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Investigation of the optical properties of Ferricyanide aqueous solution

Obaida Amer AbdulHussein[1], Reham. Q.AL-Shemary[2], Azhr Abdulzahraa Raheem [3]
[1]Department of Physics, College of Education, Al-Iraqia University, Baghdad, Iraq
[2]Department of Chemistry, College of Science, University of Kerbala, Karbala, Iraq.
[3]Department of Physics, College of Science, University of Kerbala, Karbala, Iraq.
Email: dr.obaida.amer@gmail.com

Abstract :

Transition metal complexes have been widely studied to understand charge-transfer reactions in the solid and liquid phases. In particular, aqueous solutions of transition metals have wide applications in the physical and biological fields. Among many transition metal complexes, hexacyanoferrate has usually received much attention as a suitable model system for studying the optical and electronic properties. In particular, ferricyanide $[FeIII(CN)_6]^3$ molecules consist of an iron (III) ($Fe^{3+/2+}$) center coordinated to six cyanide ligands. Many optical properties, including the absorption, transmittance, and refractive index of $[FeIII(CN)_6]$, are investigated in this paper. The results show promising optical properties, including absorption and reflectance behavior, making this material a good candidate for optoelectronic devices.

Keywords: Transition metal complexes, optical properties, ferricyanide $[FeIII(CN)_6]^3$, absorption, transmittance, energy gab.

المائي $[FeIII(CN)_6]^3$ دراسة الخصائص البصرية لمحلول الفيريسيانيد

عبيدة عامر عبد الحسين [1] ، رهام قائد عبيد الشمري [2] ، أزهر عبد الزهرة رحيم [3]
[1] قسم الفيزياء، كلية التربية، الجامعة العراقية، بغداد، العراق
[2] قسم الكيمياء، كلية العلوم، جامعة كربلاء، كربلاء، العراق
[3] قسم الفيزياء، كلية العلوم، جامعة كربلاء، كربلاء، العراق
البريد الالكتروني: dr.obaida.amer@gmail.com

مستخلص:

خضعت معقدات الفلزات الانتقالية لدراسات واسعة النطاق لفهم تفاعلات نقل الشحنة في الطورين الصلب والسائل. وعلى وجه الخصوص، تتمتع المحاليل المائية للفلزات الانتقالية بتطبيقات واسعة في المجالات الفيزيائية والبيولوجية. ومن بين العديد من معقدات الفلزات الانتقالية، حظي سداسي سيانوفرات باهتمام كبير باعتباره نظامًا نموذجيًا مناسبًا لدراسة الخصائص البصرية والإلكترونية. وعلى وجه التحديد، تتكون جزيئات فيريسيانيد $[FeIII(CN)_6]^3$ من مركز حديد ($Fe^{3+/2}$) (+III) مرتبط بستة روابط سيانيد. تتناول هذه الورقة البحثية دراسة العديد من الخصائص البصرية، بما في ذلك الامتصاص والنفاذية ومعامل الانكسار لـ $[FeIII(CN)_6]^3$. تُظهر النتائج خصائص بصرية واعدة، بما في ذلك سلوك الامتصاص والانعكاس، مما يجعل هذه المادة مرشحًا جيدًا للأجهزة الكهروضوئية.

الكلمات الافتتاحية: معقدات الفلزات الانتقالية ، الخصائص البصرية ، فيريسيانيد $[FeIII(CN)_6]^3$، الامتصاص، النفاذية، فجوة الطاقة.

Introduction

The transition metal elements are of great importance in the periodic table due to their electronic and optical properties. Particularly, the first transition series in group 8 and period 4 [1,2]. Coordination compounds are defined as those that contain a central metal ion or atom surrounded by many ions or molecules (ligands) [3]. The central metal ion is represented by transition metals, i.e., d- or F-block elements, which have different magnetic and spectral properties [4]. In general, these compounds result from the combination of two different atoms: one of which has a tendency to undergo electron pairing and is called a ligand. The other atom group provides empty orbitals for the electron pair to occupy and is called metals [5,6].

