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Understanding the Dynamics of Molecular Solids

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I would like to dedicate this thesis to my family
for their spiritual support throughout my entire life.

Abstract

Superconductors, single-molecule magnets, and spin-ladders materials are at the center of interest in condensed matter science. All of these materials have incredibly important potential applications and their exploration is the key to the future technologies. We carried out various measurements on representative compounds of each group of interest. The main tool for all these projects was optical spectroscopy, varied in each case to apply magnetic field or change temperature. In our magneto-optical measurements of κ -(ET)₂Cu[N(CN)₂]Br and κ -(ET)₂Cu[N(CN)₂]Cl, we sought to understand correlations between intramolecular vibrations and superconductivity. We found several totally symmetric intramolecular modes that change significantly at the field-induced superconducting to normal state transition. In our polarized vibrational and electronic spectra of [(C₆H₁₅N₃)₆Fe₈(μ_3 -O)₂(μ_2 -OH)₁₂]Br₇(H₂O)Br.8H₂O, we aimed to understand the charge excitations and benchmark electronic structure calculations. We found excellent agreement with theoretical work. And finally, in our low temperature measurements of (DT-TTF)₂Au(mnt)₂, we sought to understand phase transitions and investigate the possibility that this material may be a spin-ladder. We identified and characterized two low temperature magnetoelastic and structural transitions. The overall goal of entire work was to understand mechanisms that drive complicated and challenging physical phenomena.

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Chapter 1

Introduction

Molecular solids are an enormous group of flexible and interesting materials that display many unusual physical properties. Many of them have already been well-studied, but some are still enigmatic like superconductors, molecular magnets, and spin ladder materials. Fundamental investigations of physical properties can bring us closer to the knowledge that will allow us to explore these phenomena in new technologies.

One of the most interesting and desirable problems to understand in physics is superconductivity. It is obvious that many materials have the opportunity to be superconducting (especially at low temperatures, high pressures, etc.), but no one fully understands the mechanism. Additional investigations can also help us to succeed in the ongoing search for a room temperature superconductor. Since 1964, when the superconductivity was suggested to appear in organic materials [1], charge transfer organic solids have been studied as a “key to superconductivity”. These layered materials provide possibilities for many experiments that can not be performed on other superconductors and can provide important knowledge.

Another group of molecular solids that has been of particular interest are molecule-based magnets. This field is quite new, however, there has been a lot of leading theoretical work done on these materials, and reliable information coming from ex-

periments is very precious. Such experiments can help to support “benchmark” theory, check calculations, or “shade light” on low-temperature quantum properties. At the same time these materials have potential applications in information technology [2]. For instance single molecule magnets can decrease the size of the information storage devices and, simultaneously, increase capacity.

Spin-ladder materials are also in the center of interest not only because of their potential applications, but also due to their intermediate structural and magnetic dimensionality. It is important to note that even though the structure of these materials can form a low dimensional ladder shape, the word “dimensionality” also refers to magnetic exchange constants, $J_{\parallel}$ and $J_{\perp}$, of such values that magnetic interactions can take a spin ladder-like form. Materials that are between quasi one-dimensional chains and quasi two-dimensional lattices [3–5] have very interesting relations with magnetic interactions. This specific dimensionality can also lead us to the identification of a new family of high- T_c superconductors [4, 6, 7].

To compare with theoretical predictions many experiments have to be done. Optical spectroscopy is a sensitive technique that allows us to determine various physical properties of materials using electromagnetic radiation. There are three criteria according to which we can define different types of spectroscopy:

- considering the way the light interacts with matter. Here we have absorption, emission, and scattering (Raman, neutron) spectroscopy.
- considering the form of energy of molecules that, because of quantization, creates possibilities of transition between energy levels. This criterium gives us electronic, vibrational, rotational, electron paramagnetic resonance (EPR), and nuclear magnetic resonance (NMR) spectroscopy.
- the energy of the electromagnetic radiation that is absorbed, emitted or scattered - a spectrum range of the radiation. As a result of this criterium, we have radiospectroscopy, microwave spectroscopy, infrared spectroscopy, and others.

Table 1.1: Types of spectroscopy - schematic [8]

Spectroscopy			
radiospectroscopy	microwave	infrared (IR)	visible and ultraviolet (UV-VIS)
NMR	rotational EPR	vibrational (Raman)	electron (Raman)

Note that all these different spectroscopies can overlap, and the last two criteria are tabulated in Table 1.1 [8].

Optical spectroscopy is a perfect method of investigating local microscopic behavior - the source of macroscopic properties. Conditions, according to which the radiation can interact with the molecules, are called the selection rules. For optical spectroscopy the following has to be fulfilled:

- the common condition for any absorption spectroscopy $h\nu = \Delta E$, where h is the Planck's constant, ν - frequency, and ΔE - difference of energy levels,
- during oscillations dipole moment of a molecule changes $\frac{d\mu}{dq} \neq 0$, where μ is dipole moment and q normal coordinate of an oscillation [8].

The selection rules for possible transitions in optical spectroscopy formally specify that only asymmetric modes can be activated in infrared spectroscopy. However, some of totally symmetric oscillations (normally only Raman active) can be activated due to electron-phonon coupling (further discussed in Chapter 2.1.2) and other symmetry-breaking mechanisms.

In this thesis, we investigate the optical properties of three molecular materials. These include κ -(ET)₂Cu[N(CN)₂]Br superconductor and quasi-isostructural κ -(ET)₂Cu[N(CN)₂]Cl insulator (where ET, also known as BEDT-TTF, stands for bis(ethylenedithio)tetrathiafulvalene), the molecule-based magnet [(C₆H₁₅N₃)₆Fe₈(μ_3 -

$\text{O})_2(\mu_2\text{-OH})_{12}]\text{Br}_7(\text{H}_2\text{O})\text{Br}\cdot 8\text{H}_2\text{O}$ (Fe_8Br_8 for short), and $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ (where DT-TTF is dithiophentetrathiafulvalene and $\text{Au}(\text{mnt})_2$ stands for gold maleonitrile dithiolate) a spin-ladder candidate. Our results are compared with ongoing theoretical work.

Chapter 2

Physical Properties of Molecular Solids

2.1 Organic Superconductors

2.1.1 Structure and Arrangement of ET Layers

One of the characteristic features of low-dimension organic materials is quasi-one-dimensionality of their electronic structure, as a consequence of the specific order of molecules within the crystal structure. These systems show a columnar structure and very strongly anisotropic physical properties. Mostly, the columns consist of flat, linearly layered, symmetric, organic molecules (Fig. 2.1) [9]. This particular molecular layout causes strong overlapping of π -orbitals of adjoining molecules in a column (Fig. 2.2). This allows electrons to move within a column. When a conductor, instead of one column, has a whole layer conducting, then this system is called quasi-two-dimensional (Q-2D).

In Q-2D systems, crystals can grow in different phases (Fig. 2.3). In a θ -type layout, each ET molecule is almost isotropically surrounded by six other molecules ET. Depending on electronic interactions, material in this phase can be an insulator,

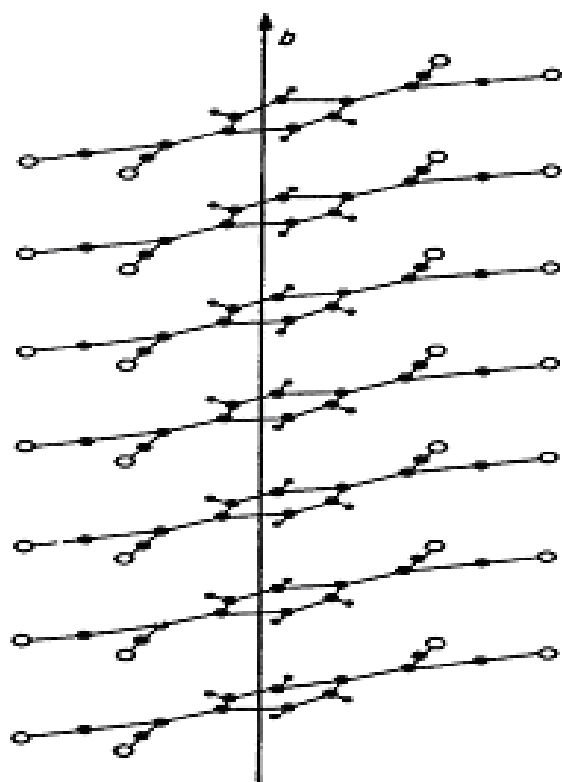


Figure 2.1: Linear alignment of TCNQ molecules along the axis [9].

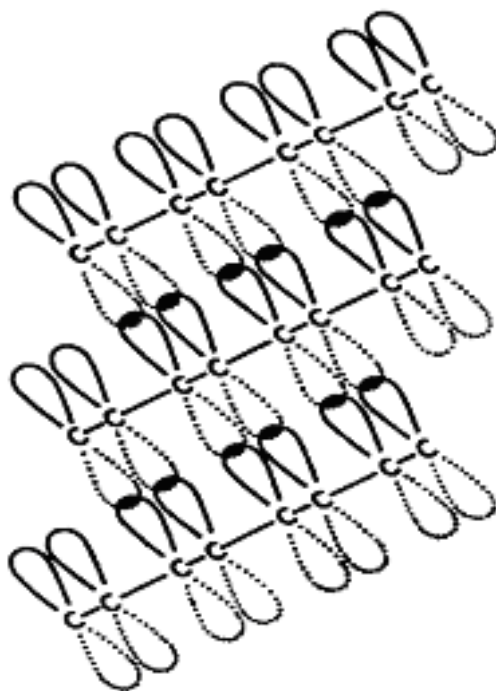


Figure 2.2: Overlapping of π orbitals in a column of TCNQ [9].

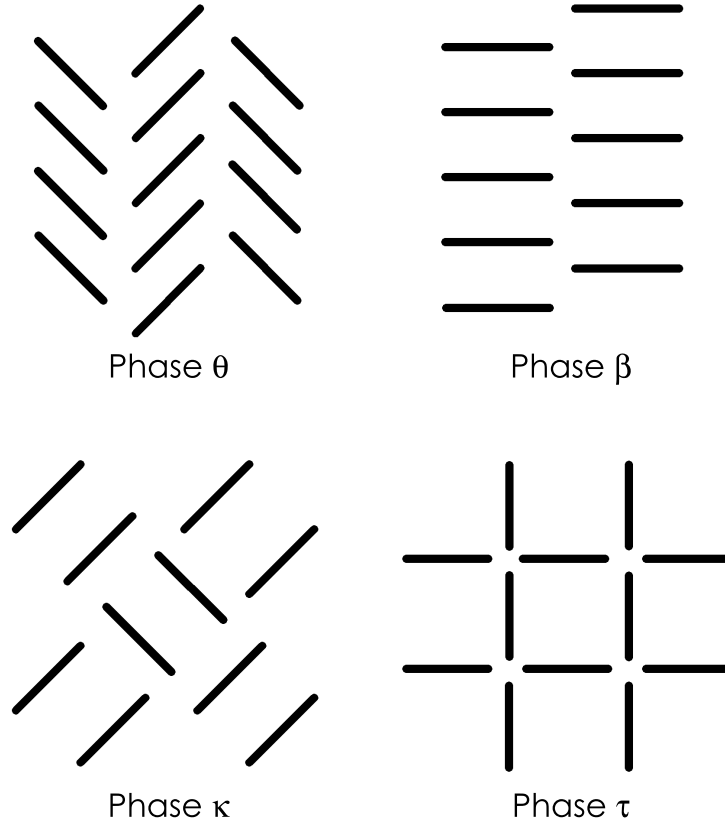


Figure 2.3: The ET molecules layout in various crystallographic phases.

metal or superconductor at low temperature. Materials in β phase consist of regular columns of ET dimers. Short contacts sulfur-sulfur exist only between columns. Intra-dimer interactions are two dimensional. There are many various modifications of β systems dependent on the electronic structure. In κ phase, there are no columns and the conducting layers consist of mutually perpendicular dimers of ET, between which, two dimensional interactions occur. Many ET-based salts, showing the superconducting phase at ~ 10 K, crystalize in the κ phase. The τ -type ordering is more likely to take place when the system consists of asymmetric variations of ET molecule. Here, molecules of the donor are mutually parallel and connected with close contacts. In this type of crystals, electronic conductivity is isotropic within a donor layer.

2.1.2 Electron-Phonon Coupling

Electron-phonon coupling is a cooperative interaction between electron system and lattice vibrations. The consequence of these interactions in a macroscopic view is most pronounced in the temperature dependence of the specific resistance, which grows with temperature. It means that the higher temperature, the stronger electrons are scattered by phonons. In the atomic view, electron-phonon interactions significantly increase the electron's mass, because during its motion, the electron “drags” heavy ions. This effect is very obvious in ionic crystals because of the strong interactions between electrons and ions. Thus low dimensional organic systems have ionic character, electron-phonon coupling (Fig. 2.4) is very important. The coupling between conducting electrons and intermolecular vibrations in these materials shows clearly in the polarized absolute reflectance spectrum. Those vibrations, activated

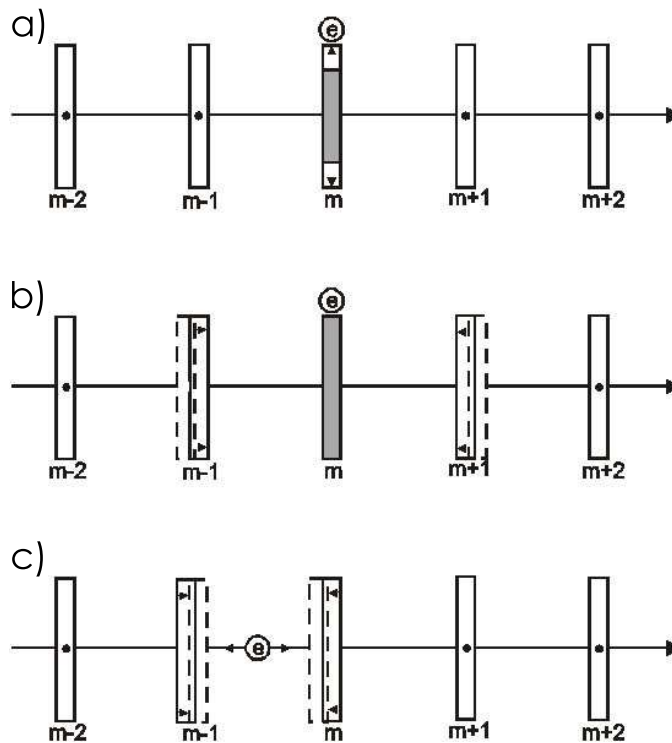


Figure 2.4: The electron-phonon coupling mechanism. Modulation of the electron energy on the core caused by intramolecular vibrations of that core (a), dislocations of the neighbor molecules (b), change of the molecular layout (c) [9].

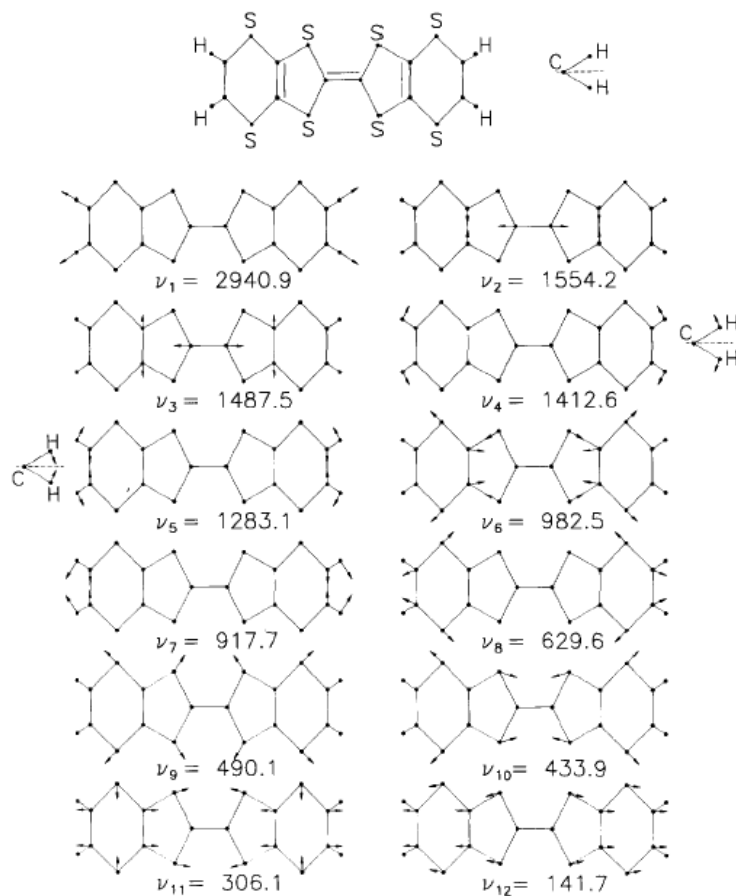


Figure 2.5: Totally symmetric (A_g) vibrations of ET molecule in D_{2h} point group [10].

as a consequence of the coupling, are polarized in the plane perpendicular to a flat organic molecule forming one dimensional column, meaning in a plane perpendicular to the normal vibrations of the molecule. The coupling takes place mostly involving totally symmetric A_g modes, normally not active in infrared spectroscopy. The totally symmetric modes of ET molecule in D_{2h} point group are shown in Fig. 2.5. In the spectrum, they appear as very strong and relatively wide peaks, shifted toward lower energies. The size of this shift depends on the coupling constant [9].

