Chapter 5

Photometallic nature of organic polyiodide chain complexes
1 INTRODUCTION

The Peierls transition from metal to semiconductor state in one-dimensional conductor was proposed long ago [1]. A one dimensional metal is unable and undergoes a static lattice distortion as soon as it is perturbed by external forces like pressure, temperature, field, frequency, intensity of light etc. That is why it is also termed as Peierls instability. The dynamic anomaly like Kohn anomaly arising from strong $Q = 2k_F$ scattering and nesting of Fermi surface [2,3] leads to a static distortion of the lattice at low temperature when the amplitude of vibration reduces. In Peierls instability, the resonance structures of one-dimensional systems are unstable according to valence bond theoretical criteria [4] or has a screening instability [5]. In phonon spectrum, there is a softening of $Q = 2k_F$ phonons and the frequency of acoustic branch at $Q = 2k_F$ reduces in Kohn anomaly. When it becomes zero, the phonon dispersion relation splits into optical phonon branches in the reduced zone scheme. Lattice constant increases and unit cell becomes larger as superlattice is formed and this includes more than one number of atom or ion leading to optical phonon branches.

Here photometallic nature is discussed in some organic polyiodide chain complexes in context with their UV-visible near IR spectra.

2 EXPERIMENTAL PROCEDURE

Benzamide - KI-I₂, benzophenone- KI-I₂ ,deoxycholic acid- KI-I₂ and lithocholic acid- KI-I₂ , were prepared by mixing organic matrix, potassium iodide and molecular iodine in 1 : 1
molecular weight proportions and grinding in a mortar till the colour changed remarkably. The colours changed to brown, blue or black with the inclusion compounds of iodine were formed.

Samples for UV-visible –near IR spectra were pasted sticking by paraffin oil (spectrograde) on semi transparent strips. The strips were placed in UV-visible –near IR λ19 model spectrometer of Perkin Elmer Company.

The spectra were recorded in the full range from 200 nm to 2500 nm. Molecular structures of all organic matrices which form cavities for polyiodide chains to go in, which were used here, are shown in Figure 1.

Figure 1 Molecular structures of organic compounds used in the present work.
3 RESULTS AND DISCUSSION

Benzamide - KI-I_2 and Benzamide - HI-I_2 were studied earlier by crystallography [6]. This study revealed hydrogen bonded network of benzamide molecules and two iodine chains residing in each cavity. Reflectivity of these materials showed anisotropic nature of optical densities [7]. Some other like benzophenone- KI-I_2 and others were also studied earlier [8,9]. Reviews can be found elsewhere [10-13]. Deoxycholic acid – iodine and lithocholic acid-iodine complexes are mentioned elsewhere [14].

The UV-visible-near IR spectra of benzamide - KI-I_2, benzophenone- KI-I_2, deoxycholic acid- KI-I_2 and lithocholic acid- KI-I_2 in full range are shown in Figure 2. The band assignments were discussed elsewhere in details [15].

![Figure 2 (a)](image)

![Figure 2 (b)](image)
Here the relevance of these spectra in relation with photometallic nature will be elucidated.

In all four cases, the following function is found

\[ A = A_0 \lambda \exp(-b\lambda) \]

where \( A \) is the absorbance and \( \lambda \) is wavelength, \( A_0 \) and \( b \) are constants. This function has maximum at \( \lambda_m = 1/b \). This is the same function we found in high pressure resistivity of polyiodide chain complexes.

Figure 2 (c) UV-visible near IR spectra of
a. benzamide- KI-I₂
b. benzophenone- KI-I₂
c. deoxycholic acid- KI-I₂
d. lithocholic acid- KI-I₂

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The high pressure function \( \rho = \rho_0 P \exp(-bp) \) gives
\[
\rho(x) = \frac{b}{b^2 + X^2} = (\pi X \text{ Cauchy distribution}) \text{ as the Fourier transform.}
\]
Thus lattice displacements are Cauchy distributed. Here \( A = A_0 \lambda \exp(-b\lambda) \) gives Cauchy distribution in wave number
\[
A = A_0 \frac{b}{b^2 + K^2} \quad [16-22].
\]

This asymmetric function is an inverse Fourier transform of the symmetric Cauchy distribution [23, 24]. Thus,
\[
A(K) = \frac{b}{b^2 + K^2}
\]
also
\[
\int \frac{b}{b^2 + K^2} \, dK = \frac{1}{b} \tan^{-1}\left(\frac{K}{b}\right)
\]
So, \( \tan^{-1}\left(\frac{K}{b}\right) \) is identified with the phase angle in \( K \) (wave vector) space.

Thus
\[
\frac{\partial^2 \theta}{\partial \lambda \partial k} = A_0 \lambda e^{-b\lambda} e^{-ik\lambda}
\]
thus, there is a second order fluctuation in phase angle of charge density waves along polyiodide chains when light is incident. Thus this function arises out of necessary condition for thermodynamic stability of the system.

The spectral function of \( b\lambda e^{-b\lambda} \) is \( \frac{b}{b^2 + K^2} \), where \( K \) is the wave number.