Among the most famous transition elements used in the formation of the transition complexes is iron [7]. The photosensitive ferrocyanide system $Fe(CN)_6$ provided a compound that received special attention as a photo-transformable molecule, as it is a strong ligand located on the high-energy side of the spectrochemical series [8,9]. Cyanide forms a low-spin complex with iron. This molecule has unique properties that can be directly controlled by light. Ferricyanide compound is an important coordination that can be used in advanced technological including optical applications [9]. The optical and electronic properties of ferricyanide offer advanced options for many applications in energy conversion and light storage devices due to its molecular excitation in the uv-vis range of the electromagnetic wavelength. Studies during the last century and in recent years have focused on the optical properties of transition elements and their application in catalysis and energy conversion, as well as in optical devices such as sensors and detectors [10,11]. These devices rely on the absorption/transmission ranges of metal complexes, either as thin films or as homogeneous aqueous solutions, using solvents that match the ionic properties of the metal complex [12,13,14].

Ferricyanide consists of an iron metal center ($Fe^{3+/2+}$) linked by six bonds to cyanide (CN). Such a complex is considered a stable coordination material

with an octahedral geometry and has varying solubility in water depending on the attached cation [15]. However, most ferrocyanide salts form colloidal solutions or are sparingly soluble. At high concentrations, ferrocyanide is relatively stable and has low toxicity due to the very strong Fe–C bond, making it less toxic compared to the other ion-cyanide complexes. Therefore, it can be applied in biocompatible fields. However, when this bond reacts with strong mineral acids, it releases highly toxic hydrogen cyanide gas.

Experimental Part

A homogeneous solution was prepared by dissolving ferrocyanide in ionically neutral distilled water at a concentration of 10^{-3} mM, as ferrocyanide is sparingly soluble at high concentrations. The aqueous solution is diluted as we need to measure the uv-vis spectra. All chemical reagents were purchased from Sigma-Aldrich. The purity is 99% and is used without further purification. A UV-Vis spectrophotometer (Implen, Nano) was used to measure the absorption of the prepared solution with a precision of 1 nm. A 1 cm thick quartz cell was used to hold the sample solution, and the absorption spectrum was measured in the range of 230 to 650 nm.

Results and Discussion

The absorption spectrum of the solution of a 10^{-3} mM sample concentration of ferrocyanide is shown in Figure 1. The absorbance was studied for wavelengths from 230-650 nm, as shown in the figure. It is clear from Figure 1 that there are many obvious optical windows for the ferrocyanide solution. The first group of these windows, which are located at 398, 422, 303, and 262 nm, is attributed to the ligand-to-metal-charge-transfer (LMCT) transitions. The second group of is positioned at 286 nm and 324 nm and attributed to the ligand field (LF) transition. The absorption of a wide range of electromagnetic energy from ultraviolet to visible light of the spectrum is attributed to the delocalization of electronic charges in the orbitals of such molecules. The electron delocalization in the ferrocyanide complex provides at least two strong optical operating windows that can be utilized in optical systems such

as detectors. These peaks at 303 nm and 422 nm are assigned to the electronic localization in the metal center via LMCT transition.

