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Inelastic X-Ray Scattering Studies on Organic Semiconductors and Organic Superconductors

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INELASTIC X-RAY SCATTERING STUDIES ON ORGANIC SEMICONDUCTORS AND ORGANIC SUPERCONDUCTORS

by

Chaminda Nalaka Kodituwakku

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Physics

Western Michigan University
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To Akki
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CHAPTER I

INTRODUCTION

1.1 Scientific Purpose and Importance

Organic electronics have began to make significant contributions to electronic devices, from LED bulbs (organic light emitting device - OLED) to military devices. The electronic behavior of these materials is very different from material to material. These behaviors are as varied as quasi-one-dimensional charge density waves to exotic superconductivity. Some of these materials are capable of self assembling, while others are used as thin films or printed directly onto surfaces. Therefore the production cost of these devices is lower compared to conventional semiconductor products. Organic solar cells and displays can be printed onto flexible surfaces. Thus the devices are light weight. Also, some of these organic materials have been used in gas sensors and as field effect transistors.

Currently, organic displays are used in digital cameras, cell phones etc. But more widespread applications are expected as the technology matures. In par-
ticular, highly efficient and inexpensive solar cells would provide great economic and social benefits. On the scientific level, the understanding of the properties of organic electronic materials is an area of strong interest in physics and chemistry [3], [4] and [5].

Conventional semiconductors have been used from the beginning of the 20th century but it became a viable business around 1960. Since then there has been a tremendous amount of effort and money invested into studying and developing conventional semiconductors. The level of fundamental understanding in organic electronic materials lags far behind that of conventional semiconductors. Organic electronic materials are very complex due to their large number of atoms in a molecule. Furthermore, some organic solids tend to have localized charges on individual molecules which are much more polarizable. Charge transfer at most temperatures is believed to proceed by hopping of polarons. A polaron behaves as a negatively charged particle with a mass greater than that of an isolated electron because of its interaction with the surrounding atoms of the solid.

Most of the solids based on organic compounds are generally bonded by weak Van der Waals forces while the inorganic semiconductors have much stronger covalent bonds. For intermolecular spacing $r$, Van der Waals forces fall off as $1/r^6$ while for a covalent bond, as $1/r^2$. Therefore, the general properties of organic electronic materials are soft, fragile and easily oxidized; whereas inorganic semiconductors are hard and brittle. Therefore, most of the time making devices
from organics requires new methods instead of the standard conventional methods.

An exciton is a bound state of an electron and a hole pair in a material. We present electronic excitations and excitons of organic semiconductor copper phthalocyanine (CuPc) and phonon measurements above and below the transition temperature ($T_c$) of the organic superconductor $\kappa$-(BEDT-TTF)$_2$-Cu(NCS)$_2$ ($\kappa$–ET Salt). Electronic excitation and exciton measurements were done using medium resolution inelastic x-ray scattering (IXS) at sector 9 at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Electronic excitation calculations were done at the Jazz supercomputer at ANL using the software Gaussian03 [6]. Phonon measurements were done using high resolution IXS at sector 3, APS. Besides the organic conductor research work, we have developed a preparation method for medium energy resolution, Cu K-edge Ge(337) analyzers.

A molecule is in its ground state if the electrons of the molecule stay in the lowest possible energy states. By supplying an external energy, electrons can be excited and moved to a higher energy level in the molecule. The possible excited states for a given external energy are determined from quantum mechanics.

Electron-hole pair of an exciton are held together by the Coulomb force. Excitons are common in insulators and semiconductors. There are two kinds of excitons. If the binding energy of an exciton is in the order of 0.1 eV then it called a Mott-Wannier exciton. In this case the potential energy between the electron-hole pair is small and the distance between the electron-hole pair is larger than the
lattice spacing. Thus, the lattice potential can be incorporated into the energy of the exciton. If the exciton energy is in the order of 1 eV, then the exciton is called a Frenkel exciton. In Frenkel excitons the Coulomb interaction between electron-hole pair is stronger than in Mott-Wannier excitons. When the bond is so tight the exciton tends to stay in the unit cell. The reason for these bonding differences is the dielectric constant of the material. In general the dielectric constant is low the effective mass becomes high. Then the potential energy becomes low and vice versa.

Part of this thesis is to observe and understand the excitons in CuPc. CuPc belongs to the phthalocyanine group and it is one of the most common and stable phthalocyanines in the group. Having a robust knowledge of CuPc would help to understand the electronic properties of most other phthalocyanines. This would improve devices which are using low energy excitations and excitons of CuPc.

Quantized lattice vibrations in atoms and in molecules in a medium are called phonons. These vibrations depend on the crystal directions of the solid. Studies of phonons help us understand physical properties of solids such as thermal and electrical conductivities. Also, by using low energy (higher wavelength) phonons one can calculate the velocity of sound in the medium.

According to the BCS (Bardeen, Cooper, and Schrieffer) theory, when the temperature is below the superconducting transition temperature, free electrons with opposite spin become paired together. These pairs are called Cooper pairs.
They can travel through the medium without any resistance. The superconducting mechanism of \( \kappa \)-ET Salt yet to be determined. This material has two-dimensional, layered structure, which may provide significant insight into the nature of superconductivity. Therefore, it is useful to study the interaction between the phonons and the electrons of these materials. The ET Salt studied here has a \( T_c \) of 10.4 K. We have measured phonon spectra at temperatures of 5 K and 15 K, along different crystal directions.
CHAPTER II

THEORETICAL BACKGROUND

With the creation of the third generation of synchrotron radiation sources, x-ray spectroscopy has become a powerful probe to study the properties of matter. Photons interact with matter in many different ways. There are several experimental techniques that help understand these interactions. This thesis work is related to an x-ray experimental technique called Inelastic X-ray Scattering (IXS). IXS is a very important experimental tool to probe both the ground and excited states of atoms, liquids and solids. In this chapter the main focus is on the theory of IXS for electronic excitations and phonons.

Figure 2.1: A schematic diagram of an inelastic x-ray scattering process.

A schematic IXS process is shown in Fig. 2.1. A photon with incident energy
wave vector $\vec{k}_1$ and polarization unit vector $\vec{e}_1$ interacts with the sample and emits a photon into a solid angle $d\Omega$ under the scattering angle $2\theta$. The scattered photon has energy $E_2$, wave vector $\vec{k}_2$ and polarization unit vector $\vec{e}_2$. In IXS the energy can be lost or gained. In the case of x-rays usually the transferred energy ($E$) is much smaller than the x-ray energies ($E_1, E_2 >> E$).

$$\vec{Q} = \vec{k}_1 - \vec{k}_2$$

(2.1)

$$|\vec{Q}| \approx 2|\vec{k}_1|\sin(\theta/2)$$

(2.2)

$$E = \hbar\omega = E_1 - E_2$$

(2.3)

The momentum transfer is given by Eqs. (2.1) and (2.2). The energy transfer is given by Eq. (2.3).

Depending on energy and momentum transfers, quite distinct information can be obtained from IXS. Interaction of the electromagnetic field (photons) with matter (electrons) can be given from the non-relativistic interaction Hamiltonian as explained in [7, 8],

$$H_{\text{int}} = \sum_j \frac{e^2}{2mc^2} \vec{A}_j \cdot \vec{\tilde{p}}_j + \sum_j \frac{e}{mc} \vec{p}_j \cdot \vec{\tilde{A}}_j$$

(2.4)

where $\vec{p}_j$ is the momentum of the $j^{th}$ target electron and $\vec{\tilde{A}}_j$ is the vector
potential of the electromagnetic field. The charge of electron, the mass of electron and the speed of light are labeled as $e, m$, and $c$ respectively. The scattering intensity depends on the double-differential cross section, $d^2\sigma / (d\Omega d\omega_2)$ given Eq. (2.5) [7, 8] as,

$$
\frac{d^2\sigma}{d\Omega d\omega_2} = r_0^2 \left( \frac{\omega_2}{\omega_1} \right) \sum_b \langle b | \sum_j e^{iQ \cdot r_j} | a \rangle - \frac{1}{m} \sum_r \left[ \frac{\langle b | \sum_j (e_2 \cdot p_j) e^{-ik_2 \cdot r_j} | i \rangle \langle i | \sum_j (e_1 \cdot p_j) e^{ik_1 \cdot r_j} | a \rangle}{E_i - E_a - \hbar \omega_1 - i\Gamma_1/2} \right] + \left[ \frac{\langle b | \sum_j (p_1 \cdot p_j) e^{ik_1 \cdot r} | i \rangle \langle i | \sum_j (e_2 \cdot p_j) e^{-ik_2 \cdot r} | a \rangle}{E_i - E_a + \hbar \omega_2} \right]^2 \delta (E_b - E_a - \hbar \omega) \quad (2.5)
$$

Here, $r_0$ is the classical free electron radius. Subscript 1 is for the incident beam and subscript 2 for the scattered beam. The frequency is given by $\omega$ (energy, if multiplied by $\hbar$), the wave vector is given by $\vec{k}$ and the polarization unit vector is given by $\vec{e}$. The electronic states are denoted as $|a\rangle$ - initial state, $|i\rangle$ - intermediate state and $|b\rangle$ - final state. $E_a$, $E_i$ and $E_b$ are the corresponding energies of these states. In Eq. (2.4), $(\vec{A} \cdot \vec{A})$ is responsible for scattering (including diffraction and non-resonant inelastic scattering), whereas the second term, $(\vec{p} \cdot \vec{A})$ is related to absorption processes and resonant inelastic scattering. The average life time of the intermediate state $i$ is given by $\tau_i = \hbar / \Gamma_i$.