The function \( A(k) = \frac{b}{b^2 + K^2} \left( \frac{A_0}{b} \right) \) has the same form as in Drude’s model [25].

\[
\sigma_1 = \frac{\sigma_{dc}}{1 + \omega^2 \tau^2}
\]
With $\omega = c k$, $\tau = \frac{1}{bc}$ and $\frac{A_0}{b^2} = \frac{Ne^2 \tau}{m} = \frac{\omega p^2 \tau}{4\pi}$

Thus the function $A = A_0 \lambda e^{-\lambda \tau}$ reveals photometallic nature.

On the other hand, for ac photoconductors [26],

$$\Delta I = \frac{eV}{L^2} \left( \frac{\mu_n \tau_n}{1 + i\omega \tau_n} + \frac{\mu_p \tau_p}{1 + i\omega \tau_p} \right) Qo e^{i\omega t}$$

where $\tau_n$ and $\tau_p$ are lifetime of charge carriers leading to

$$\text{Re} \Delta I = \frac{eV}{L^2} \left( \frac{\mu_n \tau_n}{1 + \omega^2 \tau_n^2} \right) Qo e^{i\omega t} + \Delta I_p$$

for $\omega \tau_n \gg 1$ and $\omega \tau_n \ll 1$

where $\mu_n$ and $\mu_p$ are mobilities. $Q = Qo e^{i\omega t}$ is the production rate of electron–hole pairs.

Here, $\frac{A_0}{b^2} = \frac{eV}{L^2} \mu_n \tau_n Q$ and $\tau_n = \frac{1}{bc}$

Similar function arises from orientational polarizability giving [27]

$$\alpha_d = \frac{\alpha_0}{1 + i\omega \tau} \quad \text{and} \quad \text{Re} \alpha_d = \frac{\alpha_0}{1 + \omega^2 \tau^2}$$

$$\tau = C \exp \left( \frac{\phi}{k_b \tau} \right)$$

where $\phi$ is the potential barrier. This leads to

$$\sigma = \frac{\omega \varepsilon}{4\pi} = \frac{\omega}{4\pi} \left( \frac{4\pi N \alpha_0}{1 + \omega^2 \tau^2} \right)$$

Using $\chi = N \alpha$ and $\varepsilon = 1 + 4\pi \chi$. Then $\frac{A_0}{b^2} = N \alpha_0 \omega$ and $\tau = \frac{1}{bc}$.

However, this possibility is discarded because the phenomenon occurs in the range of far-infrared or microwave range of frequencies.

The Cauchy distribution is symmetric and thus absorbance is a symmetric function of momentum ($\lambda k$). Also

$$\frac{\hat{\Omega}}{\hat{u} \hat{v}} = \frac{\hat{\alpha} \lambda e^{-i\tau \lambda - \ln \lambda}}{\hat{a} \hat{b} \hat{d}} = \frac{A_0 e^{i\lambda f}}{\hat{a} \hat{b} \hat{d}}$$
where \( K = ik + b \) is complex. \( \ln \lambda \) logarithm is fluctuation in phase of the system, \( \lambda \) has dimension of length and \( K \) can be considered as absorption coefficient.

The above function is verified by plotting \( \log (A/\lambda) \) vs \( \lambda \) (nm) for all four complexes which is a straight line graph as it should be shown in Figure 3-5, except in the case of benzamide KI- I\(_2\). In the benzamide complex a half power beta density is verified according to \( A = A_0 + A_1 \lambda^{*1/2} (1 - \lambda^{*1/2}) \), where \( \lambda^{*} = (\lambda - a)/b \), \( a \) being initial value of \( \lambda \) for the peak and \( b \) being the base width of entire flat peak. This is also shown in Figure 6.

![Figure 3](image1.png)  
**Figure 3** Log (A/\(\lambda\)) vs \(\lambda\) (nm) for benzophenone - KI-I\(_2\)

![Figure 4](image2.png)  
**Figure 4** Log (A/\(\lambda\)) vs \(\lambda\) (nm) for deoxycholic acid - KI-I\(_2\)**
The Fourier transform of half power beta density is beta density only because the Fourier transform of $\frac{1}{X^{1/2}}$ is $\frac{1}{\tau^{1/2}}$ if $X$ and $\tau$ are Fourier conjugates. Here we consider probability $p$ and complimentary $1-p$ as independent variables.

In terms of wave number, absorbance is a Fourier transform of half power beta density. Similar beta density peaks in UV-visible spectra were found for the charge transfer
complexes of lead phthalocyanine [28]. The integration of the reciprocals of beta densities related to the Bessel functions which can exist in the cases of cylindrical Fermi surfaces in one dimensional conductors. This case is somewhat clear because beta density in the reduced variable based on wavelength $\lambda$ is observed and not the wave numbers.

The photometallic nature is also observed in four iodine complexes of biopolymers recently [29].

4 CONCLUSIONS

The photometallic nature occurs by the intensity of incident light through photoelastic coupling in the four organic polyiodine chain complexes. Although the incident light has energy of the order of 2-3 eV, the coupling related with photoelasticity is an order of magnitude less i.e. 0.2 eV which is one of the order of the Peierls gap. This is related to the coupling of IR phonons with electron gas having transition or resonance in UV-visible range, as described elsewhere [30]. Photometallic nature is also found to occur in iodine complexes of four biopolymers.
REFERENCES


[22] Babita Tyagi, S K Arora and A T Oza, (an interim Report)