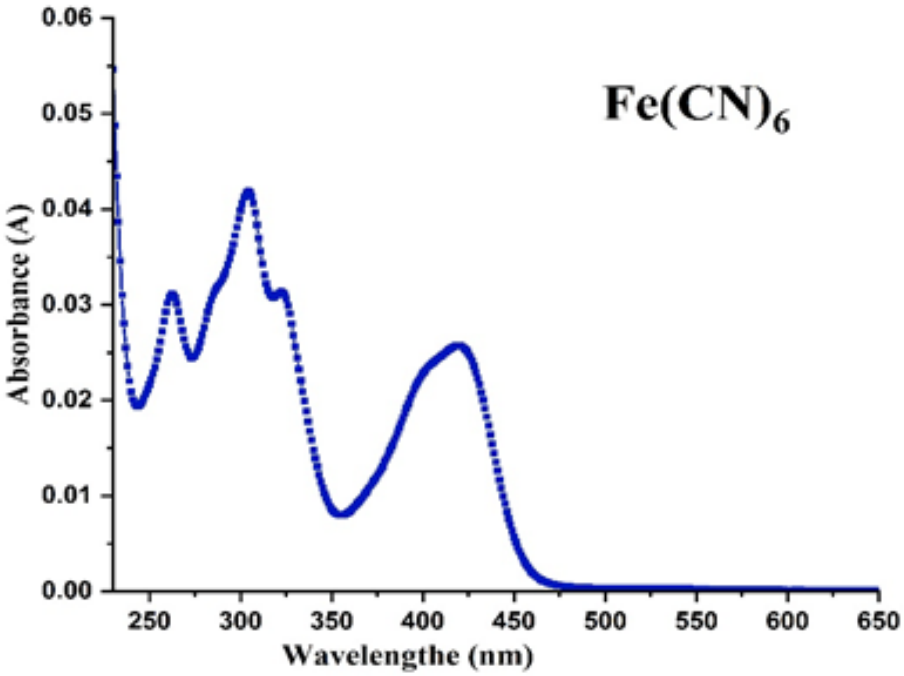

Figure (1): the absorption spectrum (A) of ferrocyanide solution.

The transmittance (T) curve for ferrocyanide was calculated using the following mathematical relationship:

A= - logT ……. (1)

As shown in Figure 2, ferrocyanide exhibits high transmittance for wavelengths greater than 450 nm, reaching approximately 99% of the beam energy. Below this window, the incident wavelengths exhibit low transmittance, which is attributed to the interaction between the wavelengths and the ferrocyanide molecule. However, as the wavelengths shorten and approach the violet region, the transmittance of ferrocyanide decreases.

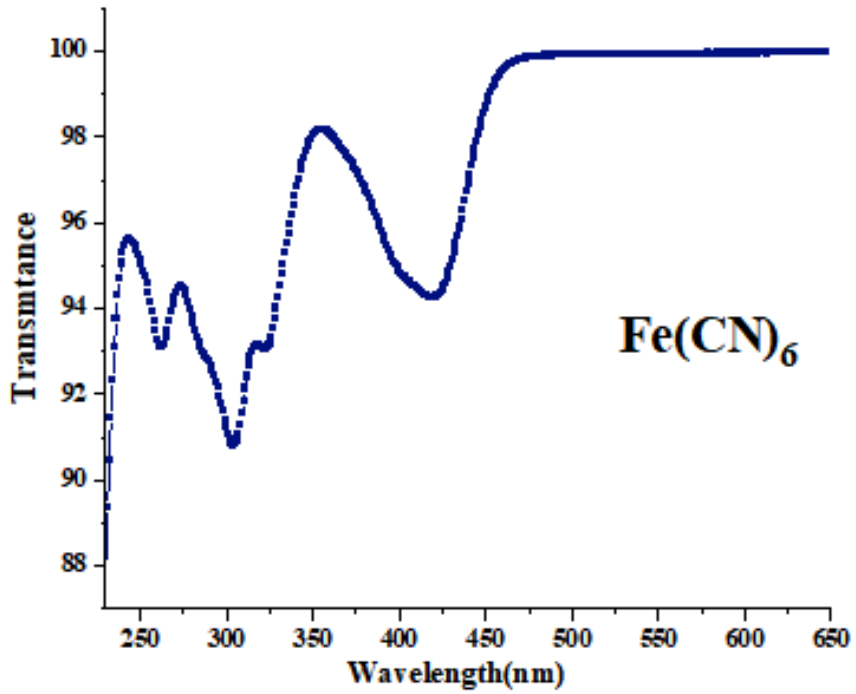

Figure (2): The transmittance spectrum (T) of ferrocyanide solution.

The reflectance, which is provided in Figure 3, is calculated from the following equation:

R+T+A=1 ……. (2)

It is clear from the figure 3 that the reflectance behaves similarly to the absorbance curve. Where the peaks appear at nearly the same position as the absorption peaks and decrease as the incident wavelengths increase. From this behavior, we can conclude that the reflection of light in the ferrocyanide materials is strong in the region between the visible and ultraviolet range of the electromagnetic spectrum. This property can be employed for utilities such as materials in a reflection mirror for ultraviolet applications.