The scattering process can be elaborated using a set of space-time (Feynman)
Figure 2.2: Graphical illustration of photon scattering processes described by Eq. (2.5): (A) inelastic scattering, (B) resonant inelastic scattering and (C) non-resonant inelastic scattering [1].

In the diagram the time goes upward and solid lines represent the atom and the wavy lines represent photons. (A) - a photon with energy $\hbar \omega_1$ hits the sample and a photon with energy $\hbar \omega_2$ is emitted. In this case there is no intermediate state. (B) - The atom absorbs a photon and is excited to an intermediate state, $i$. After time $\tau$ atomic state $i$ emits a photon and becomes the atomic state $b$. In the intermediate state there is only one atom present with no photons. The $i\Gamma/2$ factor eliminates the singularity which occurs at the resonance. (C) - A photon is emitted from atomic state $a$, which becomes the new intermediate state $i$, and after time $\tau$, the atom absorbs an incident photon and becomes state $b$. $\tau$ is called the mean life of the intermediate state and is given by $\tau = \hbar / 2\Gamma$. Depending on the momentum and energy transfers, Compton scattering, valence electron excitations, inner-shell excitations and phonons experiments can be carried out. In this thesis the focus is on phonons and electronic excitation experiments.
2.1 IXS for Phonons

In general, phonon scattering belongs to the non-resonant IXS case. If the incident energy is much different than the electronic state energy, \( E_1 \gg E_a \) or \( E_1 \ll E_a \) the denominator of the second part of Eq. (2.5) becomes much larger than the first part. Hence the contribution from the non-resonant IXS part becomes dominant. Then the Eq. (2.5) with fixed incident energy can be rewritten as in [8],

\[
\frac{d^2\sigma}{d\Omega_2 d\omega_2}(\vec{Q},\omega) = r_0^2 \frac{\omega_2}{\omega_1} \sum_b |\langle e_1 \cdot e_2 | \sum_j e^{-i\vec{Q} \cdot \vec{r}_j} | a \rangle|^2 \delta (E_b - E_a - \hbar \omega) \]

\[
\frac{d^2\sigma}{d\Omega_2 d\omega_2}(\vec{Q},\omega) = \frac{d\sigma}{d\Omega_0} S(\vec{Q},\omega) \]

\[
\left( \frac{d\sigma}{d\Omega} \right)_0 = r_0^2 \frac{\omega_2}{\omega_1} (e_1 \cdot e_2)^2 \]

\[
S(\vec{Q},\omega) = \sum_b |\langle b | \sum_j e^{-i\vec{Q} \cdot \vec{r}_j} | a \rangle|^2 \delta (E_b - E_a - \hbar \omega) \]

The double-differential cross section in Eq. (2.6) is reduced to two terms. Eq. (2.7) gives the Thomson scattering factor. Eq. (2.8) gives the dynamical structure factor. The Thomson scattering factor, \( r_0^2 \) depends only on the characteristics of the electron and has a value of the order \( \sim 10^{-25} \text{cm}^2 \). The \( S(\vec{Q},\omega) \) carries the cross sectional information of the target system independent of the x-ray beam.

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A detailed derivation of the dynamical structure factor is given in [9].

2.1.1 X-ray Scattering Intensities from Phonon

Phonon intensity is one of the important factors that needs to be considered in an IXS experiment. A description about phonon intensity for a single atom unit cell is given in [10]. Eq. (2.9) is crafted for a single atom per unit cell, for small angle scattering \((Q \to 0, \vec{e}_1 \parallel \vec{e}_2)\) and \(E_2/E_1 \approx 1\).

\[
S(Q, \omega) = e^{-2\omega(Q)} \frac{\hbar}{2M\omega_0} |\vec{Q} \cdot \vec{e}_Q|^2[(n + 1)\delta(\omega - \omega_0) + (n)\delta(\omega + \omega_0)]
\] (2.9)

where \(\omega_0\) is the phonon frequency, \(M\) is the effective mass of the atom, \(e^{-2\omega(Q)}\) is the Debye-Waller factor and \(\vec{e}_Q\) is the eigenvector for the longitudinal acoustic phonons. Phonons are bosons thus, the average occupancy number \(n\), is given by,

\[
n = \frac{1}{e^{\hbar\omega/k_B T} - 1}
\] (2.10)

In which \(k_B\) is the Boltzmann constant and \(T\) is the absolute temperature. For small \(\omega_0\), \(n \approx \frac{k_B T}{\hbar \omega_0} \gg 1\).

A few important points yielded by Eqs. (2.9) and (2.10) are worth describing here. Phonons can be created or annihilated. The negative phonon energy transfer
case is called phonon annihilation and the positive energy transfer case is called phonon creation. When the phonon energy transfer is negative \((-\hbar\omega_0)\) the phonon intensity is lower than when the phonon energy transfer is positive \((\hbar\omega_0)\). As worked out in [10], the phonon intensity can be expressed as,

\[
\frac{I}{I_0} = \frac{\pi^2 \hbar^2 c^2 (\delta Q)^2}{2eE_1^2} \frac{Z^2 \rho \lambda_{\text{abs}} k_B T}{M v^2} \tag{2.11}
\]

where \(I_0\) is the incident intensity and \(I\) is the scattered intensity. \(\delta Q\) is the momentum resolution, \(\rho\) is the number density, \(Z\) is the total number of electrons, \(\lambda_{\text{abs}}\) is the absorption length of the material for the given incident energy and \(v\) is the sound velocity of the sample.

Typical values for the incident flux is \(\approx 10^9 \text{s}^{-1} \text{meV}^{-1}\) and for the scattered intensity is \(\approx 1 \text{ count per sec or lower}\).

Calculating phonon frequencies for a simple lattice is moderately straightforward and can be found in standard solid state text books. Molecular crystals have covalent and Van der Waals bonds. Hence calculating phonon frequencies is very demanding. The most challenging part for calculation is choosing the correct potential energy model for these systems.
2.2 IXS for Electronic Excitations

Scattering off electronic excitations with high energy x-rays can be resonant or non-resonant. In the resonant case the incident photon excites an electron to a virtual orbital, and an electron with higher energy falls into the vacancy. In the non-resonant case, the first excitation does not depend on the incident energy. In each case there will be an electron and hole. These electron-hole pairs can bind and become excitons.

Figure 2.3: Left; Resonant scattering - the incident photon makes an intermediate state electron-core hole pair with exciton effects, the emitted photon and final state with electron-valance hole pair with exciton effects. Right; Non-resonant effect from core electrons. This process creates an electron-hole pair with exciton effects[2].
2.2.1 Non-Resonant Electronic Excitation

The dynamic structure factor in Eq. (2.6) contains information about electronic excitations. The scattering cross section is proportional to the imaginary part of the dielectric response function [11, 12].

\[ S(Q, \omega) = \frac{\hbar Q^2}{4\pi^2 e^2 n_e} \text{Im} \left[ \frac{-1}{\epsilon(Q, \omega)} \right] \] (2.12)

Here, \( n_e \) is the electron density and \( \epsilon(Q, \omega) \) is the dielectric function of the scattering system.