In some cases, the local symmetry of ET molecule is lowered in the solid state. The most common symmetry breaking subgroups for ET molecule are eclipsed (C_{2h}) and staggered (D_2) (Fig. 2.6). These distortions change dynamics considerable (be-

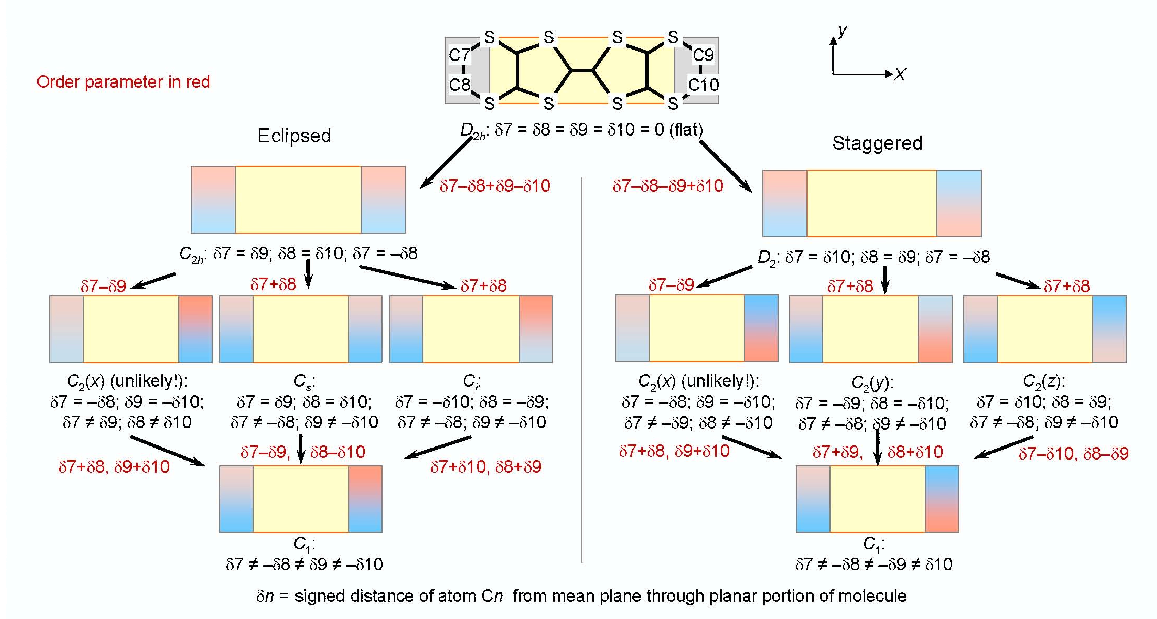


Figure 2.6: Schematic of distortion from planarity in ET molecule [11].

cause the molecule is no longer flat) and increase the number of the totally symmetric modes from twelve to eighteen in C_{2h} and nineteen in D_2 subgroup. In both situations the deformity takes place in the lateral ethylene groups causing the “splitting” of molecular modes [12–18].

2.1.3 Superconductivity

Superconductivity was discovered in 1911 by H. Kamerlingh Onnes [19–21]. The most general definition explains superconductivity as a state in which the electrical resistance of a material disappears. Onnes observed this phenomenal behavior while studying resistance in various metals such as mercury, lead, and tin in small temperature range at a critical temperature T_c , characteristic of the material. The complete disappearance of resistance is most sensitively demonstrated by experiments with persistent currents in superconducting rings, as shown schematically in Fig. 2.7. The next major step toward understanding of superconductivity was an establishment of the existence of an energy gap between the ground state and

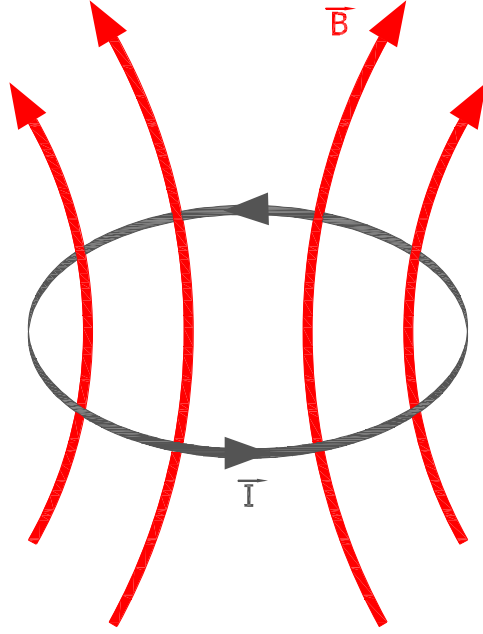


Figure 2.7: Schematic diagram of persistent current experiment [22].

the quasi-particle excitation of the system. This concept was suggested in 1946 by Daunt and Mendelssohn as an explanation the observed absence of thermoelectric effects [23]. The theoretical work was supported by experiment eight years later in precise measurements of the electronic specific heat of superconductors by Corak's group [24, 25]. These measurements showed that the electronic heat well below T_c was dominated by an exponential dependence:

$$C_{es} = \gamma T_c a e^{-\frac{bT_c}{T}}, \quad (2.1)$$

where the normal-state electronic specific heat is $C_{en} = \gamma T$, and $a \approx 10$ and $b \approx 1.5$ are numerical constants [22].

Few years later, another group: Bardeen, Cooper, and Schrieffer (BCS) [26] produced their epoch-making pairing theory of superconductivity. The BCS theory says that even a weak attractive interactions between electrons, such as that caused in second order by the electron-phonon coupling, causes an instability of the ordinary

Fermi-sea ground state of the electron gas with respect to formation of bound pairs of electrons occupying states with equal and opposite momentum and spin. These so-called Cooper pairs comprise the superconducting charge carriers anticipated in the phenomenological theories [22]. The base of this theory was a prediction that a minimum energy $E_g = 2\Delta(T)$ should be required to break a pair, creating two quasi-particles excitations. This $\Delta(T)$ was predicted to increase from zero at T_c to a limiting value such that:

$$E_g(0) = 2\Delta(0) = 3.528kT_c, \quad (2.2)$$

for $T \ll T_c$, where: T_c is the temperature of a superconducting to “normal state” phase transition, k is the Boltzman’s constant. Not only this result agreed with the measured gap widths, but BCS prediction for the shape of the absorption edge above $h\nu = E_g$ (h - Planck constant and ν - frequency) was also in quantitative agreement with the data of Glover and Tinkham [27, 28]. This agreement provided one of the most decisive early verification of the microscopic theory.

Another explanation of superconductivity goes in a different direction, epitomized by Ginzburg-Landau (GL) theory. This theory concentrates entirely on the superconducting electrons rather than on excitations. Already in 1950, Ginzburg and Landau [29] introduced a complex pseudowavefunction ψ as an order parameter for the superconducting electrons such that the local density of superconducting electrons was given by:

$$n_s = |\psi(x)|^2. \quad (2.3)$$

Then, using a variational principle and working from an assumed expansion of the free energy in powers of ψ and $\nabla\psi$, they derived a differential equation for ψ :

$$\frac{1}{2m^*} \left(\frac{\hbar}{i} \nabla - \frac{e^*}{c} \vec{A} \right)^2 \psi + \beta |\psi|^2 \psi = -\alpha(T) \psi, \quad (2.4)$$

where: m^* is the effective mass, $\hbar = \frac{h}{2\pi}$, $i = \sqrt{-1}$, e^* - effective charge, c - speed of light, and $\vec{A}$ - vector potential. This equation turned out to be analogous to the Schrödinger equation for a free particle, but with a nonlinear term. The corresponding equation for the supercurrent (Eq. 2.5) is also the same as the usual quantum-mechanical one for particles of charge e^* and mass m^* .

$$\vec{J}_s = \frac{e^* \hbar}{i 2 m^*} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{e^{*2}}{m^* c} |\psi|^2 \vec{A} \quad (2.5)$$

Two years later, Gor'kov showed that the GL theory was basically a limiting form of the microscopic theory of BSC, where ψ can be thought of as the wavefunction of the center of mass motion of the Cooper pairs [30]. The GL theory embodies, in a most simple way, the microscopic quantum-mechanical nature of the superconducting state crucial for understanding its unique electrodynamic properties. The GL theory introduces a characteristic length: the temperature-dependent coherence length:

$$\xi(T) = \frac{\hbar}{\sqrt{|2m^* \alpha(T)|}}, \quad (2.6)$$

which describes the distance over which $\psi(\vec{r})$ can vary without undue energy increase. In a pure superconductor far from T_c , $\xi(T) \approx \xi_0$, where ξ_0 is the Pippard coherence length defined as follow:

$$\xi_0 = a \frac{\hbar v_F}{k T_c}, \quad (2.7)$$

where v_F is the Fermi velocity and a is a numerical constant [31]. Near T_c , however, $\xi(T)$ diverges as $(T_c - T)^{-1/2}$, since α vanishes as $(T - T_c)$. The ratio of the penetration depth λ and the coherence length ξ defines the GL parameter:

$$\kappa = \frac{\lambda}{\xi}. \quad (2.8)$$

For typical pure superconductors $\lambda \ll \xi$, therefore $\kappa \ll 1$.

The 1950's were very important for the history of superconductivity. In the same year as BCS, Abrikosov published a very significant paper in which he investigated a case of GL theory where κ was large instead of small, meaning $\xi < \lambda$ [32]. This should lead to a negative surface energy, so that the process of subdivisions into domains should proceed until it is limited by the microscopic length ξ . The superconductors that show this different behavior were called “type II superconductors”, to distinguish them from the earlier known “type I” variety. The exact breakpoint Abrikosov calculated as $\kappa = \frac{1}{\sqrt{2}}$ [32]. For materials with $\kappa > \frac{1}{\sqrt{2}}$ instead of a discontinuous breakdown of superconductivity in a first-order transition at H_c , there was a continuous increase in flux penetration starting at a first critical field H_{c1} , and reaching $B = H$ at a second critical field H_{c2} . This situation is shown schematically in Fig. 2.8. Because of the partial flux penetration, the diamagnetic energy of holding the field is smaller, so H_{c2} (given by $H_{c2} = \sqrt{2}\kappa H_c$) can be much greater than the thermodynamic critical field H_c . The state between H_{c1} and H_{c2} is called the mixed state or vortex state. Macroscopically, type II superconductors are not perfectly diamagnetic, and since $|\psi|^2$ goes to zero in the centers of the vortices, there is no energy gap in the cores. In an ideal homogeneous material the flux motion is resisted only by a viscous drag, and type II superconductors show a resistance comparable to that of the normal state, but reduced by a factor of $\sim \frac{B}{H_{c2}}$. In real materials, however, there is always some inhomogeneity to pin the flux, so there is no resistance until a finite current is reached, such that the Lorence force ($\vec{J} \times \frac{\vec{\Phi}_0}{c}$, where $\vec{J}$ is the current density and $\vec{\Phi}_0$ is the flux) is capable of exceeding the pinning force. Actually, even with pinning, the resistance is extremely small, but is not exactly zero. This behavior is due to thermally activated fluctuations that can occasionally overcome the pinning, leading to a small resistance due to flux “creep” [22]. If the material has enough flaws to pin the vortices in place, it forms a well defined vortex lattice.

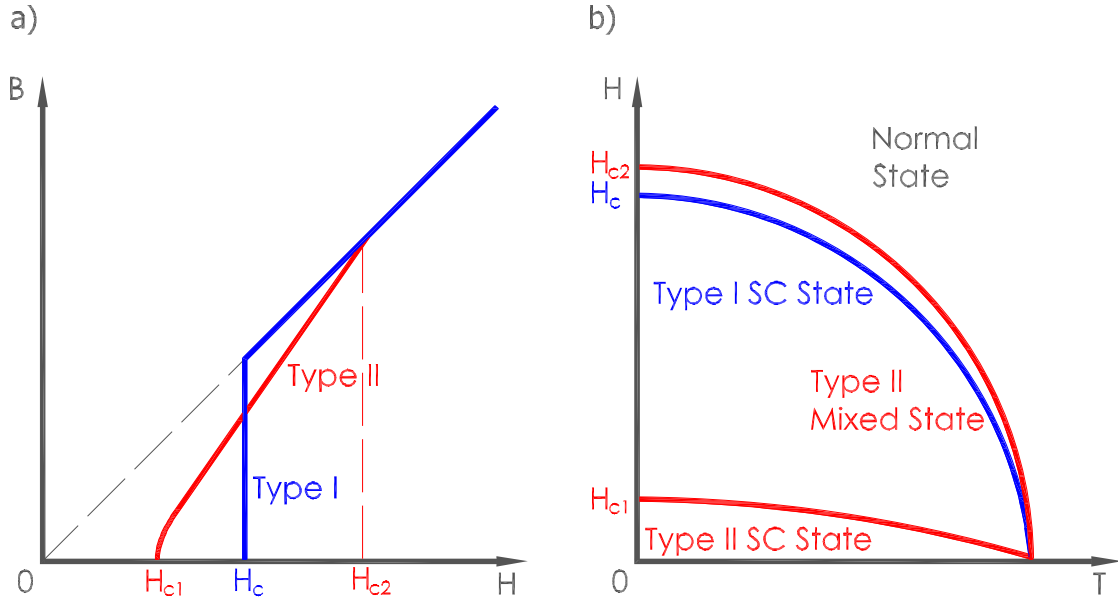


Figure 2.8: (a) A comparison of flux penetration behavior of type I and type II superconductors with the same thermodynamic critical field H_c . $H_{c2} = \sqrt{2\kappa}H_c$. The ratio of $\frac{B}{H_{c2}}$ from this plot also gives the approximate variation of $\frac{R}{R_n}$, where R is the electrical resistance for the case of negligible pinning, and R_n is the normal-state resistance [22]. (b) A schematic plot of the phase diagrams (magnetic field versus temperature) of type I and type II superconductor.

This lattice is two-dimensional in nature, and in two dimensions true long range structural order cannot exist. The nature of the vortex lattice in superconductors, and the subtle role that pinning plays in the properties of superconductors, has been a topic of interest for decades [33].

Superconductivity in organic materials was discovered in 1979 by Bechgaard [34] in $(\text{TMTSF})_2X$ salts (TMTSF stands for tetramethyltetraselenafulvalene and X is a monovalent anion). Since then, there has been on-going research trying to find other organic superconductors that consist of large, flat, organic CT (charge-transfer) molecules. Some of these building blocks are shown in Fig. 2.9. The search for organic superconductors with higher T_c has since made great progress. There are currently more than a hundred examples of such superconductors, including families of superconductors with the same base-molecule. The molecule most often studied, which leads to organic superconductors with the highest T_c , is ET.

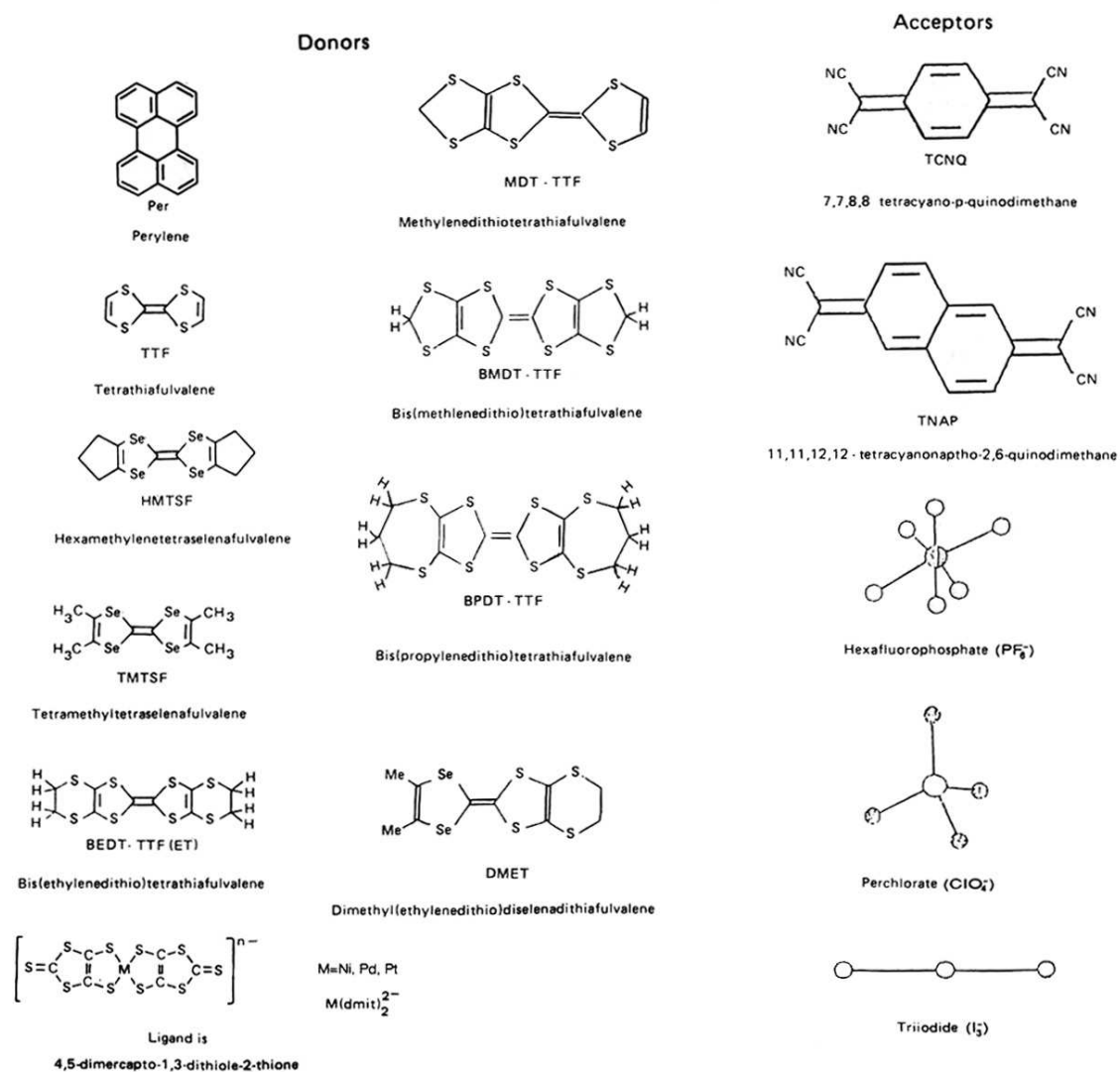


Figure 2.9: Structures of several donor and acceptor species, and anions found in organic CT salt superconductors [15].

2.2 Molecule-Based Magnetism

2.2.1 Magnetic Materials

The essential component of any magnetic material is the presence of the spin associated with an unpaired electron. The way these spins interact with each other determines the magnetic behavior of a magnet. Note, that strong interactions between spins lead to the formation of chemical bonds that lack significant magnetic response. The behavior of magnetic materials is frequently measured in terms of response or susceptibility χ of the material to an external magnetic field (attraction or repulsion). Independent spins, those that do not interact with other spins, exhibit paramagnetic behavior (Fig. 2.10(a)), which as a function of temperature obeys the Curie law:

$$\chi \propto \frac{1}{T}. \quad (2.9)$$

When we start bringing the spins closer to each other, they begin to couple with a tendency toward parallel ($\uparrow\uparrow$) or antiparallel ($\downarrow\downarrow$) alignment. This increases (or decreases) the susceptibility, and this behavior can be modeled as a function of temperature by the Curie-Weiss expression:

$$\chi \propto \frac{1}{T - \theta}, \quad (2.10)$$

where θ is the paramagnetic Curie temperature characteristic of the material. When the spins align parallel, χ is enhanced ($\theta > 0$), whereas in the antiparallel configuration, χ is suppressed ($\theta < 0$), where the magnitude of the Curie-Weiss θ is proportional to the strength of the coupling between adjacent spins [35].