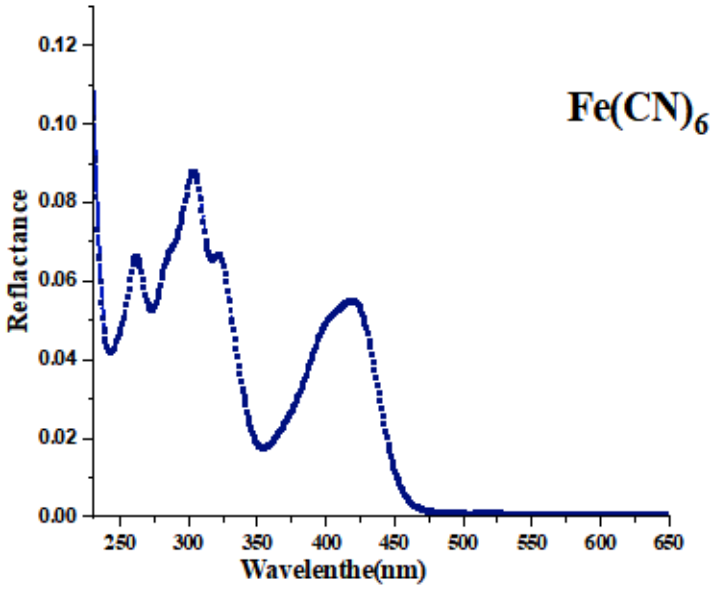

Figure (3): The reflectance (R) coefficient spectrum of ferrocyanide solution.

The Extinction coefficient, which is presented in Figure 4, was calculated from the following equation:

$$k_o = \frac{\alpha\lambda}{4\pi} \quad \ldots\ldots\ldots (3)$$

Where λ is the wavelength, α: represents the amount of attenuation of the incident photon's energy.

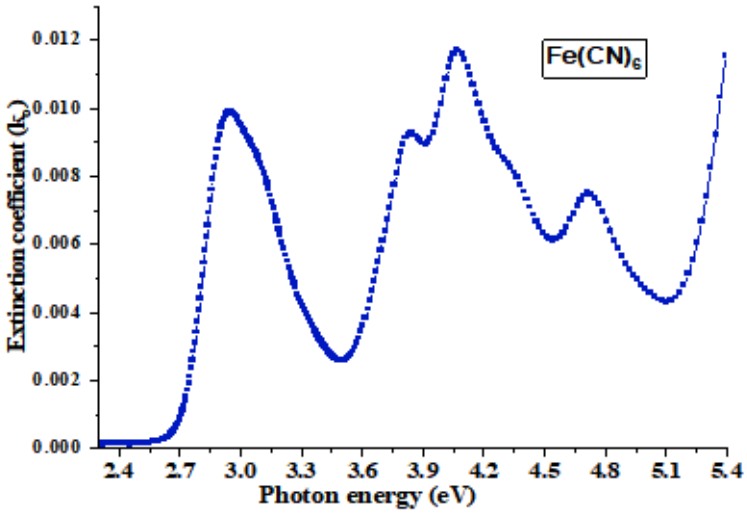

Figure (4): the Extinction coefficient (k_o) spectrum of ferrocyanide solution.

Figure 4 shows that higher-energy photons experience greater attenuation than lower-energy photons. This makes ferrocyanide a suitable material for coatings or as a medium that can inhibit the energy of incident photons and convert it into energy through electron interactions in the orbitals.

Figure 5 represents the optical refractive index of the ferrocyanide solution, which is calculated using the following equation:

$$n_o = \left[\frac{(1+R)^2}{(1-R)^2} - (k_o^2 - 1)\right]^{1/2} + \frac{(1+R)}{(1-R)} \quad \ldots\ldots\ldots\ldots (4)$$

where R is the reflectance.

It is observed that the ferrocyanide molecules exhibit an unstable refractive index. Where the refractive index fluctuates, and many increments of its amount appear with respect to the wavelength used in the electromagnetic spectrum. This is an important consideration when designing optical systems for devices that require a distinct refractive index at specific wavelengths.