2.2.2 Resonant Electronic Excitation

Resonant scattering can be explained using the last two terms of Eq. (2.5). In this case the incident photon needs to have the same energy as the energy of an electron in an occupied orbital. The second order process consists of the x-ray absorption from \( |a> \) to \( |i> \) and x-ray emission from \( |i> \) to \( |b> \). If state \( |b> \) is the same as state \( |a> \), it is called resonant elastic scattering. If not it gives the resonant inelastic x-ray scattering (RIXS) spectrum. The intensity of RIXS is stronger than that of Thomson scattering because of the resonance effect. Thomson scattering is a function of \( (E_1 - E_2) \) rather than individual \( E_1 \) and \( E_2 \), whereas RIXS scattering depends on \( E_1 \) and \( E_2 \) separately. Therefore, RIXS gives more information about electronic excitation by tuning \( E_1 \) so that different
intermediate states \( |i \rangle \) can be studied.

2.3 Instrumentation

An IXS spectrometer consists of three main parts [13]. They are the monochromator, the analyzer and the detector. The photons from the undulator have about 100 eV bandwidth. The monochromator passes a narrow bandwidth beam to the sample. In nested channel-cut geometry, high energy resolution can be achieved. More technical details about high resolution monochromators can be found in [14]. The scattered beam from the sample is spread out over \( 4\pi \) steradians. It is challenging to do energy analysis on the photons scattered from the sample. Conventional solid state detectors are not capable of giving the higher resolution required. To overcome this problem, crystal analyzers are used together with detectors. An analyzer is a high quality, spherically bent single crystal (usually diced to minimize the stress and strain on the crystal from bending) with a diameter of \( \sim 10 \) cm. The scattered x-ray from the sample has different energies. The task of the IXS analyzer is to reflect back photons with a unique energy to the detector. The crucial quantity is the energy resolution. The energy resolution \( \Delta E \) is given by [15],

\[
(\Delta E)_{geo} = E \frac{\sqrt{3}}{2} \frac{\cos \theta_B}{\sin^2 \theta_B} \frac{D}{L}
\]  

(2.13)
where $D$ is the pixel size, $L$ is the distance between the sample and the analyzer and $\theta_B$ is the Bragg angle.

In general, IXS experiments need an energy resolution of 1 eV or better energy resolution. Usually, higher the resolution, lower the count rate. It is important to decide on the appropriate compromise level. Also, there are technological limits for monochromators and analyzers. More details about the medium resolution IXS spectrometer (120 meV) is given in [16] and a detailed description of the high resolution IXS spectrometer is given in [10], [17] and [18].

In the case of phonon shift measurements on $\kappa$-ET Salt, the best resolution we achieved was about 2 meV at beamline 3ID-C at the APS. For phonon measurements, the analyzers and the detectors were kept at a constant angle and scanning was done by changing the incident energy from the monochromator. In the medium resolution spectrometer, sample, analyzer and the detector are in the Rowland circle [19]. Here we kept the incident energy constant and measured the energy change by moving the analyzer and the detector on the Rowland circle. We have previously measured electronic excitations on a CuPc polycrystalline sample with 300 meV resolution. It came to our attention that with 300 meV resolution, the low energy excitations were not resolved. Once the 2 m arm spectrometer was commissioned with the 120 meV energy resolution Cu $K$-edge (see Appendix A) analyzer, low energy electronic excitations were resolved.
CHAPTER III

COPPER PHTHALOCYANINE (CuPc)

3.1 Introduction

In the field of organic electronics phthalocyanines are useful materials. Among them, CuPc is very important since it has been using for solar cells [20, 21, 22], organic field effect transistors [23] and gas sensors [24]. Understanding the electronic behavior of these phthalocyanines helps to improve the performance of these devices.

Phthalocyanine was discovered by chance in 1928 at Scottish Dyes, Ltd [25]. In 1934 Dent et. al [26] have synthesized CuPc. There are more than twenty different kinds of phthalocyanines available today. Most of the differences among them come from the central atom of the molecule. The center atom could be a metal (including Li, Si, Ti, Fe, Co, Ni, Cu, Zn, Ag, Sn, Sb, and Pb) or two H atoms. Phthalocyanines are almost flat monomers. There are few different phases of CuPc. The $\beta$-CuPc phase is stable up to 560 °C and it is claimed to be the
Figure 3.1: A schematic representation of the molecular structure of copper phthalocyanine molecule (top and side view).

most stable one among the different phases of CuPcs. These different phases come from different orientations of CuPc molecule in the crystal. The solubility of CuPc is minimal but it increases somewhat in highly concentrated sulfuric acid. The CuPc molecule is shown in Fig. 3.1. It is structurally similar to the biologically important molecules, chlorophyll and hemoglobin [27].

Fielding and Gutman [28] estimated the activation energy of CuPc to be 1.64±0.2 eV. This estimation was based on electrical conductivity measurements taken perpendicular to the (010) crystal face. They used the $\sigma = \sigma_0 \exp(-E/kT)$ relationship to calculate the activation energy assuming these materials follow the same relation as in the conventional semiconductors; $\sigma(\sigma_0)$ is the conductivity at temperature $T(T=0)$.

STM measurements by Lippel et al.[29] on CuPc lead to the observation that not
only the inner heavy atoms but also the lighter atoms in the outer benzene rings contribute to highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Optical measurements on CuPc thin films were done by Nahass et al. [30] to determine both absorption and transmission indices. They estimated the fundamental and onset energy gaps at 2.74±0.02 eV and 1.64±0.02 eV, respectively. Ab-initio calculations were done on copper tetraazaporphyrin molecule by Carniato [31]. They used this molecule instead of CuPc molecule to reduce the computational cost, hoping the result would be similar. The calculated energy gap along the molecular plane is 3.1 eV and perpendicular to the plane is 3.5 eV. Their HOMO and LUMO do not agree with the measured values previously reported [29]. CuPc was tested in [22], [32] and [33] for solar cell applications. In all cases the energy gap was determined to be 1.7 eV.

Knupfer et al. [34] have carried out electron energy-loss spectroscopy (EELS) on a α-CuPc thin film sample. Their result was interesting physics, but without data from single crystals the interpretations were limited. These measurements were taken for momentum transfer very roughly perpendicular to the b crystal direction. Electronic excitations/excitons were observed below 0.6 Å⁻¹ momentum transfer region, having some momentum dependence. According to the authors, these excitons could be a mix of intramolecular Frenkel and intermolecular charge transfer excitons.

In this chapter we discuss the β-CuPc crystal preparation method, crystal
properties, HOMO LUMO gap and electronic excitations around 1.3 eV, 1.7 eV.

3.2 CuPc Crystals

3.2.1 CuPc Crystal Growing Method

![Diagram of CuPc crystal growing apparatus setup.]

$\beta$-CuPc crystals were grown by using the method of sublimation. The procedure is slightly altered with respect the procedures described in [35] and [36]. The apparatus was set up as shown in Fig. 3.2. The diameter of the Pyrex tube is about 30 mm and its length is about 1 m. Commercially purchased (Alfa Aesar) CuPc of $\sim$95% purity was used to grow the crystals. About 500 mg of CuPc powder was placed on the copper boat. Copper was chosen in order to minimize the reaction with CuPc. The left end of the Pyrex tube was connected to a carbon dioxide tank and the right end was connected to a liquid gas trap and then to the fume hood. The flow rate of carbon dioxide gas through the system was about
1-1.5 bubbles per sec. Instead of carbon dioxide, any non-interacting gas with CuPc powder (eg: Argon and Nitrogen) can be used. The crystal size is slightly higher when carbon dioxide is used rather than argon. This may be due to the angular shape of the carbon dioxide molecule.

Figure 3.3: Temperature vs. Time plot - Heating pattern for CuPc crystal growing.

A Lindberg/M-55035 oven was used to grow CuPc crystals. The temperature curve is shown in Fig. 3.3. The preheating section was used to remove the impurities. The powder was heated up to 560 °C at the rate of 9 °C/min and kept at this temperature for 3 hours. After that the oven was turned off and allowed to cool down gradually.

The crystals accumulated in one area of the tube. This accumulation area
depends on the temperature of the tube. If the accumulation area is small, the crystals are larger compared to when the accumulation area is big. In order to make the crystal growing area smaller, a simple condenser (a copper wire wrapped around the Pyrex tube with its two ends dipped in cooled water) was added. The resulting crystals were about 1-2 cm long and up to 700 microns wide and their thickness went up to 250 microns.

![CuPc Sample](image1.png) ![CuPc crystal zoomed](image2.png)

Figure 3.4: CuPc Crystal: (a) CuPc sample on the sample mount and (b) zoomed part of the sample.