The θ value reflects only short-range spin coupling. Pairwise ferromagnetic coupling ($\uparrow\uparrow$), albeit rare, can lead to long-range ferromagnetic order (Fig. 2.10(b)), whereas antiferromagnetic order may arise from pairwise antiferromagnetic coupling

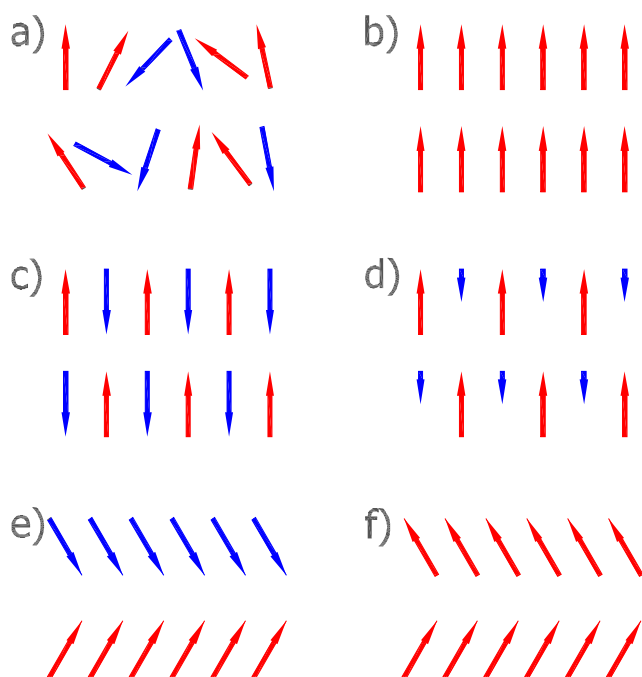


Figure 2.10: Schematic illustration of spin-coupling behaviors, including (a) paramagnetically disordered spins (2D), (b) ferromagnetic ordered (aligned) spins (2D), (c) antiferromagnetically ordered (opposed) spins (2D), (d) ferrimagnetically ordered (opposed) spins (2D), (e) canted antiferromagnets (2D), and (f) weak ferromagnets (2D) [35].

($\uparrow\downarrow$), as shown in Fig. 2.10(c). Ferrimagnets (e.g. magnetite Fe_3O_4) come from antiferromagnetic coupling, which does not lead to complete cancelation, and thus they have a net magnetic moment (Fig. 2.10(d)). All three types of ordering, ferro-, antiferro-, and ferrimagnetic, occur below a critical magnetic ordering temperature T_c . This technologically important ferro- or ferrimagnetic behavior is not a property of a molecule, it is more likely akin to superconductivity - a cooperative solid-state (bulk) property [35].

2.2.2 Origin of Single-Molecule Magnetism

Molecule-based magnets are a broad, emerging class of magnetic materials that shows many interesting properties, more than just typically associated with magnets [35]. Essentially, all of the common magnetic phenomena with conventional

transition-metal and rare-earth-based magnets can be found in molecule-based magnets [35]. Information storage is, certainly, one of the most technologically important uses of magnets. The size of the memory elements is determined by the superparamagnetic size, unfortunately, below which information cannot be permanently stored because the magnetization freely fluctuates [36]. It occurs at room temperature for the particles in the range of 10-100 nm. However, even smaller particles can in principle be used either by working at lower temperature or by taking advantage of the onset of quantum size effects, which make nanomagnets candidates for the construction of quantum computers. An important point is that the properties of magnetic particles scale exponentially and therefore either it must be possible to address individual particles or ensembles of absolutely identical particles must be available. This has presented a formidable challenge, but an attractive solution is provided the recent realization that molecules containing several transition-metal ions can exhibit properties similar to nanoscale magnetic particles (nanomagnets). For this reason, polynuclear metal complexes displaying superparamagnetic-like properties have been referred to as single molecule magnets [36, 37].

The first single molecule magnet, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}\cdot 2\text{CH}_3\text{CO}_2\text{H}$, was discovered in 1993 [36, 38, 39]. Variable-field magnetization and high-frequency electron paramagnetic resonance (HF-EPR) data indicate that this Mn-based magnet has an $S = 10$ ground state [40]. The large spin ground state arises from antiferromagnetic interactions between the $S = \frac{3}{2}$ spins of Mn^{IV} ions and the $S = 2$ spins of Mn^{III} ions, which do not compensate. This lack of mutual compensation of spins is the source of all single molecule magnets existence. An axial zero-field splitting is present, and this leads to a splitting of the $S = 10$ state into 21 levels, each characterized by a spin projection quantum number, m_s , where $-S \leq m_s \leq S$ [36]. The behavior of the magnetization M , in this and other single molecule magnets, is also unique and shows an enormously long relaxation time. It has been conclusively

established that this slow magnetization relaxation is due to an individual molecule rather than to long-range ordering as observed in nanoscale magnetic domains of bulk magnets. Support for this conclusion comes from several experiments, such as magnetization relaxation data for frozen solutions or polymer-doped samples, the absence of any anomaly in heat-capacity measurements (no long-range magnetic ordering), and HFEPR data [36, 40–42]. One exciting phenomenon in single molecule magnets is quantum tunneling of magnetization at low temperatures.

2.2.3 Correlation between the Electronic System, Spin System, and Structure in Fe_8Br_8

The properties of a nanoscale system of coupled spins depend on the strength of the exchange parameters and also on the spin-orbit coupling. It is therefore essential to understand its electronic structure in order to correctly predict the corresponding magnetic behavior. Calculations of the properties of correlated systems present a challenge to mean-field frameworks such as density-functional theory (DFT), because of the difficulty in treating strong ligand-metal interactions [43, 44]. Earlier DFT calculations of magnetic anisotropies in a wide variety of single molecule magnets have shown excellent agreement with experiment [45, 46]. The Fe_8Br_8 system ($[(\text{C}_6\text{H}_{15}\text{N}_3)_6\text{Fe}_8(\mu_3\text{-O})_2(\mu_2\text{-OH})_{12}]\text{Br}_7(\text{H}_2\text{O})\text{Br}\cdot 8\text{H}_2\text{O}$), exceptionally, has been a consistent challenge [47, 48]. The disagreement between theory and experiment in this important test case may originate from an inadequate description of the electronic interaction of the d electrons within DFT. For example, although the theoretically calculated (spin-forbidden) gap between highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO) of Fe_8Br_8 is found as 0.15 eV, the experimentally measured transport gap in the Fe_8Br_8 semiconductor is 1.4 eV [49]. If the transport gap represents the smallest gap in the problem, the difference between theory and experiment would be large even considering the fact that density functional theory

tends to underestimate the gap.

The octanuclear Fe_8 -cluster has the chemical formula $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$, where $\text{tacn} = 1,4,7\text{-triazacyclononane}$ ($\text{C}_6\text{N}_3\text{H}_{15}$). The approximate D_2 symmetry observed in the molecule is formally broken by the presence of halide atoms and waters of crystallization [50, 51]. The central atoms are connected by oxo-hydroxo bridges. The Fe^{III} ions have a d^5 electron configuration. The ferrimagnetic coupling of spins between the eight Fe atoms results in an $S = 10$ spin ground state [52]. The organic tacn -rings are very important for stabilizing the magnetic core of the molecule because the three lone pairs of nitrogen complete a quasi-six-fold environment for the Fe atoms. Further, the tacn rings separate the Fe_8 -clusters in the crystal, resulting in negligible intermolecular dipole fields, typically on the order of 0.05 T [53]. The resulting formal charge states are nominally Fe^{3+} , $(\text{OH})^{-1}$ O^{-2} , and tacn^0 , leading to a molecule with an overall formal charge state of +8 which may then be compensated by the eight negatively charged halide ions. The $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ molecule is the building block of the Fe_8Br_8 molecular crystal.

2.3 Properties of Ladder-Like Materials

2.3.1 Intermediate Dimensionality and Magnetic Interactions in Spin Ladders

Spin ladders are low-dimensional magnetic quantum systems that consist of a finite number of magnetically coupled chains of spins. This coupling causes the intermediate dimensionality of these systems that is between one-dimensional chain and two-dimensional lattice (Fig. 2.11). Especially interesting are ladders with $S = \frac{1}{2}$ spins, which show antiferromagnetic isotropic coupling between the nearest neighbors, and that are generally known as $S = \frac{1}{2}$ Heisenberg antiferromagnetic spin

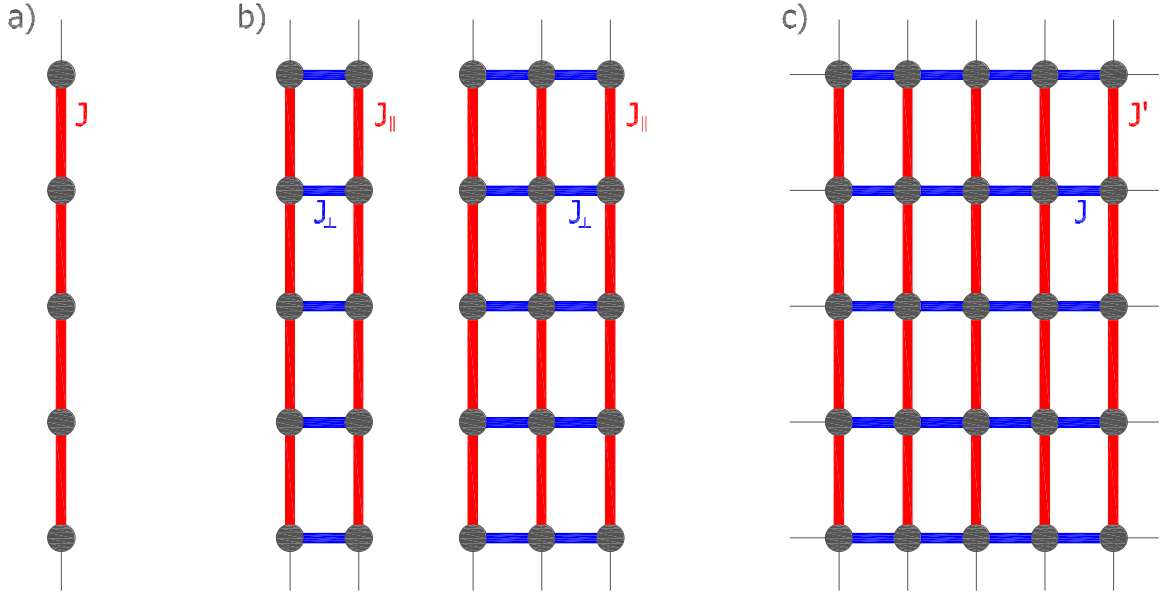


Figure 2.11: Schematic illustration of different kinds of low dimensional magnetic Heisenberg systems with antiferromagnetic couplings: (a) one dimensional chain; (b) two- and three-leg spin ladders, in which $J_{\perp}$ is the coupling along the rungs and $J_{\parallel}$ is the coupling along the rails (called legs or chains as well); (c) two-dimensional square lattice with different exchange coupling constants, J and J' . Black dots denote $S = \frac{1}{2}$ spin-containing units and blue and red lines represent antiferromagnetic interactions of different strength [54].

ladders. The Hamiltonian (Eq. 2.11) defines such magnetic systems,

$$H = J_{\parallel} \sum_{a=1}^L \sum_{i=1}^L S_{i,a} S_{i+1,a} + J_{\perp} \sum_{i=1}^L S_{i,1} S_{i,2}. \quad (2.11)$$

In Eq. 2.11 $S_{i,a}$ is the spin operator at the site i ($i = 1, 2, \dots, L$) on the leg a ($a = 1, 2, \dots$) of a ladder with L rungs; $J_{\perp}$ and $J_{\parallel}$ denote the intra- and inter-rung exchange coupling constants, respectively. According to the definition, $J_{\perp}$ and $J_{\parallel}$ should be positive for antiferromagnetic interactions.

Magnetic properties of spin-ladder systems are particularly interesting as a result of the increased importance of the quantum-mechanical effects operating within them. Theoretical calculations have predicted that spin ladders with an even number of legs have a spin-liquid ground state, so called because of their purely short-range

spin correlations along the legs. These even-leg ladders consist of spin singlet pairs, with a spin-spin correlation length along the legs that shows an exponential decay due to the presence of a finite spin gap. In contrast, a ladder with an odd number of legs behaves quite differently and displays properties similar to those of a one-dimensional antiferromagnetic Heisenberg chain at low temperatures; a gapless spin excitation spectrum and power-law spin-spin interactions which are magnetically ordered [3, 6, 54–64].

Another interesting prediction for two-leg ladders is that light hole-doping can lead to superconductivity, as an effective attraction between “extra” holes arises from the magnetic interactions between the spins of the ladders [55]. On the other hand, odd-leg ladders should exhibit different behavior, because singlet pair formation on their rungs is not possible [57].

Ideal spin ladders are those in which the exchange coupling along the rungs is very similar to the exchange coupling along the rails, that is $\frac{J_{\perp}}{J_{\parallel}} \approx 1$. These systems are intermediate between two extreme cases of isolated dimers ($\frac{J_{\perp}}{J_{\parallel}} \rightarrow \infty$), and isolated one-dimensional chains ($\frac{J_{\perp}}{J_{\parallel}} \rightarrow 0$). Spin ladders of experimental interest are those that have both exchange coupling constants of the same order of magnitude, that is $0.1 \leq \frac{J_{\perp}}{J_{\parallel}} \leq 10$. In addition, ladders should be quite well isolated one from another, since appreciable interladder coupling (J' in Fig. 2.12) can promote a quantum phase transition from the spin-liquid ground state to a magnetically ordered state. It is known that a critical ratio of the interladder to intraladder coupling is $\frac{J'}{J_{\perp}} \approx 0.1$, which separates the spin liquid from an antiferromagnetic-ordered state [65].

2.3.2 Phase Transitions

Any discontinuous change in the physical properties of a system during a continuous alteration of external parameters, is called a phase transition. There are two main kinds of phase transitions, the first and the second order transition. The first order

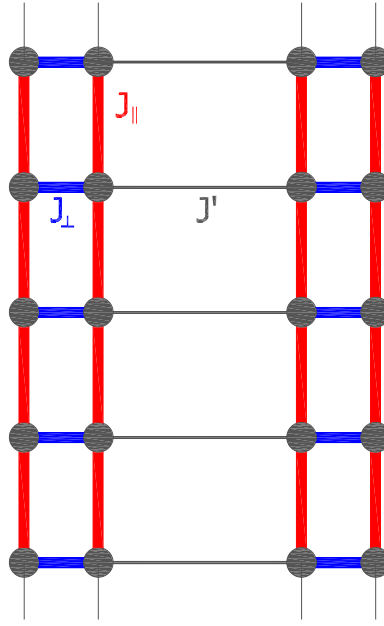


Figure 2.12: A schematic of two-leg ladders showing intraladder ($J_{\perp}$ and $J_{\parallel}$) and interladder (J') exchange couplings. Black dots denote $S = \frac{1}{2}$ spin-containing units [54].

transitions are the change between states of matter where there is a steep change of thermodynamics functions ($\frac{\partial G}{\partial x}$). In the second order transition there is no change in the heat of phase transition, but there is a steep change of, i.e.: specific heat or compressibility constant ($\frac{\partial^2 G}{\partial x^2}$). As an example of the second order transition we have transitions: metal-insulator, metal-semiconductor, metal-superconductor, and also paramagnetic-ferromagnetic, paramagnetic-diamagnetic, or the spin-Peierls transition, etc. Structural transitions are second order, as well.

Chapter 3

Experimental Methods

3.1 Materials of Interest

We have chosen three materials as representative of different groups of molecular solids. First, κ -(ET)₂Cu[N(CN)₂]Br and its chlorine equivalent, κ -(ET)₂Cu[N(CN)₂]Cl (abbreviated as κ -Br and κ -Cl, respectively), were chosen for the opportunities that presents a comparison of a superconductor with a nearly isostructural non-superconducting compound. According to the transport measurement, dc resistivity of κ -Br shows the superconducting transition at $T_c = 11.6$ K (also the glass transition $T_g = 77$ K and the anomaly at $T^* \approx 40$ K) [66–68]. Second, the molecule-based magnet [(C₆H₁₅N₃)₆Fe₈(μ_3 -O)₂(μ_2 -OH)₁₂]Br₇(H₂O)Br·8H₂O, (for short Fe₈Br₈) was selected for study due to the known discrepancies between theoretical and experimental results for the electronic structure. The final material, (DT-TTF)₂Au(mnt)₂, was investigated due to its intermediate dimensionality and potential to be a spin-ladder material.

High quality single crystals of κ -Br, κ -Cl, and (DT-TTF)₂Au(mnt)₂ were grown using electrocrystallization techniques [5, 69–73]. Fe₈Br₈ was obtained by the procedure of Wieghardt *et al.* [50] through a slow evaporation technique. Both κ -ET layered organic compounds were synthesized at Argonne National Laboratory,

USA, (DT-TTF)₂Au(mnt)₂ at Departamento de Quimica, ITN, Portugal, and the molecule-based magnet at the Department of Chemistry, Florida State University, USA.

All the samples are particular and unique. One of the few things that they have in common is their physical dimensions; the size of an average crystal was at most $\approx 0.5 \text{ mm}^3$. To obtain reliable results from such small samples, we had to solve in an appropriate, to their properties, way. κ -Br and κ -Cl were prepared for the high magnetic field measurements. Note, that the signal from the source through the spectrometer, transfer line, sample, to the detector, has a long distance to defeat, therefore there is about 80% - 90% loss of the signal strength. To receive appropriate amount of reflected photons, so that the signal differs significantly from the noise, we built a crystal mosaic on a brass plate (Fig. 3.1). All crystals were oriented facing up the conducting two-dimensional *ac* plane and attached using rubber cement. Since both κ -Br and κ -Cl were prepared to proceed experiment in magnetic field, all materials to create the mosaics were, obviously, diamagnetic. The picture of the crystal mosaic is shown in Fig. 3.1. Crystals of molecular magnets brought up an additional problem - short life time in any environment other than "cold" nitrogen gas. Figure 3.2 displays the comparison of a good sample versus a completely dissolved one. To slow down the process of crystal decomposition additional nitrogen purging was necessary. The crystal was oriented to show the *ab* plane, which allowed us to examine the sample in the two main optical directions: parallel to *b* and perpendicular to *b* (Fig. 3.2). (DT-TTF)₂Au(mnt)₂ challenged us with very low response. Such a low signal is caused by the cryostat (low temperature experiment), and very small crystal area. Looking at Fig. 3.3 we can see, that the small width ($\approx 0.3 \text{ mm}$) of the sample significantly limits the reflecting area of the crystal. We again obtained reliable and consistent results on these needle-like crystals, using knife-edge apertures Fig. 3.3. For the purpose of this experiment we wanted to

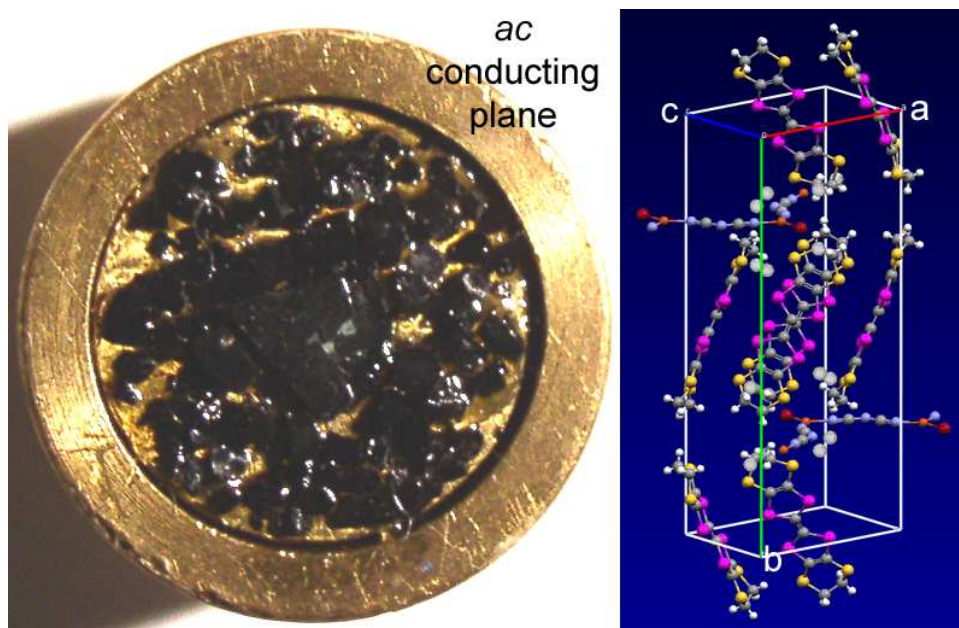


Figure 3.1: Left side: the mosaic of κ -Br prepared on a 9 mm diameter brass plate, attached using rubber cement. All crystals are oriented to show the two-dimensional conducting plane (ac). Right side: a rendering of the molecular structure, showing crystallographic directions [51].

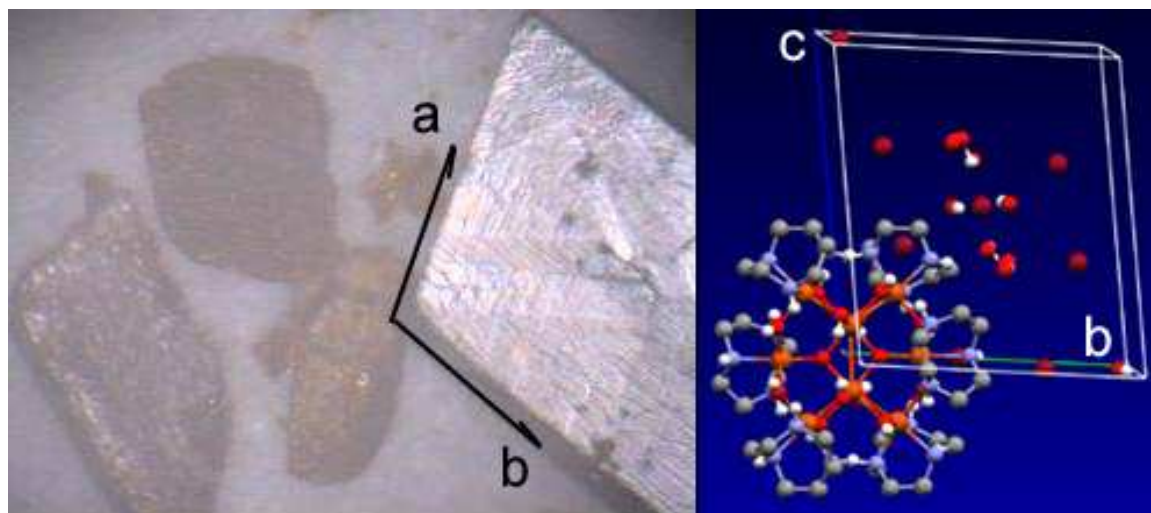


Figure 3.2: Left side: a picture showing comparison of the Fe_8Br_8 the examined crystal was $1 \times 1 \times 0.5 \text{ mm}^3$. Right side: a rendering of the single molecule, with visible Fe–O core, tacn ligand and free Br and water molecules; this structure repeats throughout the whole crystal with different orientations [51].

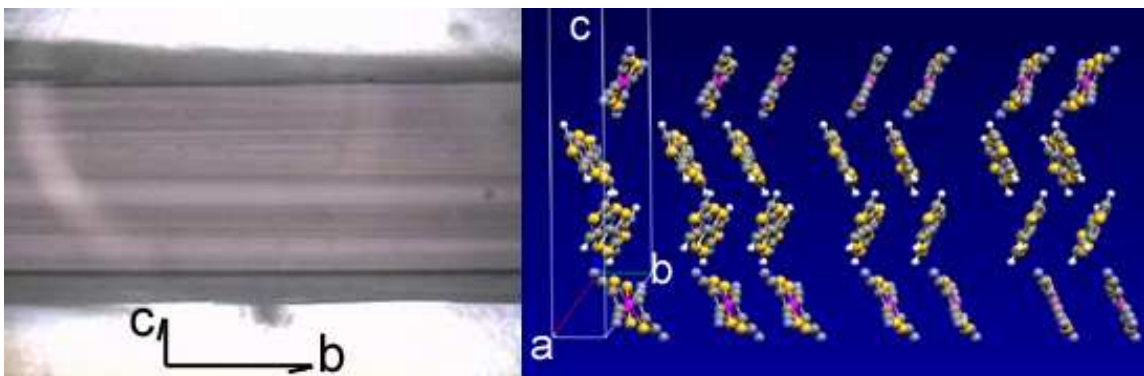


Figure 3.3: Left side: a picture of the $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ crystal, showing the middle infrared aperture. The size of this crystal was $\approx 3 \times 0.3 \times 0.1 \text{ mm}^3$. Right side: a rendering of the crystallographic structure showing columns of DT-TTF (inner columns) separated by the column of gold maleonitrile dithiolate molecules (outer columns) [51].

proceed our measurement in two directions, along the stacks (for legs) and parallel to them (for rungs). Fortunately, the largest plane (bc) of this crystal, corresponds to the desired directions.

3.2 Equipment and Methods

We employed several spectrometers in these measurements: Bruker 113V, Bruker Equinox 55 equipped with a Bruker IRScope II infrared microscope (both Fourier transform, based on the Michelson interferometer, Fig. 3.4), and Perkin Elmer Lambda 900 (a grating instrument). Table 3.1 summarizes technical details of the following spectrometers:

- The Lambda 900 spectrometer features an all-reflecting, double-monochromator optical system. Details of the alignment are shown and describe in Fig. 3.5. To cover the range $3500 - 50000 \text{ cm}^{-1}$ this spectrometer is equipped with two radiation sources: a halogen lamp for the near infrared and visible, and a deuterium lamp for the ultraviolet. Lambda 900 also has two detectors, a photomultiplier for the UV-Vis range and a lead sulfide detector for the NIR range.

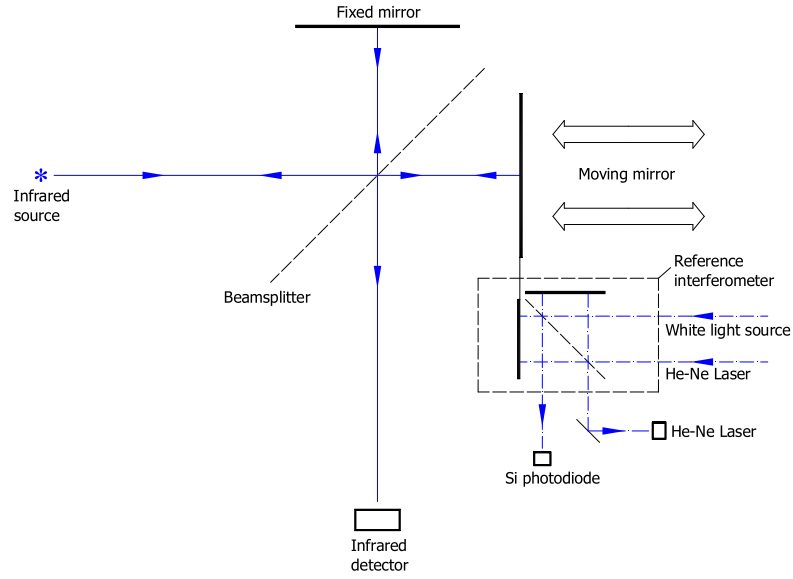


Figure 3.4: The optical diagram of the Michelson interferometer [8].

Table 3.1: Characteristics of employed spectrometers.

Frequency Range (cm^{-1})	Instrument	Source	Beam Splitter/ Monochromator	Detector
20-50	Bruker 113V	Hg Arc	50μ Mylar	4.2 K Silicon Bolometer
35-110	Bruker 113V	Hg Arc	23μ Mylar	4.2 K Silicon Bolometer
80-210	Bruker 113V	Hg Arc	12μ Mylar	4.2 K Silicon Bolometer
180-630	Bruker 113V	Hg Arc	3.5μ Mylar	4.2 K Silicon Bolometer
600-3000	Bruker 113V	Globar	KBr	4.2 K Silicon Bolometer/DTGS
600-7500	Bruker Equinox 55	Globar	KBr	MCT
3500-15000	Bruker Equinox 55	Tungsten (W)	Quartz	InSb
3100-14250	Perkin Elmer Lambda 900	Halogen Lamp	Holographic Gratings with 1440 lines/mm	PbS
11240-31330	Perkin Elmer Lambda 900	Halogen Lamp	Holographic Gratings with 1440 lines/mm	Photomultiplier
31330-50000	Perkin Elmer Lambda 900	Deuterium Lamp	Holographic Gratings with 2400 lines/mm	Photomultiplier

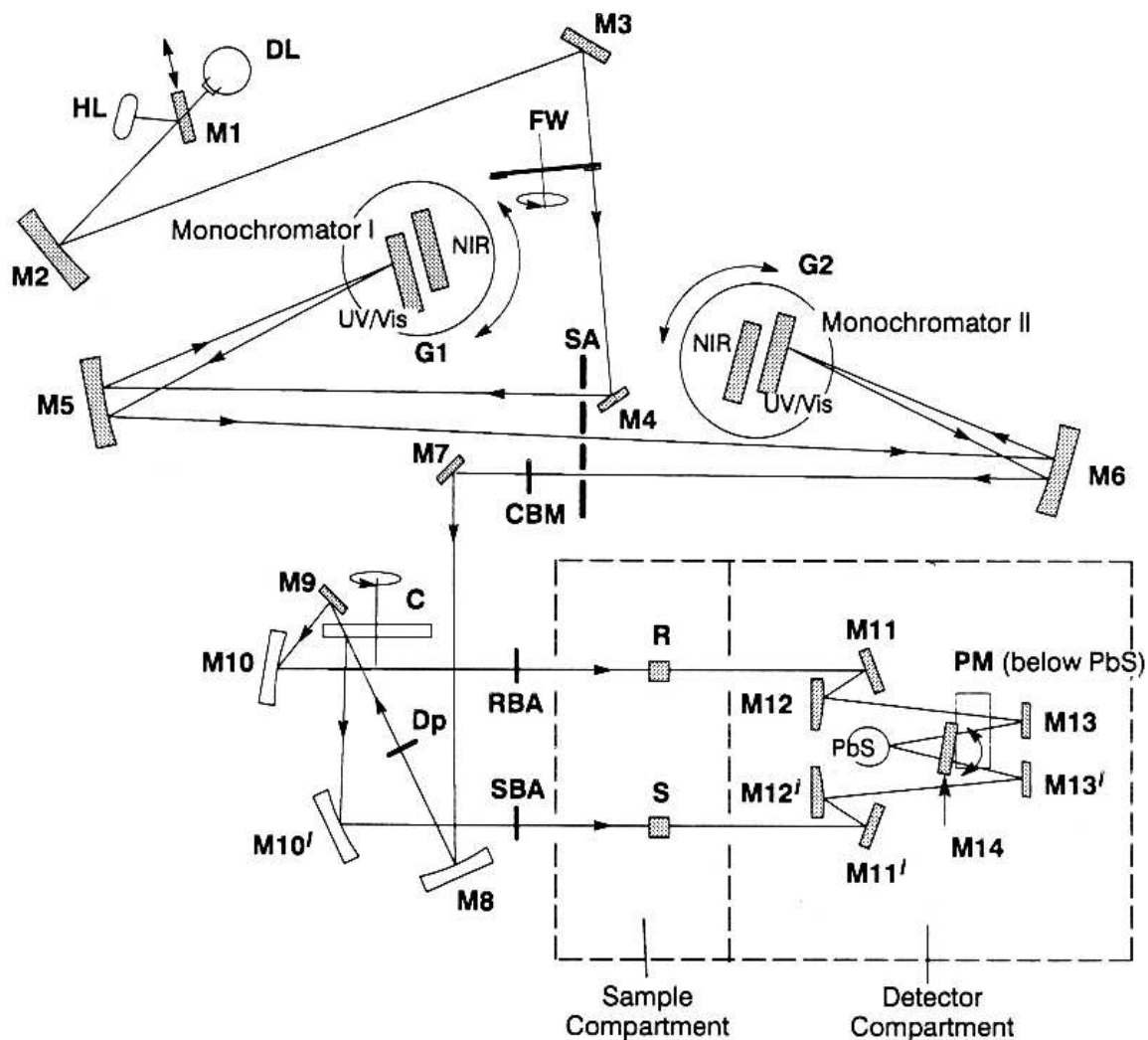


Figure 3.5: The schematic of optical paths in the Perkin Elmer Lambda 900 spectrometer. DL - deuterium lamp, HL - halogen lamp, M1 to M14 - mirrors, FW - filter wheel assembly, SA - slit assembly, NIR - near infrared monochromator, UV/Vis - ultraviolet/visible monochromator, G1, G2 - grating tables, CBM - common beam mask, Dp - depolarizing filter, C - chopper assembly, RBA - reference beam attenuator, SBA - sample beam attenuator, R - created reflected beam, S - created sample beam, PM - photomultiplier (detector), and PbS - lead sulfide detector [74].

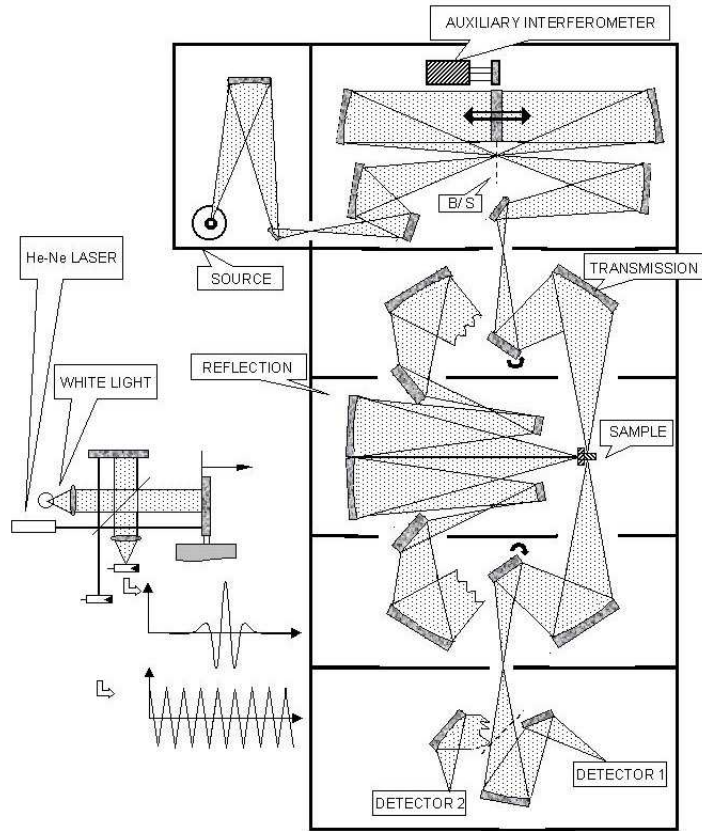


Figure 3.6: The schematic of Bruker 113V with shown optical paths [75].

- Bruker 113V was used to cover the spectrum range of the far and the middle infrared ($30 - 3500 \text{ cm}^{-1}$). The schematic of the set-up and optical path is shown in Fig. 3.6. There are two sources in this instrument: far infrared Hg Arc and middle infrared globar. For detection, Bruker 113V is equipped with 4.2 K silicon bolometer and DTGS
- For the middle and the near infrared region of spectrum ($600 - 15000 \text{ cm}^{-1}$) a Bruker Equinox 55 spectrometer was employed. The source of the middle infrared light is globar, and Tungsten (W) produces higher energy light (near infrared). In addition, the spectrometer was equipped with infrared microscope. The optical paths are shown in Fig. 3.7. Here detectors (KBr and Quartz for middle and far infrared, respectively) are located in the microscope.

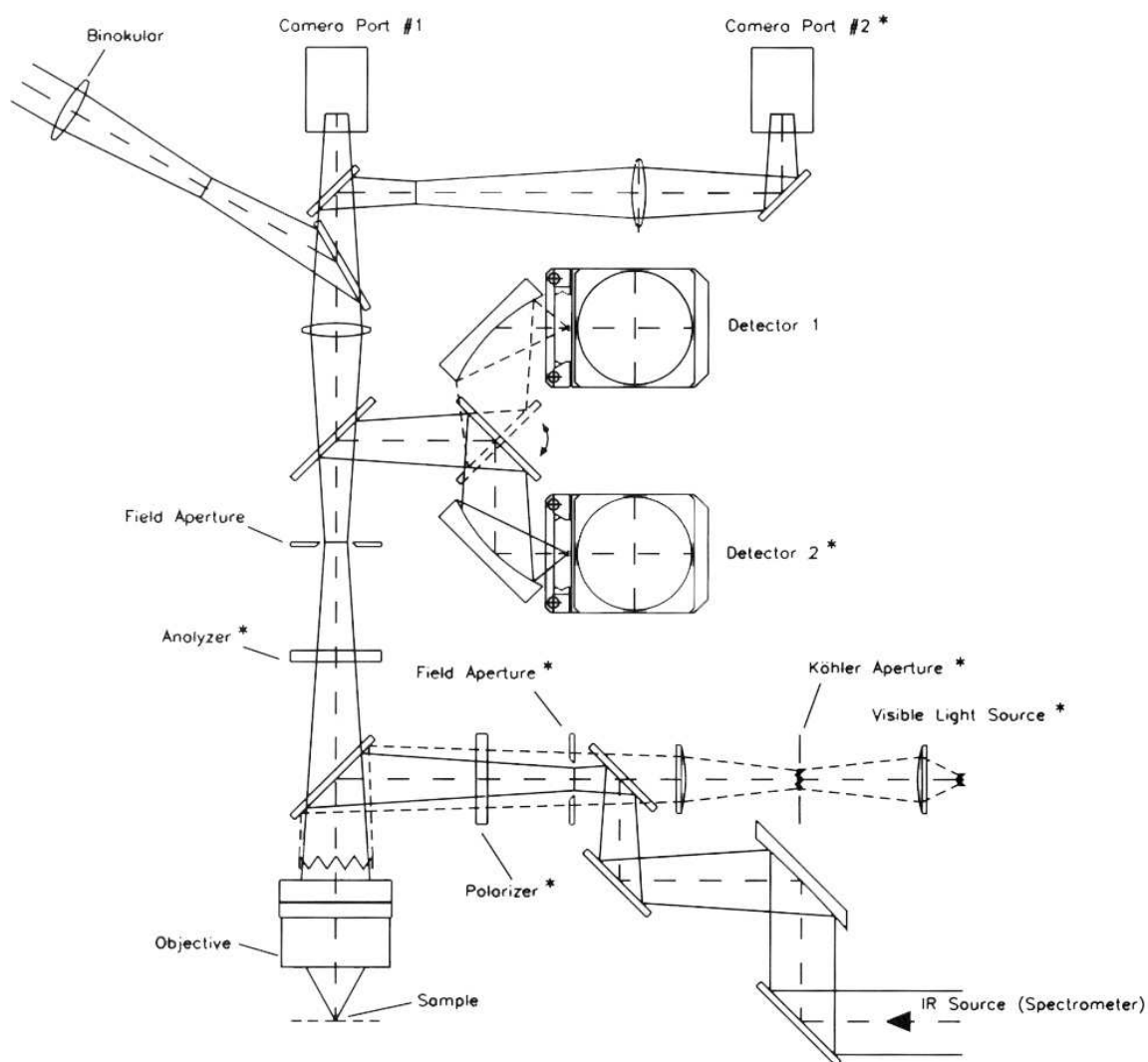


Figure 3.7: Optical paths in reflectance mode of the infrared microscope IRScope. Additional, optional parts are marked with a (*) mark [76].

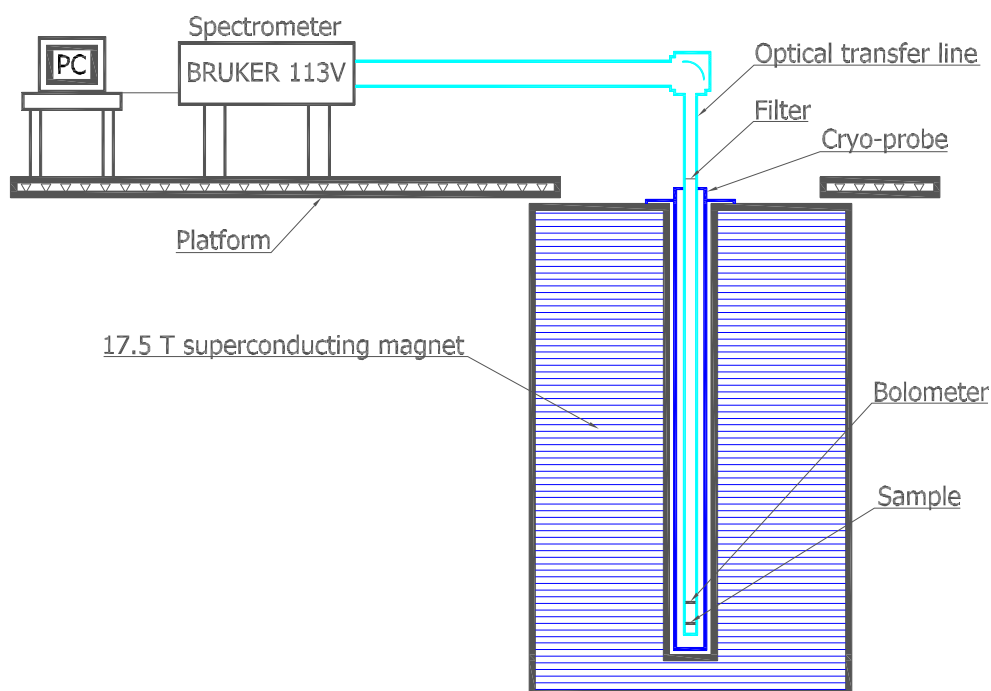


Figure 3.8: Set-up for magneto-optical measurements at the National High Magnetic Field Laboratory.

Since $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ and Fe_8Br_8 molecule-based magnet have anisotropic responses, we applied the appropriate high quality polarizers to each of the spectrometers (or the microscope, in the case of the middle infrared measurements).

Additionally, a low temperature set-up was required to obtain studies of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$. This set-up consisted of a cryostat Microstat^{HE} Oxford, an ITC 601 Oxford - PID (Proportional-Integral-Derivative) electronic temperature controller and a dewar of liquid helium, and it's considered as standard.

In order to complete magnetic field studies of $\kappa\text{-Br}$ and $\kappa\text{-Cl}$ we used a 17.5 T superconducting magnet at the National High Magnetic Field Laboratory. The schematic of the measurement set-up is shown in Fig. 3.8. The magnet consist of superconducting coils through which current flows without loss. This provides a very stable and “low-noise” magnetic field. The disadvantage of superconducting magnets is their limited low value of magnetic field (comparing to the resistive magnets), but

for the purpose of our experiment, the maximum value is sufficient.

3.3 Measurements Details

Experiments on κ -Br and κ -Cl were carried out using the superconducting magnet. We collected reflectance spectra of both materials in carefully selected values of magnetic field between 0 T and 17 T. All the measurements were done at the liquid helium temperature, 4.2 K. The spectral range that was taken with the Bruker 113V was 30 - 2500 cm^{-1} , with 2 cm^{-1} resolution. First we took a measurement with no magnetic field applied ($R(\omega, H_0 = 0 \text{ T})$), and we then started sweeping up the field, collecting spectra for several different values of magnetic field within the superconducting phase (only for κ -Br). We passed the critical field $H_{c2} \approx 6.2 \text{ T}$ [77], changing from the superconducting to non-superconducting phase, and continued taking data up to 17 T ($R(\omega, H)$). After reaching the maximum value, we swept the magnetic field back to 0 T, and took another zero-field scan ($R(\omega, H = 0 \text{ T})$). The procedure for κ -Cl was basically the same, except we did not have to be careful about a critical field, which does not exist in this case.

The Fe_8Br_8 molecule-based magnet measurement was done using Bruker 113V, Perkin Elmer Lambda 900, and Bruker Equinox 55 with IRScope. These spectrometers allowed us to cover a wide energy range (4.5 meV - 5.5 eV or 35 - 45000 cm^{-1}). Reflectance spectra of the crystals and the reference mirror were taken with 2 cm^{-1} resolution (2 nm data interval for Lambda 900). We collected data in two main optical directions of the crystal, $\vec{E} \parallel b$ and $\vec{E} \perp c$, using polarizers and analyzers. This experiment was carried out at room temperature ($\approx 300 \text{ K}$).

The spin-ladder candidate, $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$, was examined using Bruker Equinox 55 with IRScope in the middle and near infrared (600 - 15000 cm^{-1}) with 2 cm^{-1} resolution. Also, we carried out temperature studies using the low temperature station and collected reflectance spectra in two main crystallographic (and

optical) directions: $\vec{E} \parallel b$ and $\vec{E} \parallel c$. We investigated the data at twelve temperatures between 4 and 300 K, concentrating around the 70 and 220 K transitions.

3.4 Calculations

Using the reflectance mode as a measurement method, we need to recalculate all data using Kramers-Krönig (KK) analysis [78]. This allows us to obtain optical conductivity σ_1 from absolute reflectance spectrum (referring to (DT-TTF)₂Au(mnt)₂ and Fe₈Br₈ molecule-based magnet measurements).

A beam of monochromatic light hitting the surface of the crystal does not reflect fully; a small part penetrates to a typical distance of ≈ 3 to $5 \mu\text{m}$, where it is absorbed (Fig. 3.9). The reflected beam is weaker and also has a different phase than the original beam, and the dependence of the phase shift angle θ on the frequency ω , can be calculated through equation 3.1,

$$\theta(\omega) = \frac{2\omega_0}{\pi} \int_0^{+\infty} \frac{\ln \sqrt{R(\omega')}}{\omega_0'^2 - \omega^2} d\omega', \quad (3.1)$$

where: R is the reflectance, ω_0 - the frequency of the incident beam, and ω - the frequency of the reflected beam. KK analysis allows us to calculate dependent on frequency optical constants:

$$n(\omega) = \frac{1 - R(\omega)}{1 + R(\omega) - 2\sqrt{R(\omega)} \cos(\theta(\omega))}, \quad (3.2)$$

$$k(\omega) = -\frac{2\sqrt{R(\omega)} \sin(\theta(\omega))}{1 + R(\omega) - 2\sqrt{R(\omega)} \cos(\theta(\omega))}, \quad (3.3)$$

and the dielectric constants:

$$\varepsilon'(\omega) = n(\omega)^2 - k(\omega)^2, \quad (3.4)$$

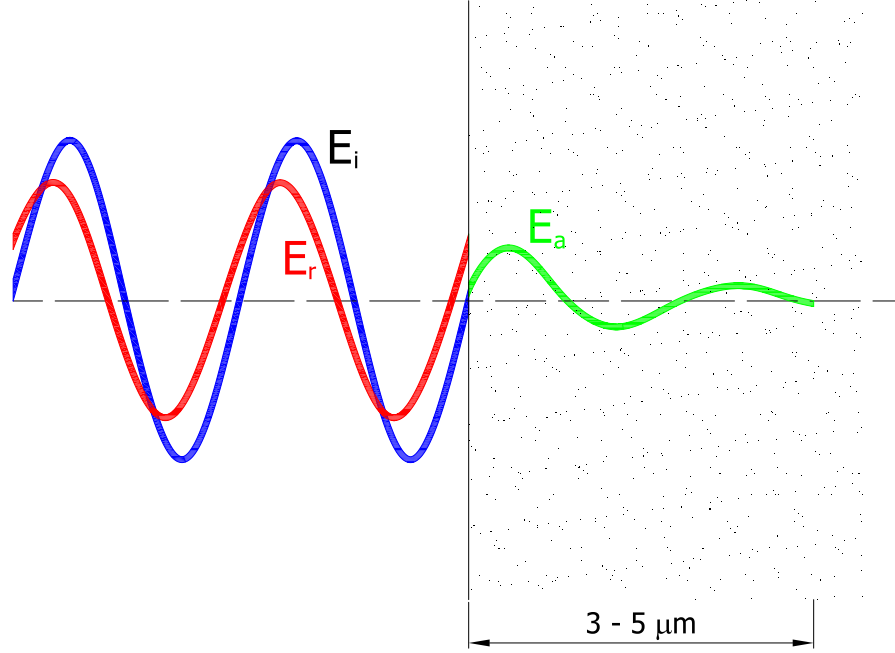


Figure 3.9: Surface reflectance phenomena in opaque solids.

$$\varepsilon''(\omega) = 2n(\omega)k(\omega), \quad (3.5)$$

and the optical conductivity:

$$\sigma_1(\omega) = \omega\varepsilon''(\omega) \quad [\Omega^{-1} \cdot cm^{-1}]. \quad (3.6)$$

The optical conductivity gives us information about the amount of energy that is dissipated in reflectance spectroscopy of solids.

The analysis of electronic bands in the optical conductivity spectrum was carried out using standard procedures of PeakFit[®] software as appropriate. We tested many parameters of fitting lines, and decided to use the Voight oscillator function for all bands. The estimated errors were about 1% for the peak position and about 10% for oscillator strength. Our choice of base line gave the largest contribution to the intensity error and it is typical for spectral fits.

All the dynamic calculations for the assignment of modes were carried out using TITAN[®] software [79]. Because these calculations were done on molecular solids, we determined molecular motions of a single molecule (a building block molecule) [80,81].

For the organic superconductor measurement and its non-superconducting equivalent, we had to use a different method of calculations - a reflectance ratio. Since the purpose of that measurement was to find differences that occurs in phonons with applied magnetic field, we divided the reflectance spectrum taken in the magnetic field ($H \neq 0$) by the spectrum taken at the beginning of the measurement in zero field (Eq. 3.7),

$$\text{reflectance ratio}_H = \frac{R(\omega, H)}{R(\omega, H_0 = 0 \text{ T})}. \quad (3.7)$$

The last measurement - with no magnetic field ($H = 0$ after sweeping down the field) - gives us a reflectance ratio:

$$\text{reflectance ratio}_0 = \frac{R(\omega, H = 0 \text{ T})}{R(\omega, H_0 = 0 \text{ T})}, \quad (3.8)$$

which is very important in further discussion of the reliability of our results. We were able to quantify these changes by integrating the area of the reflectance ratio spectrum below and above the unit line, using the following equation:

$$\text{integrated area} = \int_{\omega_0}^{\omega_1} \left| \frac{R(\omega, H)}{R(\omega, H_0 = 0 \text{ T})} - 1 \right| d\omega, \quad (3.9)$$

where ω_0 and ω_1 define the frequency range of interest (415 - 455, 850 - 900, and 1150 - 1450 cm^{-1}).

Chapter 4

Results and Discussion

4.1 Understanding the Magnetic Field-Induced Superconducting to Normal State Transition in κ -Phase Organic Superconductors

The vibrational properties of κ -(ET)₂X-type organic molecular superconductors (X = counterion) are usually interpreted as a superposition of local intramolecular and extended lattice modes [82–85]. Intramolecular modes related to the ET building block molecule are observed above 100 cm^{−1} and traditionally assigned in D_{2h} symmetry [10, 83, 85], which is an approximation that yields 12 totally symmetric modes, that are observed in the infrared spectrum due to EMV coupling [86]. The totally symmetric C=C stretch (ν_3) is the strongest mode in the optical conductivity spectrum [10, 85]. Within the D_{2h} picture, the infrared response also includes selected B_g modes [10], as well as normally infrared-active modes of B_u symmetry. Vibrational modes related to the central tetrathiafulvalene skeleton of the ET molecule seem to be reasonably described by the planar (D_{2h}) approximation. On the other hand, it is well known that distortions of the lateral ethylene groups lower overall molecular symmetry in the salts [12, 13, 15]. The two main deviations from planarity are C_{2h}

(eclipsed) and D_2 (staggered) [17,18]. Note that twisting of the ethylene group with respect to the molecular ET plane constitutes a local deformation, not a long-range change in the unit cell. At this time, only selected molecular dynamic calculations have been carried out in reduced symmetry conformations [16–18]. In the C_{2h} case, 18 totally symmetric (A_g) modes are predicted, whereas in the D_2 subgroup, 19 totally symmetric (A) modes are anticipated [16–18,87,88]. The conventional numbering scheme goes from highest to lowest frequency, therefore a proper renumbering of these modes is needed. Of particular interest in this rendering is the reassignment of the strong C=C stretching motion as ν_4 and the vibronic activation of the $\sim 880\text{ cm}^{-1}$ mode (ν_{10}) [10]. This is the first case of introducing those well known modes in non-planar symmetry [18,87].

Figure 4.1 shows the evolution of the 4.2 K reflectance ratio spectrum of κ -Br with applied magnetic field. Systematic modifications are observed in three areas, which, from the perspective of organic materials, are quite substantial. We assign these structures as the modification of EMV-activated totally symmetric intramolecular modes of the ET building block molecule [10]. Within the C_{2h} subgroup picture, the features are attributed to ν_4 (A_g), ν_{10} (A_g), and ν_{13} (A_g). The approximate eigenvector patterns are shown in Fig. 4.1. An important consequence of dynamic simulations in reduced symmetry molecular subgroups is the renumbering of the modes. We emphasize that low-frequency motion involving the outer portion of the ET building block molecule is more strongly affected by local symmetry reductions than motion involving the central skeleton of the molecule [10]. The sharp features superimposed on the broad totally symmetric C=C stretching mode near 1270 cm^{-1} in Fig. 4.1(a) are related to the narrow antiresonance dips which appear in the absolute reflectance spectrum [10]. These dips superimposed on the broad and strong ν_3 (A_g) vibronic mode in κ -(ET) $_2X$ organic superconductors are typically assigned as related to vibronic ν_5 (A_g) in D_{2h} point group symmetry. We suggest that similar

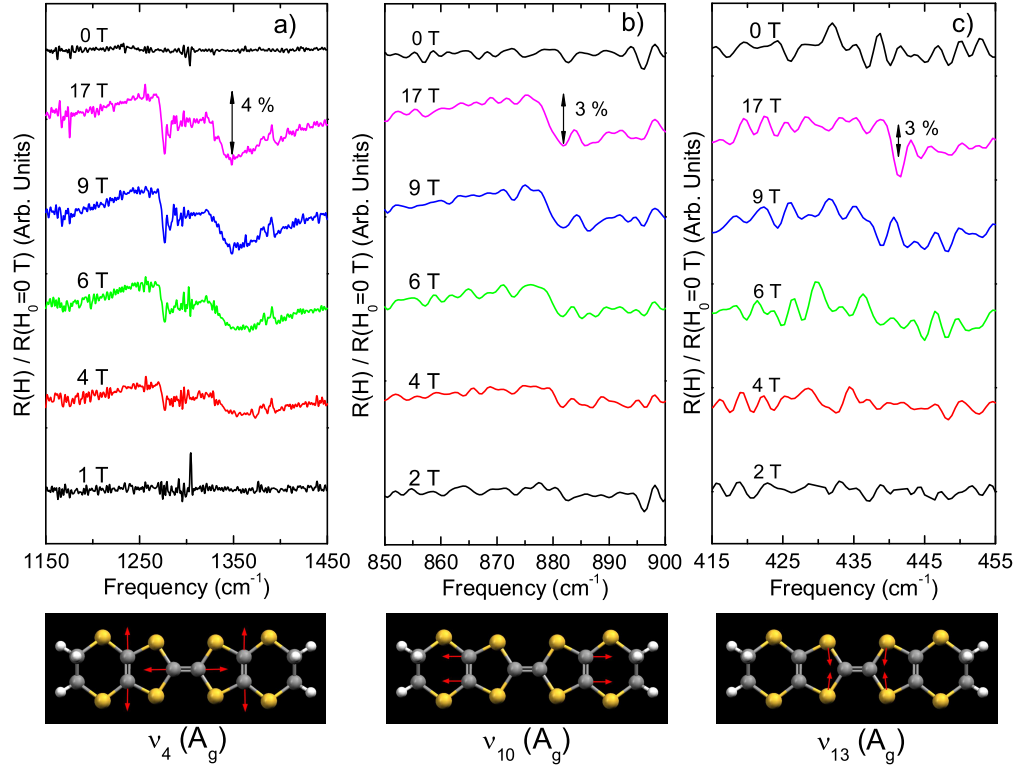


Figure 4.1: The reflectance ratio spectra, $\frac{R(\omega, H)}{R(\omega, H_0=0 \text{ T})}$, of the (a) ν_4 (A_g), (b) ν_{10} (A_g), and (c) ν_{13} (A_g) modes of κ -Br at 4.2 K. The top curve in each panel shows the reflectance ratio $\frac{R(\omega, H=0 \text{ T})}{R(\omega, H_0=0 \text{ T})}$, which provides an indication of the noise level. The double arrows indicate the size of field-induced changes at 17 T. The reflectance ratio curves have been offset for clarity. Relevant motion in C_{2h} (eclipsed) molecular symmetry [18, 87, 88] is drawn as well.

attribution can be done within the D_2 description.

Figure 4.2(a) displays a close-up view of the $\frac{R(\omega, H=17 \text{ T})}{R(\omega, H_0=0 \text{ T})}$ reflectance ratio spectrum of κ -Br in the vicinity of the C=C stretching motion compared with similar data on the two quasi-isostructural compounds κ -(ET)₂Cu(SCN)₂ (shortly, κ -SCN) and κ -Cl. We assign the broad and complex changes observed in the two organic superconductors to field-induced modifications of the totally symmetric ν_4 mode. Although of different magnitude, the field-induced spectral changes in κ -Br and κ -SCN are similar in character. Interestingly, the quasi-isostructural antiferromagnetic insulator, κ -Cl, does not display any field-induced modifications in this totally symmetric mode within our sensitivity. The magnetic field-induced effect on the totally symmetric C=C vibronic mode between κ -Br and κ -Cl seems attributable due to differences in the low-energy electronic state.

We quantify changes in ν_4 for the two organic superconductors by plotting the normalized integral area of the field-induced features vs. applied magnetic field (Fig. 4.2(b)). Strikingly, the vibrational features grow substantially with field in the superconducting phase, show a clear correlation with H_{c2} (for κ -Br $H_{c2} \approx 6.2 \text{ T}$ and for κ -SCN $H_{c2} \approx 4.5 \text{ T}$ [77, 89]), and saturate in the high-field normal state. Saturation of the magneto-infrared effect at 17 T is strong evidence for the supposition that the observed vibrational changes below H_{c2} are associated with the superconducting portions of the mixed state [90]. In the superconducting state, vortex core size goes linearly with applied magnetic field [22], consistent with the observed field-induced change in the vibronically couple modes below H_{c2} (Fig. 4.2(b)) in the κ -phase organic solids studied here. That the EMV-coupled modes show little magnetic field dependence above H_{c2} also connects this effect to the local charge environment and the idea that the low-energy electronic structure is changing with field. Experimental evidence for such a supposition comes from the recent work of Kimura *et al.* on [2,2]-D- κ -Br, where the charge transfer excitation seems to change with applied

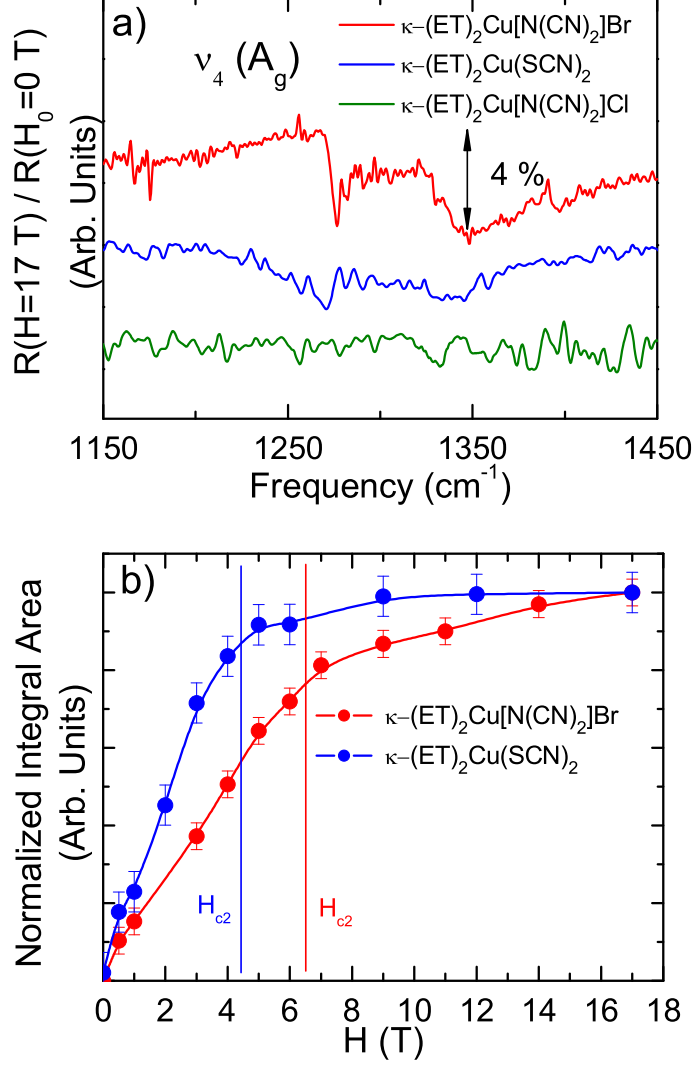


Figure 4.2: (a) Reflectance ratio, $\frac{R(\omega, H=17 \text{ T})}{R(\omega, H_0=0 \text{ T})}$, of the totally symmetric C=C stretching mode for $\kappa\text{-Br}$, $\kappa\text{-SCN}$, and $\kappa\text{-Cl}$ at 4.2 K. The double arrow shows the size of the field-induced features. The reflectance ratio curves have been offset for clarity. (b) Normalized integral area of the changes in the reflectance ratio of the totally symmetric C=C stretching mode versus applied magnetic field for $\kappa\text{-Br}$ and $\kappa\text{-SCN}$. Solid red and blue vertical lines indicate H_{c2} values for the $\kappa\text{-Br}$ ($H_{c2} \approx 6.2 \text{ T}$) and $\kappa\text{-SCN}$ ($H_{c2} \approx 4.5 \text{ T}$) superconductors, respectively [77, 89]. Lines connecting the data points guide the eye. Estimated error bars, obtained from a similar analysis of the $\frac{R(\omega, H=0 \text{ T})}{R(\omega, H_0=0 \text{ T})}$ ratio spectra are shown.

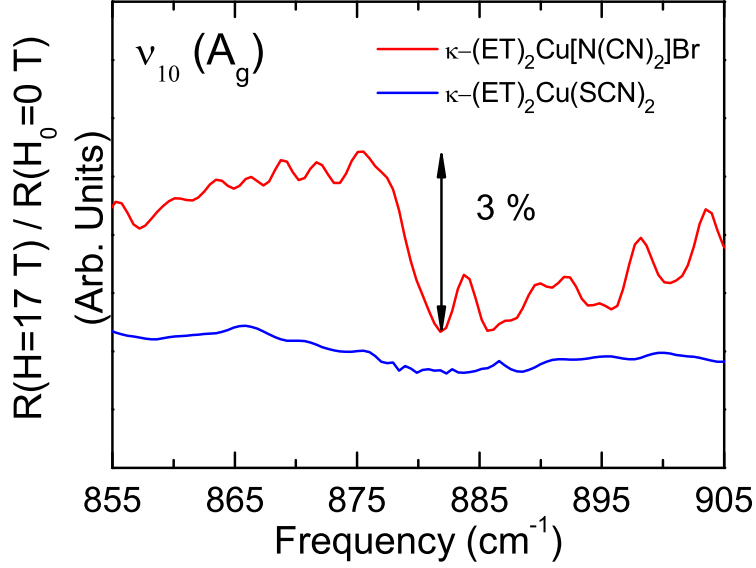


Figure 4.3: Reflectance ratio, $\frac{R(\omega, H=17 \text{ T})}{R(\omega, H_0=0 \text{ T})}$, of the totally symmetric ν_{10} mode for κ -Br and κ -SCN at 4.2 K. The double arrow shows the magnitude of the field-induced change in the reflectance ratio. The curves have been offset for clarity.

field [91]. Other isotopic decoration studies [83], particularly results on $\text{D}^{13}\text{C}^{34}\text{S}$ - κ -(ET) $_2\text{Cu}(\text{SCN})_2$ ($\Delta T_c = 0.2 \text{ K}$), show only a nascent sensitivity of the integrated area of the totally symmetric C=C stretching mode to the slightly larger value of T_c [92].

Figure 4.3 displays a close-up view of the 17 T reflectance ratio spectra of κ -Br and κ -SCN in the vicinity of the totally symmetric 880 cm^{-1} (ν_{10}) mode [10]. Field-induced modifications of this feature are much larger for κ -Br ($\sim 3\%$) compared with κ -SCN ($\sim 1\%$), a result that seems to correlate with the size of T_c and H_{c2} . This trend is in line with that for ν_4 , discussed above. Comparison of the integrated area of this structure vs. magnetic field with the response of other magnetic field dependent vibronic modes in κ -Br (shown in Fig. 4.4) demonstrates that although the field-induced response is overall similar to that of ν_4 (A_g), (growing in the superconducting

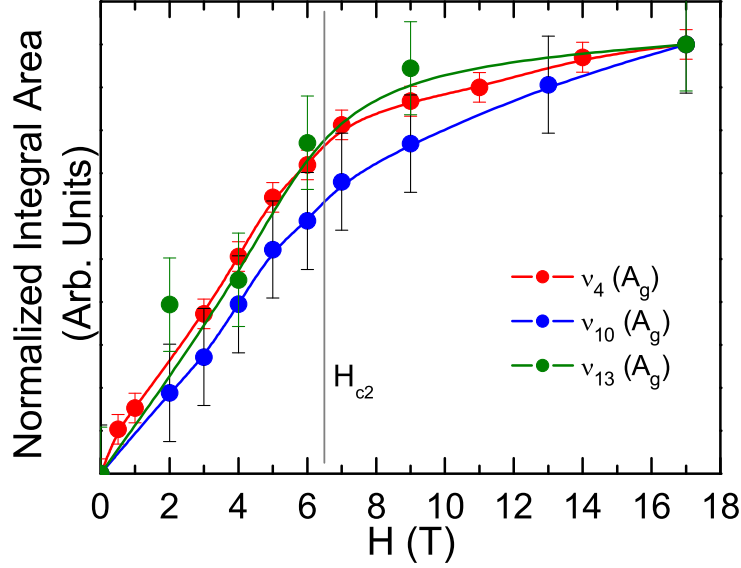


Figure 4.4: Normalized integral area of the field-induced changes in the ν_4 (A_g), ν_{10} (A_g), and ν_{13} (A_g) modes as a function of applied magnetic field for κ -Br at 4.2 K. The solid vertical line indicates H_{c2} .

phase, changing near H_{c2} , and leveling off in the high field normal state), the change is more gradual around H_{c2} . Saturation of the effect is also less pronounced.

The fairly clear field-induced spectral changes in κ -Br make it possible to identify an additional, but much smaller, magneto-infrared feature that is involved in the superconducting to normal state transition (Fig. 4.1(c)). Based on dynamic simulations in the C_{2h} point group, we assign this structure (centered around 440 cm^{-1}) as a totally symmetric intramolecular vibrational mode (ν_{13} (A_g)) [10]. Although changes in ν_{13} (A_g) were discovered only in κ -Br, we suspect that similar (but more modest) modifications are hidden beneath the noise for κ -SCN and other organic superconductors. The field-induced reflectance ratio near ν_{13} (A_g) evolves systematically, albeit with greater overall noise level than shown previously.

It has been proposed that electron-phonon coupling is fundamental to the pair-

ing mechanism in layered organic solids, with both the strongest EMV-coupled intramolecular vibrational modes as well as internal lattice modes playing key roles [93]. Our results support this prediction, and we identify the most important totally symmetric modes in κ -Br as ν_4 , ν_{10} , and ν_{13} within the C_{2h} subgroup picture. One consequence of this work is that theory for superconductivity in layered organic solids should account the lattice involvement either explicitly in the mechanism or as a consequence of the important (driving) interactions. The correlation between T_c , H_{c2} , and the size of the magneto-infrared effect also provides energy scale arguments that support the partial role of EMV coupling in driving the superconducting ground state. Phonons were also found to contribute to superconducting state of transition metal superconductors [94, 95].

4.2 Understanding the Electronic Structure of the Single-Molecule Magnet Fe_8Br_8

We first note that our results are well reproduced in the DFT (density-functional theory) calculations performed by Baruah *et al.* [80]. The calculated spin density in $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{C}_6\text{H}_{15}\text{N}_3)_6\text{Br}_6]^{2+}$ is shown in Fig. 4.5. Fe^{III} ions have a d^5 electron configuration, with spin $S = \frac{5}{2}$. The magnetic structure of Fe_8Br_8 consists of eight Fe^{III} ions, six spin up and two spin down, indicative of ferrimagnetic ordering. The total spin of the molecule is $S_{\text{tot}} = 10$. Figures 4.6 and 4.7 display the calculated total and atom-projected spin-majority (spin up) and spin-minority (spin down) density of states for $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{C}_6\text{H}_{15}\text{N}_3)_6\text{Br}_6]^{2+}$ [80]. The spin of the HOMO (highest occupied molecular orbitals) and LUMO (lowest unoccupied molecular orbitals) are different, and there is a small gap of 0.15 eV between them. The spin majority channel has a HOMO-LUMO gap of 0.54 eV. Based upon several decades of experience with the DFT method, excitation energies are generally underestimated by a factor

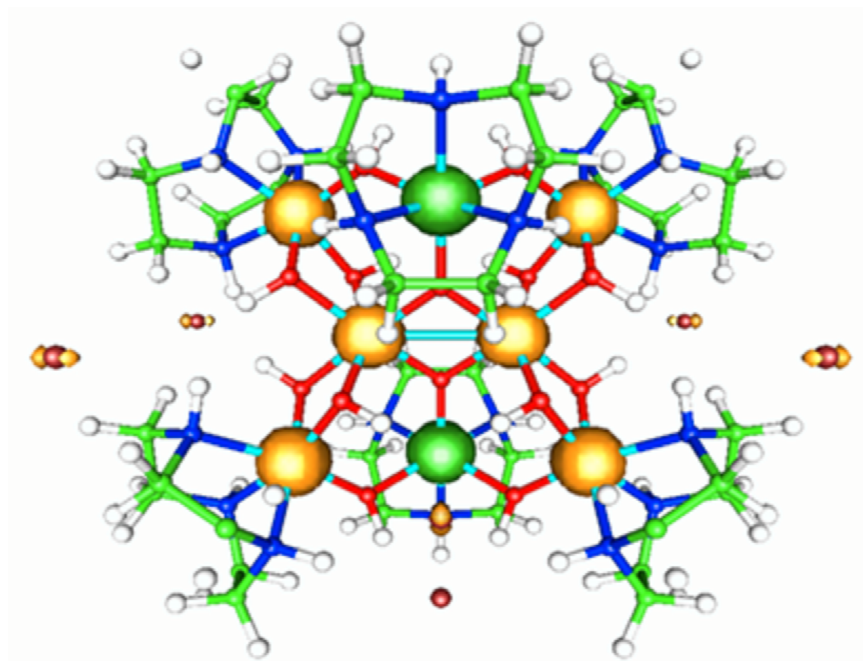


Figure 4.5: The optimized geometry of the Fe_8Br_8 cluster. Large balls show isosurfaces of the spin density, orange shows the majority spin (up), and green shows the minority spin (down) [51].

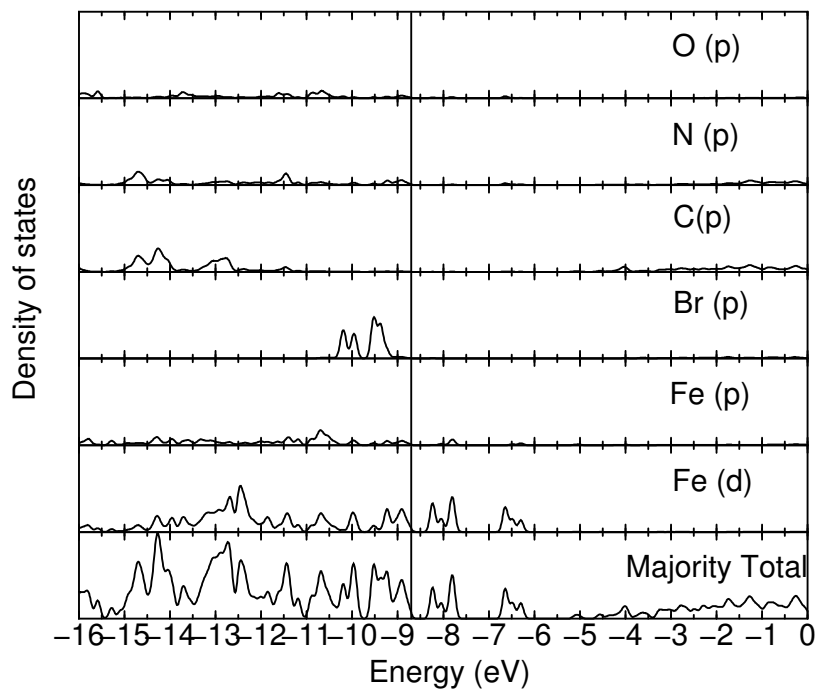


Figure 4.6: Calculated density of states for majority spin electrons [80].

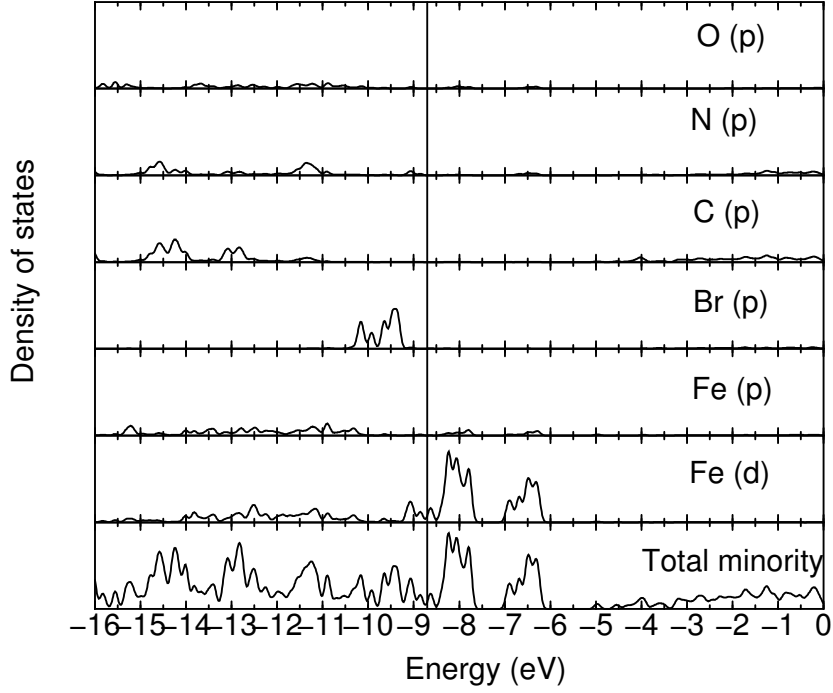


Figure 4.7: Calculated density of states for minority spin electrons [80].

of 1.4. Scaling the majority channel gap therefore yields 0.76 eV. This is the $\Delta k = 0$ transition, which should correspond to a peak in the measured optical spectrum. The states near the Fermi level (a vertical line at ~ 9 eV in Fig. 4.6 and 4.7) were derived mainly from Fe atoms, with smaller contributions from both O, N and C sites. The spin minority channel shows a HOMO-LUMO gap of 0.23 eV. Scaling this transition by a factor of 1.4 as before, this feature is expected to appear as a peak in the measured optical spectrum at ~ 0.32 eV. In this case, the states near the Fermi level originate mainly from Fe atoms.

Figure 4.8 shows the calculated optical absorption spectrum, obtained from an analysis of the dipole matrix elements of $\text{Fe}_8\text{Br}_6^{2+}$ [80]. The two projections correspond to the two polarizations along which we measured the optical response. These directions were chosen to maximize the anisotropy in the ab -plane optical properties, thus assuring that they correspond to the principal axes of the dielectric tensor. It

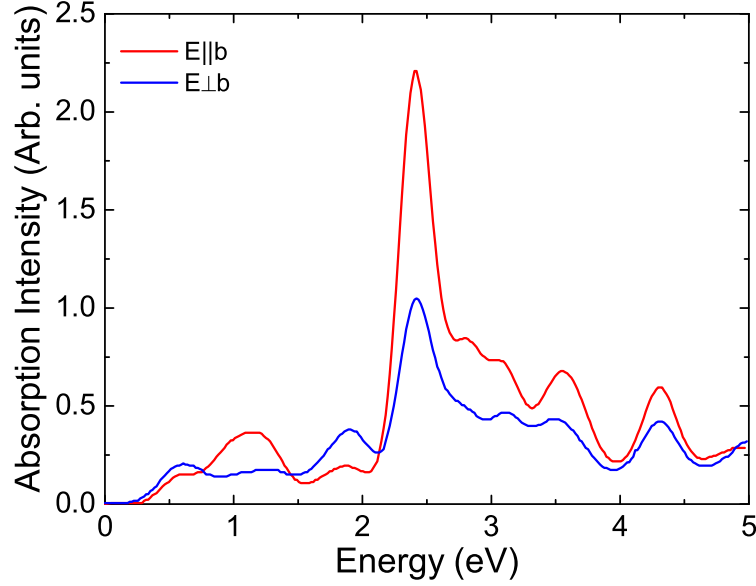


Figure 4.8: Spin-averaged joint density of states for Fe_8Br_8 . The theoretical curves are broadened by a Gaussian, with a full width half maximum of 0.27 eV, to simulate a realistic spectrum. The blue (red) curve shows the spectra along the $\parallel b$ ($\perp b$) [80].

has been confirmed that these also correspond to the two eigenvectors of the calculated bare polarizability tensor in this plane [80].

Figures 4.9 and 4.10 display the 300 K polarized optical conductivity of Fe_8Br_8 . The response is characteristic of a semiconductor, with modest spectral anisotropy. Based on a comparison of the measured optical conductivity with the calculated joint density of states, we assign the peak at ~ 0.9 eV to the theoretical 0.54 eV HOMO-LUMO gap in the majority spin channel (Fig. 4.10). When empirically scaled by an appropriate factor of 1.4, the agreement between the calculated (0.76 eV) and measured (~ 0.9 eV) features is quite good. The calculated minority HOMO-LUMO gap is 0.23 eV. When appropriately scaled, this corresponds to 0.32 eV, which is also in a reasonable agreement with a rather broad low-energy feature (centered at ~ 0.4 eV) in the experimental spectrum. However, electronic dipolar transitions between these states are forbidden by the symmetry of the $\text{Fe}_8\text{Br}_6^{2+}$ system. The other candidate

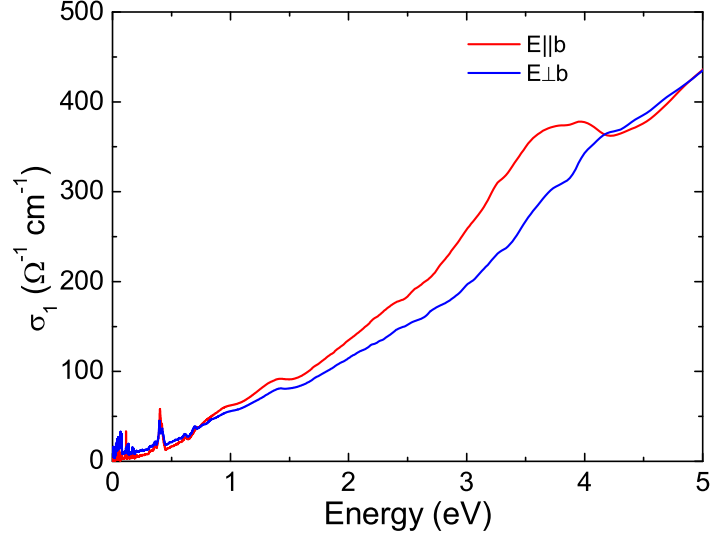


Figure 4.9: Polarized optical conductivity of the Fe_8Br_8 molecular magnet at 300 K. Higher energy excitations are due to O $p \rightarrow$ Fe d charge transfer transitions.

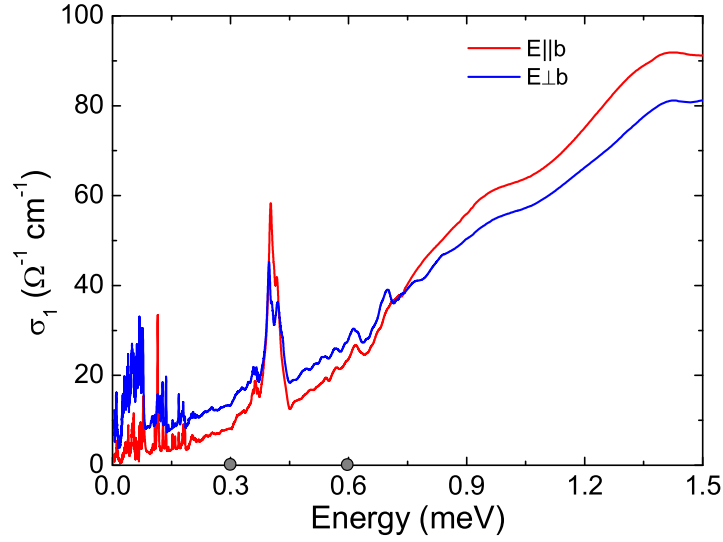


Figure 4.10: A close-up view of the rising edge of the optical conductivity in polarized optical conductivity spectra of the Fe_8Br_8 molecular magnet at 300 K. The experimental values of the spin forbidden HOMO-LUMO (see text) and majority optical gap are indicated by filled circles on the baseline in this plot; $2\Delta_{\text{opt}} = 0.3$ eV and $2\Delta_{\text{opt,maj}} = 0.6$ eV. We find that the low-energy excitations are dominated by Fe $d \rightarrow$ Fe d excitations.

is the 0.15 eV HOMO-LUMO gap (with a scaled value of 0.21 eV), although as previously mentioned, the spin channels are different. From the experimental point of view, the optical gap is typically determined by a linear extrapolation of the leading edge of the absorption band down to the baseline. Such an analysis yields optical gaps of 0.3 and 0.6 eV, which we assign as majority to minority HOMO-LUMO and majority gaps, respectively. We consider the overall agreement between theory and experiment to be excellent, considering that the experiments are done on a crystalline sample and the DFT calculations (which typically underestimate band gaps and excitation energies) are carried out on a single molecule.

The transport gap is substantially larger, 1.46 eV [49]. This difference suggests that the transport gap may be mediated by many larger energy excitations rather than a few low-energy excitations. Alternatively, the transport gap may arise from a barrier encountered by electrons hopping between two neighboring molecules. Motivated by the connection between charge transfer and hopping-related transport, we note that extrapolation of the leading edge of the absorption band centered at 3.5 eV in the experimental spectrum (Fig. 4.9) yields a value of ~ 1.5 eV. A comparison of the theoretical, optical, and transport gaps for the Fe_8Br_8 system is given in Table 4.1.

Based on an analysis of the minority- and majority-channel density of states and a comparison of the calculated joint density of states with the optical experimental spectrum, we propose the following assignments of the observed electronic excitations in the molecular solid. The 0.5 eV peak in the theoretical curve (Fig. 4.8) arises from Fe $d \rightarrow$ Fe d interionic excitations. That is, they arise from electronic excitations involving an occupied electron being moved to a hole on a neighboring antiferromagnetically coupled Fe ion. The 1.2 eV feature arises from a combination of Fe $d \rightarrow$ Fe d and Br $p \rightarrow$ Fe d transitions. The 1.8 eV peak is due to Br and O $p \rightarrow$ Fe d as well as Fe $d \rightarrow$ Fe d transitions. The predicted features in the theoretical curve near

Table 4.1: Comparison of the gap values obtained from theoretical calculation, optical conductivity experiments, and transport measurements. Theoretically, the spin minority gap is dipole forbidden. Inclusion of spin-orbit coupling activates the 0.15 eV HOMO-LUMO gap, which is otherwise spin forbidden. The experimental spectrum shows a low-energy gap at 0.3 ± 0.1 eV (with the peak at ~ 0.4 eV), the assignment of which is discussed in the text. All values are in eV.

$2\Delta_{H-L}$ (Theory)	$2\Delta_{Min}$ (Theory)	$2\Delta_{Maj}$ (Theory)	2Δ (Expt.)	$2\Delta_{Maj}$ (Expt.)	$2\Delta_{Trans}$ (Expt.)	Technique
0.15×1.4 0.21 ¹ ~ 0.4 Peak	0.23×1.4 0.32 ¹	0.54×1.4 0.76 ¹ ~ 0.9 Peak	0.3 ± 0.1	0.6 ± 0.1	1.5 ± 0.2 1.46 ± 0.2	DFT [80] Optics Transport [49]

¹The bold-font values show the results of DFT calculations, multiplied by the scaling factor of 1.4.

0.5 eV, between 1.1 and 1.3 eV, and at 1.8 eV correspond to the peaks at ~ 0.9 , 1.4, and 2.3 eV in the experimental optical conductivity spectrum. Theory predicts that the two spectra cross near 1.6 and 2.2 eV, whereas crossing of the $\parallel b$ and $\perp b$ spectra is observed near 0.75 and 4.2 eV (Fig. 4.9 and Fig. 4.10). The theoretical joint density of states (Fig. 4.8) shows maximum anisotropy near 2.4 eV. Appropriately scaled, this feature is a good match with the experimental peak centered at 3.5 eV. We note that the 3.5 eV feature (Fig. 4.9) displays substantial directional dependence, in agreement with the calculation. We assign this structure as O $p \rightarrow$ Fe d charge transfer, with smaller contributions from Br p and Fe $d \rightarrow$ Fe d states. The peaks higher in energy arise primarily from O $p \rightarrow$ Fe d transitions.

Figure 4.11 displays a close-up view of the infrared vibrational properties of Fe₈Br₈. We assign the general characteristics of these features according to our dynamic simulations [79] on the isolated molecule as well as spectral comparisons with model compounds such as FeCl₃(tacn). The features below 20 meV are assigned as low-energy wagging and rocking of the magnetic oxide core and free Br[−] motion. Structure between 22 and 35 meV corresponds to Fe–O core wagging, rocking, twist-

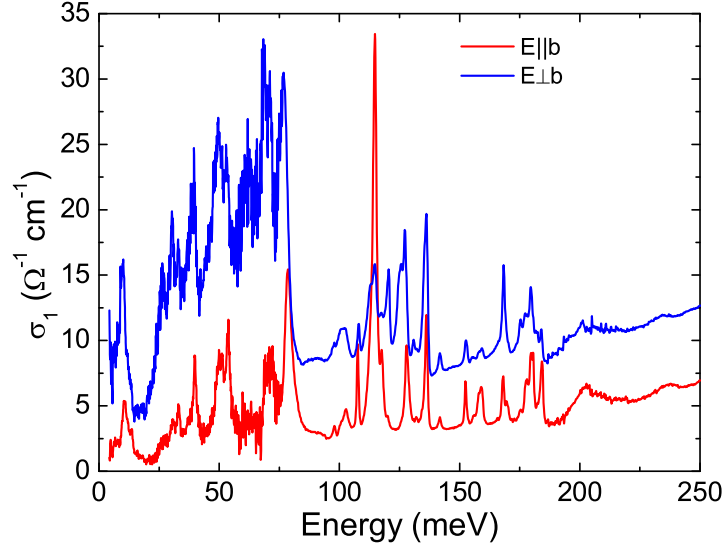


Figure 4.11: An enlarged view of the infrared region in the polarized optical conductivity spectra of the Fe_8Br_8 molecular magnet at 300 K.

ing, and bending, in addition to free Br^- motion. Wagging and bending of the tacn ligand is observed between 35 and 42 meV. We assign the complex features between 43 and 82 meV as N–Fe–N, N–Fe–O, Fe–N–C, O–Fe–O, and Fe–O–Fe bending and twisting motion. Fe–O–Fe wagging and asymmetric stretching is observed near 117 meV. Symmetric stretching of the O–Fe–O and N–Fe–N moieties appear at slightly higher energy. Most of the features between 99 and 142 meV are related to the tacn ligand. Here, the ligand features are relatively unpolarized, whereas Fe–O motion is slightly polarized, due to the disk-like shape of the building block molecule. These values are in good agreement with recent Raman data of North et al. [96]. Ligand (tacn) motion accounts for the small features between 150 and 180 meV. Well-known C–H, O–H, and N–H symmetric stretching appear at ~ 360 , 395, and 410 meV. The latter features are quite strong, and as mentioned previously, seem to be superimposed on a weak, low-energy electronic background.

Interestingly, the optical conductivity spectrum of Fe_8Br_8 displays a broad low-

energy feature centered at ~ 0.4 eV, energetic coincident with the calculated position of the minority spin gap (0.32 eV). A close-up view of the measured optical response is shown in Fig. 4.12; the green line centered near 0.4 eV illustrates the underlying electronic excitation. In view of the formal dipole-forbidden character of the spin minority gap transition, this broad peak may correspond to the aforementioned spin minority gap (perhaps activated by the symmetry breaking Br ions in the crystal structure), a phonon-assisted transition, or a spin-forbidden excitation (such as the spin majority to minority HOMO-LUMO gap). In any case, well-known C–H, O–H, and N–H vibrational modes are superimposed on the weak electronic background. To understand this broad, low-energy spectral feature better, we have carried out a similar analysis of the optical spectra of the model $[\text{FeCl}_3\text{-(tacn)}]$ compound which is chemically similar to the Fe_8Br_8 molecule.

Our interest in $[\text{FeCl}_3\text{-(tacn)}]$ (Fig. 4.13) is primarily motivated by the chemical similarity between this model compound and the Fe_8Br_8 material. Comparison of the spectral response therefore provides an important test of our assignments, and will contribute to our understanding of the low-energy electronic structure in Fe_8Br_8 . The inset of Fig. 4.12 displays a close-up view of the measured optical conductivity of the $[\text{FeCl}_3\text{-(tacn)}]$ model compound compared to that of the Fe_8Br_8 molecular magnet. C–H stretching is observed between 360 and 370 meV, and a strong N–H stretch mode is observed at 410 meV. These intramolecular vibrational modes are sharp and well-defined in the model compound, different from the broad peak shape over the same energy range for Fe_8Br_8 . We therefore assign the broad structure in the spectrum of the Fe_8Br_8 molecule-based magnet to a low-energy electronic structure, with superimposed C–H, N–H, and O–H vibrational modes.

According to calculations, the transition across the spin minority gap is dipole forbidden. One possible explanation of the low energy peak in the measured spectrum could be an admixture of the Fe p and d states in the unoccupied region due to spin-

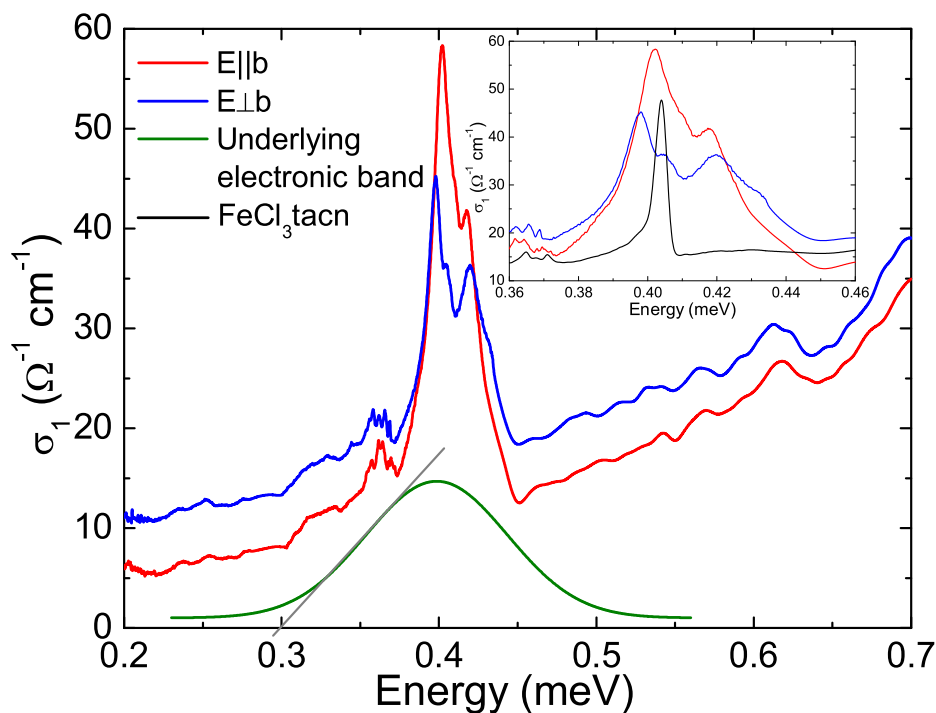


Figure 4.12: A close-up view of the 300 K unpolarized optical conductivity of Fe_8Br_8 in the b (red) and $\perp b$ (blue) directions. The weak underlying low-energy excitation was fit using a model oscillator and is drawn as a guide to the eye (green line). C–H, O–H, and N–H vibrational modes are superimposed upon this structure. The straight gray line illustrates optical gap determination for this feature. The inset compares the unpolarized vibrational response of the $[\text{FeCl}_3\text{-(tacn)}]$ model compound (black) with the polarized optical conductivity spectra of Fe_8Br_8 molecular magnet (red and blue).

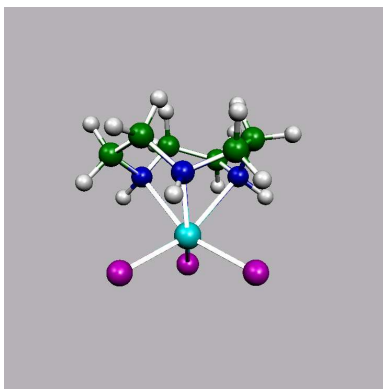


Figure 4.13: The optimized geometry of the $[\text{FeCl}_3\text{-(tacn)}]$ molecule [51].

orbit coupling [80]. The calculated peaks predicted to occur below 0.3 eV due to spin-orbit coupling are shown in Fig. 4.11. These excitations are from the HOMO and another high energy occupied state near Fermi level to the lowest unoccupied state. These excitations are of low intensity and are intramolecular in nature. The spin majority to minority nature of the transition is also consistent with the low intensity of these peaks. Such weak intramolecular transitions are not likely to contribute to the transport, where the important excitations are intermolecular in nature. This result may, in part, explain the large gap observed in transport experiments [49]. We also note that various symmetry-breaking mechanisms might activate the spin minority HOMO-LUMO gap. For instance, inclusion of the two inversion symmetry breaking Br^- ions in our calculation may change the selection rules. Another possible mechanism for activation of dipolar transitions in the low energy region could be coupling of a phonon to the electronic excitation.

4.3 Spin-Ladder Candidate

4.3.1 Vibrational Properties of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$

300 K Infrared Spectrum

Figure 4.14 displays the polarized infrared reflectance and calculated optical conductivity of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ at room temperature. The infrared spectra are anisotropic, with a different response in the two main directions. This kind of anisotropy, with a large charge transfer band polarized along the donor stack direction and a low, flat response in the other orthogonal polarizations, is typical for low-dimensional semiconducting organic charge transfer salts [97–99]. Along the b direction, the observed vibrational features have A_g symmetry. These modes are related to the motion of the DT-TTF building block molecule, and are activated by electron-molecular vibrational coupling [100, 101]. Along the c direction, we find

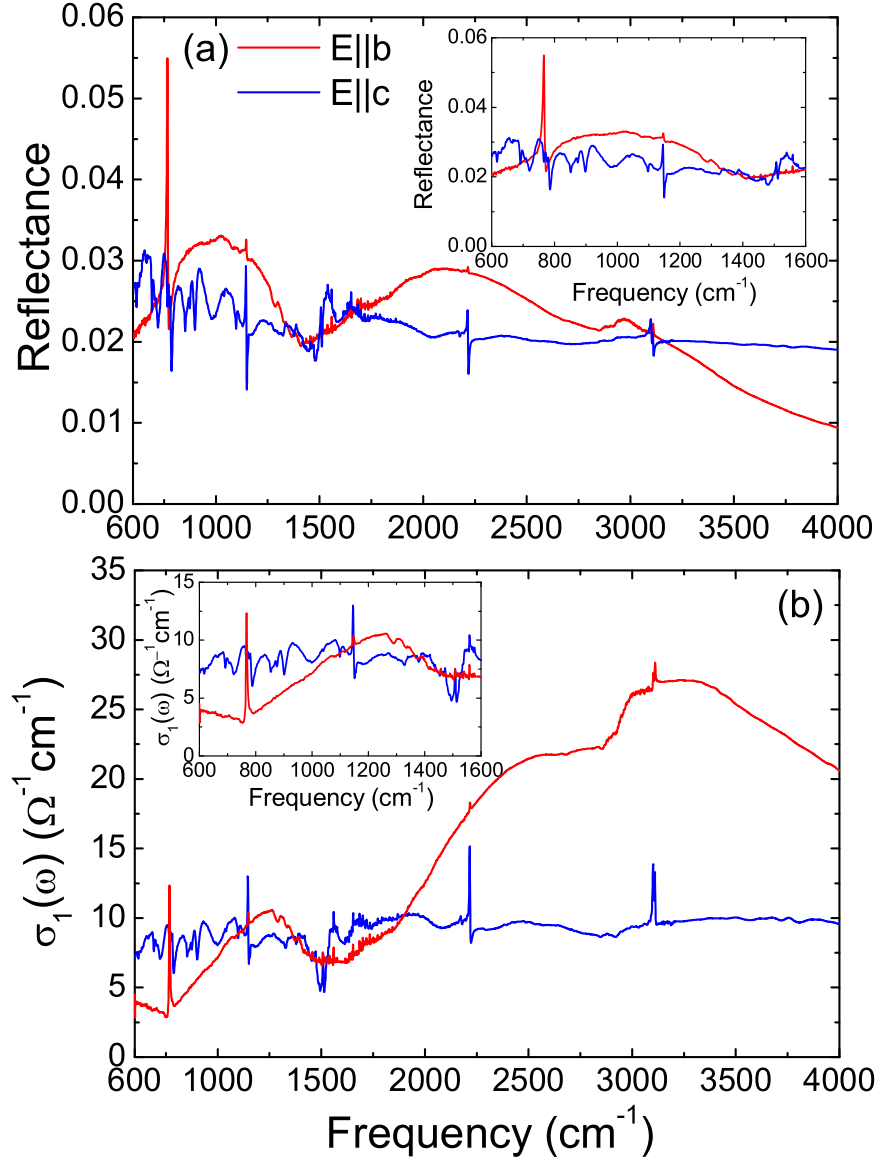


Figure 4.14: 300 K polarized reflectance (a) and optical conductivity (b) of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$. The insets show close-up views of the vibrational response.

normally infrared active B_{1u} , B_{2u} , and B_{3u} modes related to both DT-TTF and $\text{Au}(\text{mnt})_2$ building block molecules. Details of the assigned vibrational modes, based on a comparison of the spectra with our molecular dynamic simulations, are summarized in Table 4.2. The table gives the experimental frequency of each peak in the first column, the theoretical frequency in the second column, the mode symmetry in column 3, the observed polarization in column 4, the low temperature splitting in column 5, and a description of the molecular motion of each mode in column 6. As $\sigma_1(\omega) \rightarrow 0$ the result is in excellent agreement with the *dc* conductivity of $8 \text{ } \Omega^{-1}\text{cm}^{-1}$ [71].

Variable Temperature Response Along the *b* Axis

Figure 4.15 shows the optical conductivity of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ in the rail direction at 4 and 300 K. There are significant modifications in the charge transfer band with temperature. To quantify these changes, we fit the spectra with six model oscillators over the frequency range $1000 - 5500 \text{ cm}^{-1}$ (inset, Fig. 4.15). The temperature dependence of the peak position and integrated area of these six oscillators are shown in Fig. 4.16. All oscillators soften at the 70 K transition, with only occasional changes at the 220 K transition. Note, that the 4600 cm^{-1} is the least reliable as it merely simulates the charge transfer feature. Also notable are the trends in the two peaks around 3000 cm^{-1} , indicating that this splitting begins well above 300 K. Changes in the integral area of the largest peaks (Fig. 4.16(b)) are fairly substantial at the 70 K transition, although the trends are in different directions, indicating a redistribution of oscillator strength.

Figure 4.17 displays a close-up view of the variable temperature infrared properties of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ in the *b* direction. The majority of these modes have A_g symmetry, activated by the electron-molecular vibrational coupling [100, 101], and corresponding to molecular motions of the DT-TTF building block molecule (Ta-

Table 4.2: Vibrational Modes of (DT-TTF)₂Au(mnt)₂ [81].

Experimental Frequency (cm ⁻¹)	Theoretical Frequency ¹ (cm ⁻¹)	Theoretical Symmetry ²	Pol.	Low Temp. Splitting ³	Molecular Motion
697	712	<i>B</i> _{1u}	<i>c</i>	1:2	C–S Bend DT-TTF
748	784	<i>B</i> _{1u}	<i>c</i>	1:2	C–S Stretch, C=C Rocking DT-TTF
767	810	<i>A</i> _g	<i>b</i>	1:20	C–S Stretch DT-TTF
771	798	<i>B</i> _{2u}	<i>c</i>	1:2	C–S Stretch, C=C Rocking DT-TTF
818	812	<i>B</i> _{1u}	<i>c</i>	1:4	C–S Stretch DT-TTF
870	869	<i>B</i> _{2u}	<i>c</i>	1:2	C–S Stretch, C=C Rocking Au(mnt) ₂
885	885	<i>B</i> _{3u}	<i>c</i>	1:2	Out-of-Plane Rocking DT-TTF
924	964	<i>B</i> _{2u}	<i>c</i>	1:4	C–S Stretch, C–C Rocking DT-TTF
990	1016	<i>B</i> _{1u}	<i>c</i>		C–S, C=C Stretch Au(mnt) ₂
1027	1088	<i>A</i> _g	<i>b</i>	1:18	C–C, C–S Stretch DT-TTF
1047	1088	<i>B</i> _{1u}	<i>c</i>	1:4	C–C, C–S Stretch DT-TTF
1106	1124	<i>B</i> _{2u}	<i>c</i>	1:2	C–C Rocking DT-TTF
1145	1157	<i>B</i> _{2u}	<i>c</i>	1:6	C–C Stretch, C=C Rocking Au(mnt) ₂
1148	1157	<i>B</i> _{2u}	<i>b</i>		C–C Stretch, C=C Rocking Au(mnt) ₂
1311	1409	<i>A</i> _g	<i>b</i>	1:12	C–C Stretch DT-TTF
1339	1388	<i>B</i> _{1u}	<i>c</i>		C–C Stretch DT-TTF
1387	1410	<i>B</i> _{1u}	<i>c</i>		C=C Stretch Au(mnt) ₂
1515	1655	<i>A</i> _g	<i>b</i>	1:20	C=C Stretch DT-TTF DT-TTF
1652	1687	<i>B</i> _{2u}	<i>c</i>	1:3	C=C Stretch, C–C Rocking DT-TTF
2214	2231	<i>B</i> _{1u}	<i>c</i>		C–N Stretch Au(mnt) ₂
3098	3113	<i>B</i> _{1u}	<i>c</i>	1:4	C–H Stretch DT-TTF
3111	3114	<i>A</i> _g	<i>b</i>	1:4	C–H Stretch DT-TTF

¹ All theoretical peaks have been assigned to experimental data.

² *A*_g modes of the DT-TTF molecule are infrared active due to electron-molecular vibrational coupling.

³ Low temperature splitting in the *b* direction is due to the 70 K transition, whereas low temperature splitting in the *c* direction is due to the 220 K transition.

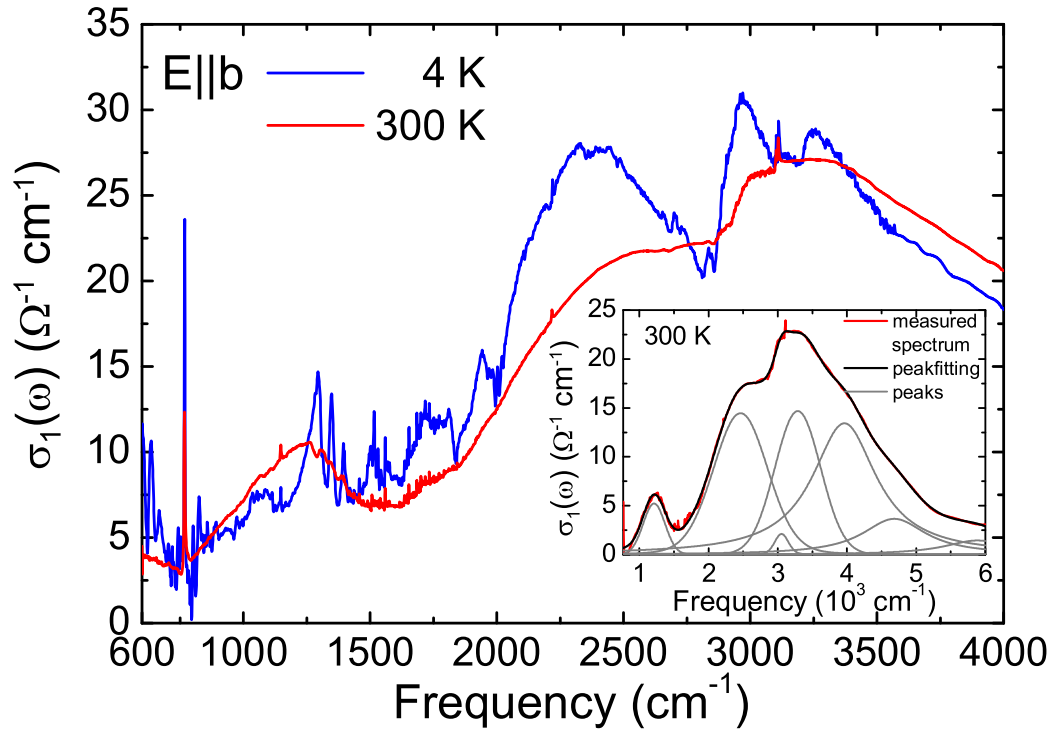


Figure 4.15: Variable temperature optical conductivity of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ polarized along the b direction. The inset shows a fit of the 300 K spectrum in the range of the charge transfer band to several model Voight oscillators.

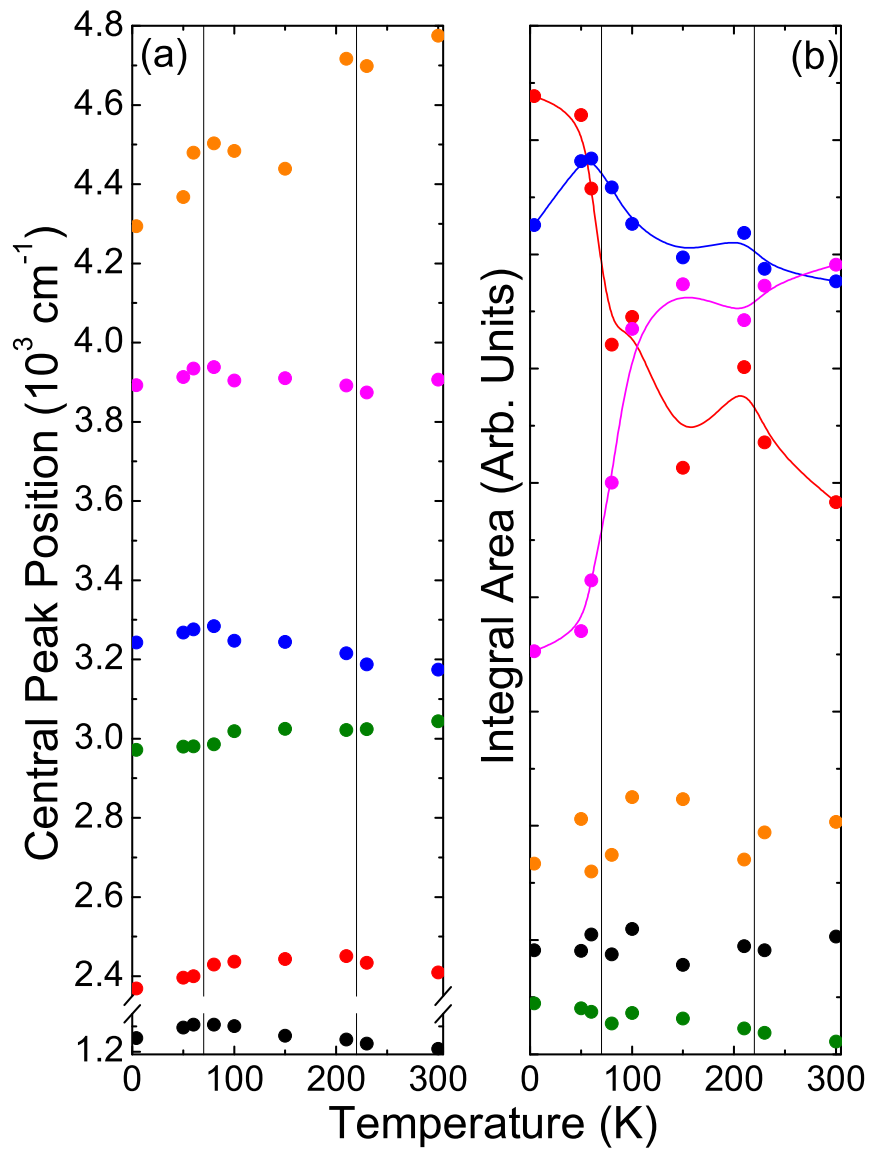


Figure 4.16: Central peak positions (a) and integral areas (b) of the fitted oscillators in the charge transfer band of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ as a function of temperature. