ. Then $\varepsilon = \hbar\omega_{APL} - \hbar\omega_e - \delta$.
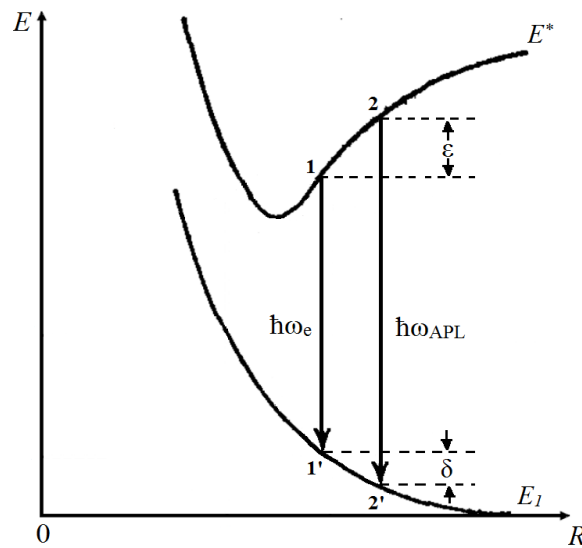
Fig.3. The origin of the diffuse emission spectrum of the excimer [10].
E1 and E * - electronic terms of the ground and excited states

The AS intensity of the PL wing is proportional to the photodissociation cross section σ_{PD}, the concentration of N_{exc} excimer states, and the energy distribution of thermally activated pre-excited states

$$e^{-\varepsilon/kT},$$

where $\varepsilon = \hbar\omega_{APL} - \hbar\omega_e - \delta$.

$$I_{APL} = \sigma_{PD} \cdot N_{exc} \cdot exp[-(\hbar\omega_{APL} - \hbar\omega_e - \delta)/kT] \qquad (1)$$

Photodissociation cross section

$$\sigma_{PD} = \frac{\pi^2 c^2 \hbar^3}{(\hbar\omega)^2 \Delta \tau_{sp}} \qquad (2)$$

here c is the speed of light, $\hbar\omega$ is the radiation quantum energy, Δ is the effective width of the emission band, τ_{sp} is the lifetime of the excited state with respect to spontaneous transitions.

In the diffuse model of the origin of PL [10], the width of the emission band is proportional to the amplitude of the monomer oscillations. In the harmonic approximation, we can write the amplitude of monomer oscillations in the form

$$a_v = \sqrt{\frac{2\varepsilon_T}{\mu\omega_0^2}},$$

where ε_T is the oscillator energy, which is generally temperature dependent, μ is the mass, and ω_0 is the natural frequency.

As is known, the average energy of the oscillator's energy, which depends on temperature, has the form

$$\varepsilon_T = \frac{\hbar\omega_O}{2} + \frac{\hbar\omega_O}{exp\frac{\hbar\omega_O}{kT}-1}$$

At high temperatures, when $kT \gg \hbar\omega_0$ can be written

$$\varepsilon_T \approx kT$$

Then for the effective width of the spectrum at high temperatures, the expression

$$n\Delta \sim \sqrt{kT}$$

And for the photodissociation cross section of the excimer is true

$$\sigma \sim \frac{1}{\sqrt{kT}}$$

## 2. The intensity of the anti-Stocks radiation

The intensity of the ASR PL in relative units will be equal to

$$I = \frac{(\hbar\omega_e)^2 \sqrt{\varepsilon_0}}{(\hbar\omega_{APL})^2 \sqrt{\varepsilon_T}} \exp\left(-\frac{\hbar\omega_{APL} - \hbar\omega_e - \delta}{kT}\right)$$

Here $\hbar\omega_{APL} - \hbar\omega_e - \delta$ is the energy of the pre-excited state, counted from state 1. From the last equation, you can find δ values depending on ω_{APL} and temperature T from a comparison with the results of [7] and, accordingly, ε values.

The intensity of radiative transitions involving pre-excited states depends not only on temperature, but also on the density of states in the excimer well. It can be assumed that the electron-oscillation spectrum of states in the excimer well will be close to quasicontinuous at energies above the bottom of this well. Taking this assumption into account, we approximate the density of states by the expression $\rho(\varepsilon) \sim exp\left(\frac{\varepsilon}{\varkappa_0}\right)$. Then the intensity of the radiative transitions can be written:

$$I_{APL} \sim exp\left(-\frac{\varepsilon}{kT}\right) \cdot exp\left(\frac{\varepsilon}{\varkappa_0}\right) \tag{3}$$
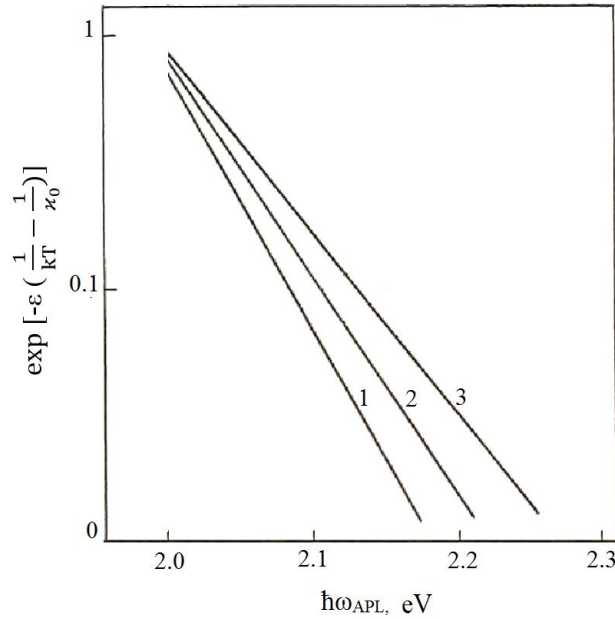
Fig.4. The intensity of radiative transitions in relative units, taking into account the density of energy states.

In Fig. 4, the calculated values of I_{APL} are calculated by formula (3) at different temperatures. The characteristic features of the particle are determined by the characteristic energy $\varkappa_0$ at various temperatures, the equals 0.023 eV (300 K), 0,026 eV (340 K) and 0.266 eV (370 K). The small increase of the maximal value of $\varkappa_0$ with the increasing of the temperature can be connected the nonparabolicity of term E*.

Conclusions

An additional feature of the PL spectra of α-C: H and collagen was the observation of anti-Stokes radiation at temperatures above the temperature of liquid nitrogen. It is proposed the dimer-excimer model of the photoluminescence of carbon quantum dots to explain the features of the spectra. The temperature dependence of the distribution function of thermally activated pre-excited states is calculated. The spectral and temperature dependence of the anti-Stokes photoluminescence wing in amorphous hydrogenated carbon α-C: H and native biopolymer-collagen are explained.

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