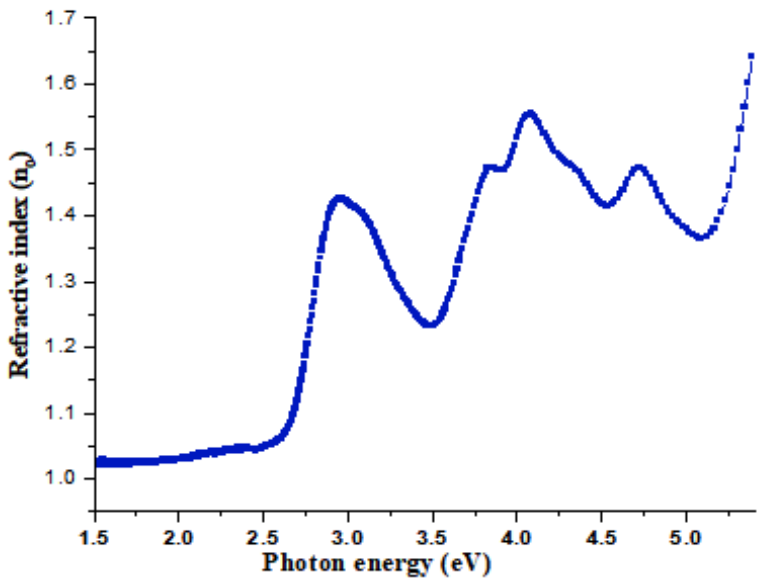

Figure (5): The refractive index (n_o) spectrum of ferrocyanide solution.

The optical absorption edge as a function of the incident photon energy is studied using the electron optical absorption coefficient α spectrum and calculated

from the following equation [10]:

$$\alpha = 2.303\ A/d \quad \ldots\ldots\ldots \quad (5)$$

Where d is the thickness of the material.

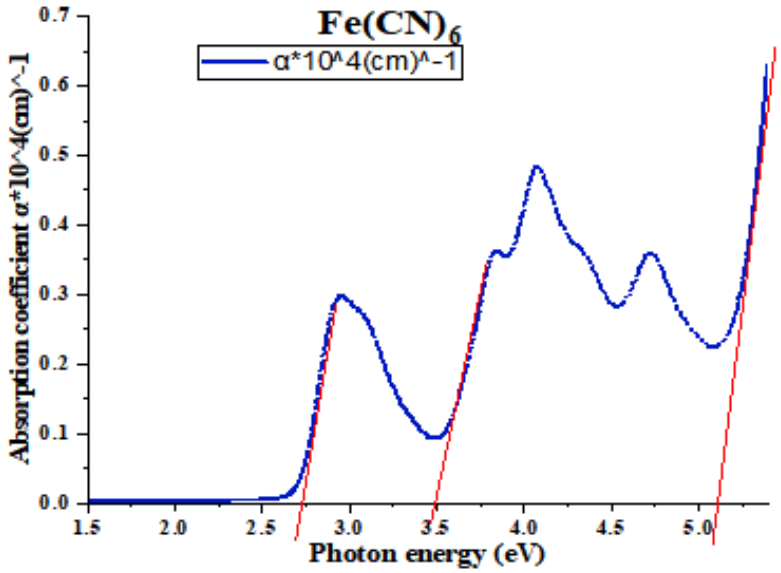

Figure (6): absorption coefficient (α) spectrum of ferrocyanide solution.

Figure 6 clearly shows three absorption regions with distinct, well-defined peaks, as shown in Table 1.

Table (1) Absorption zone of $Fe(CN)_6$ solution

Absorption zone	Absorption energy value (electron volts)
First	The first peak is at approximately 2.7–3.0 eV with a value of $\alpha \approx 0.30 \times 10^4\ cm^{1-}$
Second	The second peak is at approximately 4.0 - 4.1 eV with a value of $\alpha \approx 0.48 \times 10^4\ cm^{1-}$ (highest value)
Third	The third peak is at approximately 4.5 eV with a value of $\alpha \approx 0.35 \times 10^4\ cm^{1-}$

These peaks indicate that there are electronic transitions occurring between different energy bands in the material. The absorption coefficient curve reveals band gaps, with three distinct energy gaps (first gap ≈ 2.65 eV, second gap ≈

3.5 eV, and third gap ≈ 5.1 eV). The appearance of many band gaps is due to the complex structure of ferricyanide, which allows many transitions to occur during excitation. This confirms that $Fe(CN)_6$ is a material with a complex crystalline structure and multiple direct and indirect transitions.