Fig. 3.4 shows the CuPc crystal which was used to measure the electronic excitations and excitons: the $\beta$-CuPc single crystal on the sample mount (a) and a zoomed area of the crystal (b). CuPc crystals are needle-like. The $b$ axis is the needle axis. Crystals are fragile and the mechanical strength is stronger along the $b$ axis than any other axis. The intermolecular length is the shortest along the $b$ axis compared to all the other crystal directions [37].
3.2.2 CuPc Crystal Properties

<table>
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<tr>
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Table 3.1: Lattice parameters of β-CuPc.

The crystal structure of CuPc was determined using a Siemens SMART single crystal diffractometer available at Material Science Department (MSD), ANL. The CuPc crystal was mounted on a goniometer. Then x-rays with known energy (Mo - Kα source) were scattered off the crystal. These scattered photons were collected by a charge-coupled device (CCD camera). This procedure was repeated a few times while rotating the sample. Collected images were analyzed using the software SADABS. The measured lattice parameters are given in table 3.1. The first column of table 3.1 gives the values obtained by Brown [37] and the second column gives our measured values.

CuPc crystals grow along the b axis. The molecular organization in the crystal is essentially a hexagonal packing of linear chains (along b axis), except that the symmetry is broken by an alternating tilt of the phthalocyanine molecular plane with respect to the chain axis, and by the fact that the chain cross-section is
oblong rather than circular.

Figure 3.5: Schematic representation of the crystal structure of $\beta$-CuPc. All the corner molecules are parallel to each other. The base centered molecules are parallel to each other and are almost perpendicular to the corner molecule. The base centered molecules are located in the center of $ab$ plane.

CuPc has different crystal phases distinguished using Greek letters. Among them, $\alpha$ and $\beta$ are more common than the rest. $\alpha$ is a meta-stable state and $\beta$ is the stable form. One of the significant differences between $\alpha$ and $\beta$ is the overlapping of neighboring molecules in the molecular column; the $\alpha$ phase modification has a larger overlap and hence the lattice constant along the chain axis is shorter than that of the $\beta$ phase [38]. Heating $\alpha$ phase in vacuum at 280 °C for about 2 hours gives the stable $\beta$ phase [39].
3.3 Experimental Procedure

Figure 3.6: A picture of the 2 m arm spectrometer at 9ID-B beamline. G: Sample chamber, H: Analyzer, I: Detector

All the electronic excitations data was taken at the 9ID-B beamline of APS. A picture of the 2 m arm spectrometer at 9ID-B beamline is shown in Fig. 3.6. Fig. 3.7 is a schematic view of the 2 m arm spectrometer (Note: diagram is not to scale, and it shows only the relevant parts). The booster synchrotron injects electrons into the APS storage ring (A). These electrons go through an undulator (B). An undulator is a series of alternating dipole magnets, which oscillate the
Figure 3.7: A schematic view of 2 m-arm spectrometer at the 9ID-B beamline at APS.

Synchrotron beam and generate a tunable source of x-rays with a band pass of \(~100~\text{eV}\). These x-rays are pre-monochromatized by the high heat load (HHL) monochromator (C). The HHL monochromator is made out of a pair of Si (111) crystals. This pre-monochromatized beam has about 1.5 eV energy resolution full width half maximum (FWHM). The secondary monochromator (D) consists of a pair of Si(444) crystals. These crystals monochromatize the beam to about 70 meV resolution. The beam size can be set by two pairs of slits (E). The slit-down beam goes through an ionization chamber (F), which monitors the incident beam intensity on the sample (G). Once the beam hits the sample, the beam is scattered. An analyzer (Ge (733)) (H) is located in the vertical plane with a known angle \(2\theta\) to the incident beam. The analyzer, detector (I) and the sample are in the Rowland circle (J). A detailed description of the Rowland circle is given in [19]. This way only the photons that have a unique energy with about 120 meV band 

26
pass will reflect back to the detector. This unique energy is determined by the positions of the G, H and I elements. A brief description of the Ge(733) analyzer is given in Appendix A.

Before doing any IXS measurements on the CuPc crystal, the spectrometer energy needed to be calibrated. A copper foil 25 microns-thick was placed between an ion chamber \( (I_0) \) and a NaI detector \( (I) \). NaI detectors are capable of capturing large number of photons before getting saturated. The x-rays come through the ion chamber, go through the copper foil and reach the detector. The incident energy was varied from 8.970 keV to 9.040 keV. The results are shown in the Fig. 3.8. The curve \( (f) \) represents the Cu foil absorption spectrum. First peak (peaks were determined from the 2nd derivative of the curve-where second derivative is zero at the edges) is at 8.9805 keV (Cu K-edge). This peak was used to calibrate the energy in the spectrometer. The same procedure was repeated to get the absorption spectra of the CuPc powder sample \( (p) \), along \( a^* (a) \), \( b^* (b) \) and \( c^* (c) \) directions of the CuPc single crystal. Peak A is due to a transition to a bound state, of mostly 1s-to-3d. Peak(s) B (B1 and B2) is (are) due to 1s-to-4p shake up transition due to different ligand orbitals [40]. Peak at at 8.992 keV (B2) is due to the transition 1s-to-3d10L; \( L \) stands for ligand-hole [41]. Peak C is mostly the beginning of continuum from 1s-to-4p. The excitation from 1s-to-4s has no intensity [42].

X-ray absorption is given by \( I = I_0 exp(-\mu x) \), where \( \mu \) is the absorption coeffi-
Figure 3.8: X-ray absorption spectra of: f-25 microns copper foil, p - CuPc powder, a - along a* direction, b - along b* direction and c - along c* direction of a single crystal of CuPc. The y (ln(I₀/I)) axis is scaled separately to fit in the graph.

The absorption coefficient of the material, which depends mainly on the density of the material and the incident energy. x is the thickness of the sample, I(0) intensity after thickness x(0). A detailed theoretical and experimental explanation of CuPc absorption spectrum is given in [41].

For electronic excitation measurements a large, a good quality CuPc crystal was selected. Dimensions of the crystal were 1.5 cm x 700 μm x 220 μm. The crystal directions were found as described above. The oriented crystal was mounted
on a sample holder as shown in Fig. 3.4(a). The sample holder was mounted in a vacuum chamber. The vacuum chamber was attached to a sample stage which can be rotated and translated in order to get the desired direction (see Fig 3.6). This allowed the crystal to be aligned with the x-ray beam.

Using the sample stage, the sample was moved into the beam with the desired crystal direction. The incident energy was fixed at a selected energy and the analyzer was moved to a selected momentum transfer (constant $2\theta$) and the scattered photons with different energies were counted using the detector. This procedure was repeated for different incident energies, for different $2\theta$ values and different crystal directions.

The sample was moved frequently to prevent radiation damage. There was no visual radiation damage on the sample at the end of the experiment.

For the 300 meV resolution experiment, a stack of CuPc crystals was mounted into a sample holder. Here, all the crystals were stacked along the $b$ direction but $a$ and $c$ directions were randomly oriented.

### 3.4 Experimental Data on CuPc

Inspection of Fig. 3.9 shows a peak at around 3 eV, with a 1 eV width. The peak analysis is given in Fig. 3.10. The fitting was done using a Lorentzian
Figure 3.9: IXS Measurements of HOMO-LUMO gap of a bulk sample of CuPc. Measurements were taken at 1 m arm spectrometer at CMC with 300 meV resolution.

function:

$$y(x) = \frac{2A}{\pi} \frac{\omega}{4(x-x_c)^2 + \omega^2}$$

where $A$ is the area, $x_c$ is the position and $\omega$ is the width of the peak. The tails of the elastic peaks were fitted by a quadratic function. According to Fig. 3.10, HOMO-LUMO gap goes from 2.2 eV to 3.8 eV. This width could be due to the broadening in the HOMO and LUMO. The real HOMO-LUMO gap is where the excitation starts near 2.2 eV.

The rest of the scans on an oriented single CuPc crystal were done with the 2 m-arm spectrometer at sector 9, APS. The measured spectrometer resolution was
120 meV.

The peaks at around 1.3 eV and 1.7 eV (Fig. 3.11) are only visible when $b^*$ is parallel to $\vec{Q}$. No excitations appear with momentum transfer along the $a^*$ or $c^*$ axes (Fig. 3.13). This may be due to the way the molecules are packed in $\beta$-CuPc crystals. The effect is unlikely to result from the change in incident polarization. The molecules are tilted by approximately 45 degrees with respect to the $b$-axis (Fig. 3.5), so the component of the polarization along and perpendicular to a molecule remains essentially the same in or perpendicular to the $b^*$ axis. The allowed $\vec{Q}$ range for these excitations is less than 1.0 Å$^{-1}$. Above this value (even at equivalent points in higher zones) no excitation was visible. At low $Q (= 0.24$ Å$^{-1}$) along $b^*$ we also did not see the excitations clearly, probably due to the larger elastic background here. The maximum momentum value 1.0 Å$^{-1}$ corresponds to a real space distance of $\sim 6$ Å. Along the $b^*$ direction the
Figure 3.11: IXS spectra of CuPc. $b^*$ is perpendicular to the polarization vector and parallel with momentum transfer ($Q$). (a) Constant incident energy; $E_i = 8.9755$ keV (5 eV less than Cu $K$-edge). (b) Constant momentum transfer; 0.79 Å with different incident energies. In both plots the data are shifted vertically for clarity. Cu $K$-edge is 8.9805 keV.

molecules are tightly bound and the molecular spacing (center to center) is about 5 Å. Our interpretation is that these excitations involve charge transfer between two molecules, most likely a Mott-Wannier exciton. The excitations only occur along this direction since the molecules are closely spaced. The difference in the energy for the 1.7 eV excitation and a HOMO-LUMO transition is approximately the binding energy, about 0.5 eV for this excitation, which is a reasonable value.
Figure 3.12: Data analysis of the peak around 1.3 eV energy loss and the peak around 1.7 eV energy loss. (a) Peak position vs. momentum transfer. (b) Area of the peak vs. momentum transfer. (c) Width of the peaks vs. momentum transfer. Measurements were done at incident energy 8.9755 keV. Peak fittings were done using a Lorentzian function.

in an organic material [43].

Both peaks were fitted with Lorentzian functions. The peaks properties are given in Fig. 3.12. The error bars were generated from the fitting algorithm. According to Fig. 3.12, inside the $Q$ range of 0.40 Å$^{-1}$ to 1.00 Å$^{-1}$ peaks do not disperse. Fig. 3.11(b) shows that 1.3 eV excitation is from resonant scattering and 1.7 eV excitation is not from resonant scattering.

The resonant 1.3 eV excitation is visible with the incident energy set at the energy of peak A (Fig. 3.8) corresponding to a quadrupolar transition. It also resonates near peak B1 (Fig. 3.8), which is a 1s to 4p transition. The resonant nature indicates that the excitation involves states on the copper atoms, and its
directional dependence argues for an intermolecular excitation. The fact that this state is visible neither in our non-resonant data nor in the EELS or the optical data indicates that it is only weakly excited. It could be a more strongly bound exciton, or the proximity of the two molecules along this crystal direction may result in alterations of the electronic states from the molecular states we calculate.

![Graphical representation](image)

Figure 3.13: RIXS spectra of CuPc; $a^*$ along $\vec{Q}$ (left) and $c^*$ along $\vec{Q}$ (right) directions. In the both case $\vec{Q}$ is 0.64 Å$^{-1}$. The data are shifted vertically for clarity.

In Fig. 3.14( left) there is a resonant peak at an incident energy of 8.992 keV
Figure 3.14: Resonant scattering of CuPc. Left: Resonance scans with $b^*$ parallel to momentum transfer. The left oval in the plot shows the 1.3 eV excitation and the right oval shows the resonant excitation at 2.6 eV. The dashed line shows that the exciton at 1.7 eV is non-resonant. The data are shifted vertically for clarity. Right: Possible states involved in 2.6 eV resonant excitations.

With 2.6 eV energy loss. The incident energy is set to peak B2 which is a 1s-3d10L transition (Fig. 3.8). This excitation is even visible when $\vec{Q}$ is parallel to the $a^*$ direction (Fig. 3.13), but not much clear when $\vec{Q}$ is parallel to the $c^*$ direction. Resonant scattering involves the transition of a copper 1s atom to an intermediate state, and then subsequent decay from the intermediate state to the final state. The localized nature of the copper 1s level means that only intermediate states with copper character are likely to be resonantly enhanced. This excitation has no directional dependence and therefore is mostly likely a localized molecular
excitation. Our calculations indicate the following picture for this excitation (Fig. 3.14 right): At resonance a 1s electron of the copper atom is excited into one of the $d_{z^2-r^2}(\text{LUMO+1})$ orbitals (-2.53 eV ) of the copper atom. Then the HOMO electron (-5.14 eV) will fall into 1s state of the copper atom. The calculation technique is given in the Sec. 3.5.

![Graph](image_url)

Figure 3.15: Calculated x-ray absorption on the CuPc crystal when $a^\ast$, $b^\ast$ and $c^\ast$ parallel to momentum transfer $Q$. The calculations were done for 220$\mu$m and 500$\mu$m thickness.

The graph shown in Fig. 3.15 was obtained as it follows: The x-ray absorption coefficient ($\mu$) was calculated for the energy region of interest (8.850 to 9.100 keV) using [44] and plugged into $I = I_0 exp(-\mu x)$, for $I_0 = 100$. X-ray absorption of a CuPc crystal at 500 microns thickness for an incident energy 8.992 keV is about 94% and the elastic peak is wider in this direction due to the thickness. When $c^\ast$
is parallel to $\vec{Q}$, the sample is about 500 micron-thick. This might be the reason why we do not see this RIXS peak around 2.6 eV energy loss when $c^*$ is parallel to $\vec{Q}$.

![Graph showing IXS phonon measurements of CuPc along (2.2, 0, 2.2) direction and calculated frequencies of atomic vibrations. The small graph shows the higher energy phonons. Calculated values are marked [1].](image)

Figure 3.16: IXS phonon measurements of CuPc along (2.2, 0, 2.2) direction and calculated frequencies of atomic vibrations. The small graph shows the higher energy phonons. Calculated values are marked [1].

We also carried out high resolution IXS studies on CuPc to study the phonons in CuPc. Fig. 3.16 shows the measured phonon spectrum of CuPc along (2.2, 0, 2.2) direction. The resolution was about 2 meV. These measurements were done at 3ID-C beamline at the APS. (A detailed description of phonon measurements on ET-Salt is given in chapter IV.) Calculations of the phonon spectrum was done using Gaussian03 on a CuPc single molecule using B3LYP method and 6-311g basis set (B3LYP and basis set are described in Sec. 3.5). Calculation time...
was about 9 hours in a PC (2GB RAM and 3.2GHz). Calculated values show that possible vibrations go up to 398 meV. These higher energies are mostly from C-H vibrations. This indicates that the peaks at 1.3 eV, 1.7 eV and 2.6 eV are not phonons. One has to note that the calculation was performed on a single molecule and the measurements were done on a single crystal.

Compton scattering is given by:

$$\Delta E \propto \Delta \lambda = \frac{h}{m_e c} (1 - \cos \theta)$$  \hspace{1cm} (3.1)

According to Eq. (3.1), changes in wavelength ($\Delta \lambda$) or energy ($\Delta E$) depend on the scattering angle $\theta$. But according to the measured data (Fig. 3.17), none of
the excitons disperse with the scattering angle. Therefore these peaks at 1.3, 1.7 and 2.6 eV are not from Compton scattering but electronic excitations or excitons.

3.5 Calculations

![Figure 3.18: Structure of CuPc molecule.](image)

Electronic excitation calculations were done using time dependent density functional theory (TD-DFT) [45] as implemented in Gaussian03 [6] on Jazz, one of the supercomputer clusters available at ANL. There are two major steps involved in electronic excitation calculations. The first one is the geometrical optimization of the molecule and the second one is the electronic excitation calculations.

In the process of geometrical optimization, the minimum potential energy surface is determined, thereby predicting the equilibrium structure for the molecular
system. An optimization is complete when the forces are zero. For this purpose in Gaussian03 four parameters are checked. They are force, root-mean-square of the force, displacement to next step and root-mean-square of the displacement. For the optimized conditions these four values must be below the cutoff value. Two types of optimizations are possible. One is called the saddle point and the other is called the stable point. The second derivative of the total energies of the molecule, if all eigenvalues are positive, is a stable point. If there exists at least one negative eigenvalue, then it is a saddle point. These unstable saddle points are transition states of the structures. A detailed explanation of geometrical optimization is given in [46].

To perform a geometrical optimization, one needs the atomic coordinates of atoms in the molecule, basis sets and a calculation method. In Gaussian03 the atomic coordinates can be given as a Cartesian coordinates or as a Z-matrix. Basis sets are a set of coefficients for the functions used to described electron orbitals in an atom, which are expand as a Linear Combination of Atomic Orbitals (LCAO). Eq. (3.2) is a such LCAO. In a basis set both normalization constant and orbital exponent are given.

\[
\phi_i = \sum_{s=1}^{b} C_{si} \chi_s
\]  

(3.2)

\(\chi_s\) is a primitive basis function. There are two types of orbital functions which
have been used for these kind of calculations. They are Slater Type Orbitals (STO) \( \propto \exp^{-r} \) and Gaussian Type Orbitals (GTO) \( \propto \exp^{-r^2} \). STO has higher accuracy with respect to GTO in the vicinity and far away from the nucleus. But STO requires a higher computational cost. In Gaussian03 GTO has been used. Higher \( b \) in Eq. (3.2) will give higher accuracy but also higher computational cost. For the calculations on CuPc molecule, the basis set Wachters+f [47] was chosen for copper. This basis function has been used for similar calculations and has been known as a better basis set for copper [31]. For carbon, nitrogen and hydrogen, atomic orbitals are given by double zeta valence polarized (DZVP) basis sets. All the basis sets were obtained from [48].

Density Functional Theory (DFT) with unrestricted (since there is one unpaired electron) B3LYP [49] was used to perform the optimization. In DFT, energy of the structure is evaluated by electron density instead of calculating the wave function for each electron in the system. Unfortunately, although the results obtained from DFT are usually sufficiently accurate for most applications, there is no systematic way of improving them. Hence in the current DFT approach it is not possible to estimate the error of the calculations without comparing them to other methods or experiments. The DFT energy is given by Eq. (3.3) [50]

\[
E_{\text{total}} = T_0 + \int \rho V_{\text{nuc}} \, d^3r + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{12}} \, d^3r_1 d^3r_2 + E_{XC} \quad (3.3)
\]
where $T_0$ is the kinetic energy of the non-interacting reference system. The second term gives the nuclear interaction energy and the third term gives the electrostatic self-interaction energy. $E_{XC}$ is the density-functional exchange-correlation energy. There are many ways to estimate $E_{XC}$. Becke's three parameter functional called B3LYP is one method. B3LYP is known as a good method for hydrocarbons. B3LYP is a hybrid method that includes a mixtures of Hartree-Fock and DFT exchange-correlations. It is given by:

$$E_{XC}^{B3LYP} = (1 - A)E_{x}^{LSDA} + A E_{x}^{HF} + B \Delta E_{x}^{B88} + C E_{c}^{LYP} + (1 - C)E_{c}^{VWN} \tag{3.4}$$

The first term is from the Local Spin Density Approximation (LSDA), the second term from Hartree-Fock method and the third term from Becke’s gradient correlation. The rest of the terms are from non-local correlation functional provided by Lee, Yang and Parr (LYP) and Vosko, Wilk and Nusair (VWN). The three parameters A, B and C are determined by fitting the function to the experimental data, where $A = 0.80$, $B = 0.72$ and $C = 0.81$. A detailed explanation of the B3LYP method is given in [51, 52]

The atomic coordinates were optimized by using the methods B3LYP and unrestricted Hartree-Fock. In both cases stability checks confirmed that the geometrical optimizations are stable. All these calculations were done for a single
molecule and all the atoms in the molecule have been considered.

We used two kind of CuPc molecules for the calculations. One is based on the atomic positions measured by Brown [37]. The other is 1/8 of the CuPc molecule (see triangle in the Fig. 3.18 ) converted into completely 2D. The rest of the molecule was generated using this part (see Fig. 3.18) which provided a $D_{4h}$ symmetry. Once the optimization was done, the molecule was found to have $C_{2h}$ symmetry. Symmetric calculations were significantly faster than that of the measured molecular geometry calculations. For instance, for a single 120 excitations, the symmetry based calculation took 2.5 hours to complete on 16 nodes each with 2GB RAM. For the calculation with completely measured coordinates the calculation time was 72 hours under the same conditions. With symmetry coordinates, for 180 excitations the computational cost was 165 hours on 8 nodes each with 2GB RAM.

Fig. 3.19 shows calculated electronic excitaton spectrum (convoluted to energy widths of 300 meV). Due to the increasing calculation complexity, the theory only goes up to 5.58 eV. The measured continuum excitation was somewhat consistent with the calculated excitations. Since the oscillator strength is coupled to the dipole moment, non-dipole excitations are not visible in the calculation. They become important mostly at higher $\bar{Q}$ values. Table 3.2 gives the calculated distance between atoms in CuPc molecule with previously measured data by Brown [37]. Calculated electronic density of states (DOS), virtual orbitals (VO) and
molecular (occupied) orbitals (MO) are shown in Fig. 3.20. The low energy VOs are concentrated in few regions (2, 4 and 6 evs). They are consistent with the calculated excitations. Our calculation of the HOMO and LUMO states, as well as the states above and below them in energy, is given in Fig. 3.21. Here the color indicates the spin. There is only very little contribution to the LUMO from the copper atom. Also, it is important to note that outer atoms in the molecule contribute to the HOMO-LUMO orbitals significantly.
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Table 3.2: Distance between atoms of CuPc molecule in Å. Column one is the optimized distances from the B3LYP method for the non-symmetric case, column two is the optimized distances from the B3LYP method for the symmetric case, column three is the optimized distances from the UHF method for symmetric case and the last column is the measured distance by Brown et. al [37]. Notations are as marked in Fig. 3.18. Measured values have an error of around $6 \times 10^{-3}$ Å and for calculated values it is around $10^{-5}$ Å.
Figure 3.20: Calculated Density of States of CuPc using the B3LYP method. — shows the virtual orbitals (VO) and — shows the occupied orbitals (OO). (a) is the full set of VOs and OOs, and (b) is orbitals in between ±100 eV. Left side of (c) is OOs and VOs in between ±10 eV and right side is showing the calculated density of states with 300 meV resolution.

Figure 3.21: HOMO-LUMO orbitals: Orbitals calculated using B3LYP method. Different spins are different colors, and the surfaces shown are equal energy surfaces. (a) HOMO-1 (0), (b) HOMO (2), (c) LUMO (4) and (d) LUMO+1 (0); number of degenerate states are given in the brackets.
CHAPTER IV

ET Salt

The first organic superconductor \(((\text{TMTSF})_2\text{PF}_2 : T_c=0.9 \text{ K at 12 kbar})\) was discovered in 1979 [53],[54]. Bis(ethylenedithio) tetrathiafulvalene (BEDT-TTF) usually, abbreviated as ET, consists of two donor molecules of \([\text{C}_{10}\text{S}_8\text{H}_8]\). There is a large number of organic superconductors based on ET and they have yielded the highest \(T_c\) values for organic superconductors known to date. ET acts as an electron donor molecule and in combination with polymeric anion \([\text{Cu(NCS)}_2]\) makes \((\text{ET})_2\text{Cu(NCS)}_2\). As in \text{CuPc}, ET Salt has different phases, according to the molecular organization in the crystal. A description of \(\kappa\) phase is given under section 4.2. This phase is well-known and has a higher \(T_c\) (=10.4 K) in the family of \((\text{ET})_2\text{Cu(NCS)}_2\) [55].

\(\kappa-(\text{ET})_2\text{Cu[N(CN)}_2]\text{Br [} T_c=11.6 \text{ K}] [56] \text{ and } \kappa-(\text{ET})_2\text{Cu[N(CN)}_2]\text{Cl [} T_c=12.8 \text{ K}] [57] \) are the other members of the \(\kappa\) series of this organic superconductor. \(\kappa-(\text{ET})_2\text{Cu(NCS)}_2\) (also known as ET Salt) is the simplest model in this category. Having a robust knowledge about this ET Salt would help to understand the
superconducting mechanism of the family of ET-based organic superconductors.

ET Salt offers the potential for fine-tuning of electrical properties. This compound has a two-dimensional, layered structure, which may provide significant insight into the nature of superconductivity. These advances will help understand how organic superconductors work and may contribute to the design of new materials with higher $T_c$. Detailed descriptions on these systems are given in [58] and [59].

The phase transition and superconducting mechanism of ET Salt are not yet known. A large amount of both Raman and neutron scattering work has been done on these systems to study the superconducting behavior. In particular, Kozlov [60] et al. have done theoretical calculations of the electron-phonon coupling in these materials. Their work was followed by experimental work by Eldridge et al. [61]. They have carried out Raman spectroscopy to study the electron-phonon coupling. Two different (visible and IR) lasers have given different results due to the resonant nature of the scattering, but the frequency shifts due to electron-
phonon coupling confirmed the validity of the theoretical work. Lin et al. [62] observed phonon softening below 80 K and antiferromagnetic fluctuations. This provides evidence for interaction between phonons and magnetism. Varelogiannis [63] confirmed the argument presented by Lin et al. Also they argue that at small $Q$ electron-phonon scattering dominates the pairing.

Lin et al. [64] used both neutral and deuterated ET Salt to study low temperature softening of some Raman modes. They noticed unusual softening due to the modes involving the C-H bonds and the central double bonds. Pintschovius et al. [65] measured phonon shifts above and below $T_c$ using a deuterated ET Salt. The measurements were done by inelastic neutron scattering on single crystals. Significant frequency changes were observed for phonon energies close to the superconducting energy gap. The observed relative phonon shifts were relatively large compared to those in the classical (Nb) and high-$T_c$ ($\text{YBa}_2\text{Cu}_3\text{O}_\gamma$).

In the BCS model, superconductivity is mediated by phonons. In order to understand the nature of superconductivity, it is therefore useful to study the phonon behavior of these materials. At the superconducting transition temperature $T_c$, electronic density of states of a superconductor changes and causes a change in phonon frequency and linewidth.

In this chapter phonon measurements using IXS in ET Salt along several crystal directions above and below of $T_c$ are discussed.
4.1 Sample Preparation

The sample preparation was done at MSD of ANL by H. Wang, J. A. Schlueter and U. Geiser. The procedure consists of electrochemical oxidation of three different kind of anions (K(18-crow-6)+, (PPN)+, (n-Bu4N)+) with the solvent of 1,1,2-trichloroethane in the presence of CuSCN and KSCN. It takes a couple of months to grow a crystal on a millimeter scale. By changing the crystal growth temperature one can change the phase of the crystal. To get $\kappa$ phase the temperature should be 10 °C [66]. This crystal growing technique is explained in [55, 66, 67].

4.2 Crystal Properties

$\kappa$-(ET)$_2$Cu(NCS)$_2$ has a base-centered monoclinic crystal structure with the space group of $P2_1$. The ET molecule is a dimer. These donor molecules are almost orthogonal to each other. The $\kappa$-(ET)$_2$Cu(NCS)$_2$ unit cell contains two pairs of ET molecules and they stack parallel to each other. The stacked array of cation layers is separated by a 2D layer of Cu(NCS)$_2$ anion molecules (Fig. 4.2). The cation 3D layer of these crystals is an almost insulator, while the anion layer (parallel to $bc$ plane) acts as a 2D conducting layer. These conducting layers almost do not exchange electrons among themselves, thus the conductivity remains two-dimensional. The conductivity ($\sigma$) of the highly conducting plane $bc$ would be...
Figure 4.2: Different crystal views of $\kappa$-(ET)$_2$Cu(NCS)$_2$ (a) ET Salt unit cell, (b) a view long $b$ direction, (c) a view along $a$ direction and (d) a view along $c$ direction.

is about $20 \, (\Omega cm)^{-1}$ $\sigma_c/\sigma_b \approx 2$ and $\sigma_c/\sigma_a \approx 600$ [68]. Here the subscripts stand for the crystal directions.

4.3 Experimental Setup

Phonons have directional dependence. Therefore it is important to know the crystal direction of the sample before the experiment. Single crystal diffraction measurements were done at MSD, ANL to identify the crystal directions. The
measured lattice parameters are given in table 4.1 with values from [55] and [69].

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<th>[69]</th>
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Table 4.1: κ-(ET)$_2$Cu(NCS)$_2$ lattice parameters.

Phonon measurements on the ET Salt have been carried out at the high-energy resolution IXS beam line 3ID-C APS, ANL. A schematic view of the 3ID-C beamline and an image of the spectrometer are given in Figs. 4.3 and 4.4, respectively. White beam comes from the undulator (A). The beam size is set by a pair of silts (B). The beam is monochromated to 21.657 keV using a diamond (111) double-crystal high heat load monochromator (C). The beam passes through an ionization chamber (D), which gives the intensity of the beam. The beam will be

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Figure 4.4: Above: Image of 3ID-C spectrometer at sector 3 APS. Below: Experimental setup.
further monochromatized by a high-energy resolution monochromator (E), which consists of a Si (220) channel cut at 300 K, a cryogenically cooled backscattering monochromator [Si (15 11 9) ] at 123 K and another Si (220) channel cut at 300 K. The monochromated beam is focused on the sample using a toroidal mirror (F). An attenuator (G) is used to reduce the beam intensity when necessary. Again, the beam size is set by a pair of slits. In this experiment the beam size was 200×300 μm². Once again the flux was measured by an ion chamber. Finally, the beam hit the sample (H). The analyzers (I) reflected the scattered 21.657 keV photons back to the detectors (J). The analyzers (10 cm in diameter and 2 mm in thickness) are made out of Si (18 6 0) diced crystals and are spherically bent to a 6 m focusing radius. The 3ID-C spectrometer has four analyzers in a fixed horizontal array. This allows the measurement of four different momentum transfer values (Q) simultaneously. The overall energy resolution of the spectrometer was determined by measuring the scattering spectra of a plexiglass sample for all four analyzers and was found to be 1.9-2.3 meV (FWHM). The total flux on the sample was about 10⁹ photons/s/meV. A detailed explanation of this spectrometer is given in [10], [17] and [18].

The locations of all analyzers in reciprocal space for this experiment are given in Fig. 4.5. The gap between each analyzer is 1.73° (0.33 Å⁻¹). Alignment of each analyzer is very critical and we were not always able to collect data from all four analyzers simultaneously. Also, the signal from each analyzer is different.
Figure 4.5: Positions of the analyzers in reciprocal space. The coordinates are given in $a^*$ and $c^*$ where $b^*$ is perpendicular to the plane. The position of analyzer 1 [labeled: Ana 1] in Figs. 4.8, 4.6 and 4.7 is given in the legend.

from the others. Therefore, it is not straightforward to compare intensities among the analyzers.

The ET Salt crystal was oriented using a single crystal diffractometer at MSD. The oriented crystal was mounted in the sample holder using GE-varnish and Cry-Con thermal conducting grease. GE-varnish is a good low-temperature adhesive and a moderate thermal conductor. Cry-Con is a good thermal conductor but not an adhesive.

The sample mount was attached to an Oxford continuous flow cryostat (CF1108), whose temperature can go as low as 4 K with the correct flow of liquid He. It is necessary to cool down the sample in a controlled way so that the re-arrangement of molecules at low temperatures become more stable, thus providing a higher $T_c$. In some ET-based superconductors, this reorganization of molecules occurs in the
temperature region of 80 K to 65 K [70] and [71]. In this region, cooling needs to be done at a rate of 0.1 K/min to get the highest $T_c$. As a precaution we followed the same procedure on ET Salt. Energy transfer scans on ET Salt were done just above and below $T_c$. As mentioned earlier, the 3ID-C spectrometer is optimized for an energy 21.657 keV. Since the energy resolution is critical, the analyzers, sample and the detectors were kept stationary. The analyzers were looking for 21.657 keV. The incident energy was changed by changing the angles of the secondary monochromator crystals. The difference between the incident energy and 21.657 keV is the energy transfer. Once the $\tilde{Q}$ value for a given crystal direction was chosen the spectrometer was moved in the horizontal plane to get the desired $\tilde{Q}$ value. Due to the temperature changes in the experiment hutch, the analyzer crystals and the monochromator crystals change their lattice parameters. Temperatures were recorded during the scans and the corrections were done using a homemade software ($PADD$), available at sector 3, APS.

Since the phonon intensity drops with the temperature, the low-temperature measurements were more difficult. We have measured phonons along [0,0,$\xi$] and along [3,0,3.5] directions. In a few cases we managed to collect data from all four analyzers. Measured data is shown in Figs. 4.6, 4.7 and 4.8. We observed some phonon shifts, especially along the crystal directions [0,0,4.1] to [0,0,4.7]. The phonon shifts are mostly visible at energy transfers around 3, 12 and 18 meV. These shifted areas are zoomed out in Fig. 4.6. The incident flux was $\sim$30%
lower on the measurements on Fig. 4.6 compared to Figs. 4.7 and 4.8. All the measurements were taken on the same sample.

According to BCS theory, the BCS ratio is given by $\frac{2\Delta}{k_B T_c} = 3.52$, where $2\Delta$ is the energy gap. A significant phonon shift is expected if the phonon energy is close to $2\Delta$ [65]. For $T_c=10.4$ K, $2\Delta$ is $\sim 3.15$ meV. This agrees with the phonon shift in Fig. 4.6. The other shifts observed at 12 and 18 meV are yet to be determined. In all three figures shifts are not very consistent. The phonon around 3 meV changes its characteristics even in Fig. 4.7 it has minimal strength along [3,0,3.5]. Thus, the superconducting energy gap seems to be anisotropic. This may due to the 2D conducting planes in ET Salt, which was described in the beginning of the chapter.
Figure 4.6: Measured phonon spectrum of $\kappa$-ET Salt along crystal direction $[0,0,4.1]$ to $[0,0,4.7]$. Only Analyzer 1 was used. Note: The incident intensity was about 30% lower than the other two set of graphs.
Figure 4.7: Measured phonon spectrum of $\kappa$-ET Salt along crystal direction [0,0,5.1] to [0,0,5.9]. All four analyzers were used.
Figure 4.8: Measured phonon spectrum of $\kappa$-ET Salt along crystal direction [3,0,3.5]. All four analyzers were used.
We have carried out medium resolution IXS measurements on CuPc crystals to study the electronic excitations and excitons. This work was followed by TD-DFT calculations on CuPc molecule. Our measurements show that HOMO-LUMO gap is around 3 eV. Excitations begin at around 2.2 eV, which we call the band gap. Our DFT calculations find a HOMO-LUMO gap at 2.2 eV, in good agreement with the data. This difference is small and indicates that the MOs are only slightly different in the crystal, showing that molecular properties dominate the behavior of these excitations.

Also we observed resonant exciton around 1.3 eV and non-resonant exciton around 1.7 eV. They have a strong directional dependence. The effect is unlikely to result from the change in incident polarization. These excitations are most likely to be in between adjacent molecule along the \( b \) direction. Therefore one can call them Mott-Wannier excitons.

These excitons, especially the one around 1.7 eV, have been observed before
([28], [32] and [72]). But we are the first to report their directional dependence. This dependence is very important in device fabrication, especially in organic solar cell fabrication.

Our calculated electronic DOS show that there are low energy VO bands at \( \sim 2, 4 \) and \( 6 \) eV. Due to increasing calculation complexity, the theory only goes up to \( 5.58 \) eV. The continuum measured excitations somewhat agree with the excitations to VOs. Since the oscillator strength is coupled to the dipole moment, the non-dipole excitations are not visible in the calculation, which is important especially at higher \( \tilde{Q} \) values.

We have carried out high resolution IXS measurements on \( \kappa \)-ET Salt along different crystal directions to study the phonon shifts through the transition temperature. We were able to see evidence for an antisymmetric superconducting gap. Since the intensity drops with the temperature, the low temperature measurements were more difficult. The observed phonon shifts are mostly visible at energy transfers around \( 3, 12 \) and \( 18 \) meV. The phonon shift around \( 3 \) meV is due to the superconducting gap. The other major shifts in optical phonons around \( 12 \) and \( 18 \) meV need to be identified. Further theoretical work needs to be done to understand the phonon modes.
APPENDIX A

Cu K-edge Ge (733) Analyzer

IXS spectrometers require analyzers to analyze the scattered photons from the sample. The fabrication technique for a medium resolution germanium analyzer for IXS spectrometers at APS (sectors 9 and 30) is given below. The reflection is given by the Bragg's law

\[ 2dsin(\theta) = n\lambda \]  

where \( \theta \) is the scattering angle, \( d \) the spacing between scattering plans and \( \lambda \) the wavelength of the incident beam. In order to achieve higher resolution, the analyzer should be close to backscattering geometry. Since the cross section of inelastically scattered photons is small, the analyzer needs to cover a relatively large solid angle. A general description of this kind of analyzers is given in [73]. Ge(733) was selected to measure the energy around Cu K-edge (8.9905 eV). First a 2 mm-thick and 10 cm-diameter (10 cm will give about 0.04 Å\(^{-1}\) momentum...
resolution at 2 m distance) Ge wafer and a BK7 optical glass plate with the thickness of 500 microns were cleaned using Alconox 15%, KOH and Acetone. Then we glued the wafers using EPO-TEK 301-2. It is necessary to have a thin, even, bubble-free layer of glue between the glass and the Ge wafer. The glue was cured at 55 °C inside an oven for about 12 hours with 4 lbs of weight on top of it. The measured glue layer was about 8 microns. The glued Ge wafer was diced with a dicing machine at APS (Kulicke and Soffa 984-10 Plus) using a 50 \( \mu m \)-thick blade. Dicing parameters were: cutting speed 1 mm/s, spindle rotation frequency 20000 rpm and pixel size 450×850 \( \mu m^2 \). Since the analyzer needs to be bent, care was taken not to cut the glass. See Fig. A.1.

Figure A.1: A schematic view of glued diced analyzer

The flat-diced Ge-glass unit needed to be converted into spherical mirror with a 2 m focal length. A few drops of EPO-TEK 301-2 were dropped onto the center of the glass wafer and all the air bubbles in the glue were removed.

A convex glass lens of 1.98 m radius, about 2 cm in thickness and 12 cm in diameter was placed on a mechanical press. A thin rubber layer was placed on...
top of it. The Ge-glass unit was placed on top of it with the Ge wafer face down. A concave lens (2 m in focusing radius, 2 cm in thickness and 12 cm in diameter) was placed on top of the glued side of the glass plate. The thin rubber layer was introduced in between the Ge wafer and the convex glass lens to stop the excess glue from leaking onto convex lens and to reduce the direct force on pixels during bending. This rubber layer also helps to distribute pressure uniformly. The entire unit was pressed at about 1500 lbs overnight. The convex glass lens was used to force the thin glass plate to bend and glue to the concave glass lens uniformly. The setup is shown in the Fig. A.2.

![Diagram of sandwich analyzer](image)

**Figure A.2: Process of bending the sandwich analyzer**

It had been observed that dicing introduces some strain to Ge crystals. H$_2$O$_2$ was used to remove this strain. 30% H$_2$O$_2$ was heated to 65 °C in a wide beaker. The front side of the analyzer was submerged in it for about 1.5 hours. The etching speed depends on the H$_2$O$_2$ concentration, temperature and the crystal
Figure A.3: Ge (733) analyzer at sector 9 APS.

direction. About 20 microns was etched from each side of a pixel. The completed analyzer is shown in Fig. A.3.

In order to study the overall resolution, we used a piece of scotch-tape as a sample. Any material with low x-ray absorption and high diffuse scattering is good for this purpose. The incident energy was fixed at 8.995 keV and the scattered intensities were measured in the vicinity of 8.995 keV while keeping the momentum transfer constant. The measured resolution function is given in Fig. A.4 [16].

The resolution of crystal analyzers has many limitations. The quality of these analyzers can be improved by improving the process of dicing and gluing. Dicing
removes a significant amount of the surface area of the analyzer, which causes a smaller reflective area. Using a strainless, narrow cutting method one can improve the surface area. To get better focusing, a uniform glue layer is needed. One has to know about the curing pattern of the glue to minimize the surface errors. An alternate solution is to bond the Ge(733) wafer to a glass wafer without using any glue (anodic bonding).
APPENDIX B

Electronic Excitation Calculations using Gaussian03

B.1 Input file for the optimization

Header part of the optimization input file is as follows.

```
%RWF=a,400MW,b,400MW,c,400MW,d,400MW,e,400MW,f,400MW,h
%NoSave
%NProcLinda=8
%mem=511mb
%chk=Symmetry3.chk
# opt ub3lyp gen geom=connectivity scf=(conver=6)
```

Input data from Symmetry2-11035.log on Jazz

0 2

This part was followed by the atomic coordinates (given by Z-matrix) and by the atomic connections. Then the basis sets were included [48]. The reader is referred to [46] for details about the input file.

68
B.2 Input file for TD-DFT calculation

Header part of the TD-DFT input file is as follows.

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\%NoSave
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\%mem=1900mb
\%chk=SymmetryTD7.chk
# td=(nstates=180) symm=loose ub3lyp geom=connectivity gen

Input data from Symmetry3-13781.log on Jazz

0 2

B.3 Some useful results

Optimized stable atomic coordinates is give in the table B.1.

Fig. B.1 shows the Millikan charge separation throughout the CuPc molecule. All four benzene rings have a relatively high charge separation compared to some inner molecular atoms. Therefore, it is necessary to include the outer benzene rings in the calculations.
## Table B.1: Optimized atomic positions of CuPc molecule in units of Å. The optimization was done using B3LYP method. Cu was described using Wachters+f basis set and the rest of atoms described using DZVP basis sets

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Figure B.1: Millikan charge distribution of CuPc calculated from B3LYP method. The diameters of the circles are proportional to the value of the charges with red for (-) charge and blue for (+) charge.
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