A multiband electronic structure can explain the origin of the three energy gaps. The presence of three distinct energy gaps at 2.65 eV, 3.5 eV, and 5.1 eV is not a random phenomenon, but rather reflects a real complexity in the electronic structure of the material. The interpretation of the three gaps in the $Fe(CN)_6$ crystal structure is as follows:

The first energy position at 2.65 eV - (*d-d*) transition. This band gap is the most characteristic in coordination iron compounds and is due to crystal field splitting (Δ_o) in an octahedral environment, the *d* bands of the iron ion split into two levels: (t_2g) (lower level), which contains 6 electrons in Fe^{2+}, and (*eg*) (higher level), which is an empty energy level. Since CN^- ligand is one of the strongest ligands in the spectrochemical series, this results in a very large Δ_o compared to other iron compounds, leading to push absorption towards higher energies than in the visible range, extending to the UV edge. The coupling between spin and orbital momentum is responsible for additional splitting of the (t_2g) levels, which explains the fine structure of the peaks in the curve. The transition from (t_2g to *eg*) requires an energy equal to Δ_o, and in $Fe(CN)_6$, this energy is: $\Delta_o \approx 2.5$ - 2.7 eV, which corresponds perfectly with the gap observed at 2.65 eV [16].

The second energy position at 3.5 eV corresponds to the metal-to-ligand charge-transfer (MLCT) transition. Such an energy gap represents one of the most important and well-known transitions in coordination chemistry. This transition is well documented in the scientific literature at approximately 3.4–3.6 eV for $Fe(CN)_6$ compounds and is responsible for the characteristic yellow color of ferrocyanide solutions [16]. This electron transfer is performed as a transition from the *d* orbitals of the iron ion to the antibonding π orbitals of CN^-*

$Fe^{2+}(d) \rightarrow \pi(CN^-)^*$

Its energy is higher than that of a *d-d* transition because it involves actual charge transfer. It has a higher trans-

fer probability (greater absorption), which explains the peak in the diagram at 4.0–4.1 eV adjacent to this gap [16].

The third energy point at 5.1 eV corresponds to a deep Ligand-to-Metal Charge Transfer (LMCT) transition, which represents the exact opposite direction, where electrons transfer from σ and π orbitals in $CN^- \rightarrow$ empty (*eg)* orbitals in Fe ion. This transition requires a much higher energy (deep ultraviolet) because it transfers electrons from stable orbitals deep within the ligand. The value of 5.1 eV. is consistent with observations made in far-UV spectroscopic studies of transition metal cyanide compounds.

Based on the electronic transition values provided by the compound, the following fields can be proposed as practical applications for $Fe(CN)_6$, including modified optical applications. Fields such as dye-sensitive solar cells, multi-junction solar cells, photocatalysis, biochemical, and biological detectors can be applied in such materials [16].

The electronic transitions are governed by the following equation [10],

$$\alpha hf = B(hf - E_g \pm E_p)^r \quad \ldots\ldots\ldots\ldots(6)$$

where the value of the exponent (r) determines the type of transition, as shown in Figures (7-9) for direct and indirect allowed and forbidden transitions.

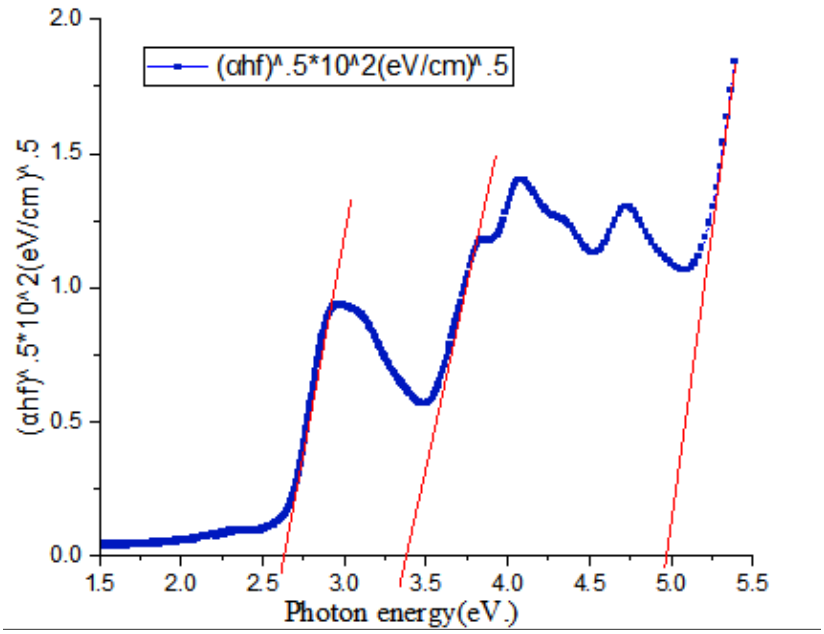

Figure (7) the direct allowed transition

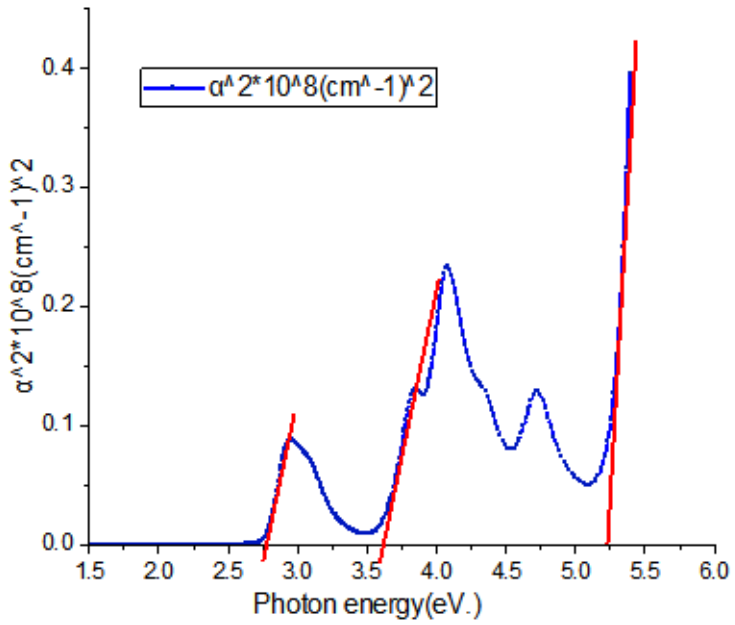

Figure (8) the indirect allowed transition

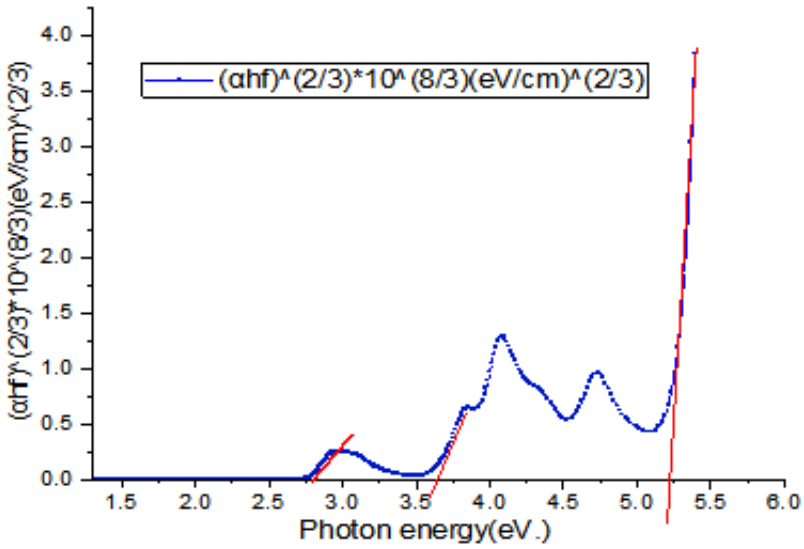

Figure (9) the direct forbidden transition

Conclusions

From the present study of the optical and spectral properties of ferrocyanide aqueous solution, we observe that ferrocyanide possesses a distinctive electro-optical window. It exhibits a unique optical spectrum due to its orbital structure, providing excellent op-

tical properties across the 230-650 nm range of the electromagnetic spectrum. It is relatively transparent for wavelengths greater than 550 nm and exhibits a relatively low, variable extinction coefficient. We also note an increase in the refractive index with increasing incident energy, particularly for shorter wavelengths approaching the violet region. Moreover, the band gap energy of the ferricyanide is so important in this study. Multiple values of the energy gap indicate that the sample can be used across a range of energy needs, from ultraviolet to visible electromagnetic photon energies.

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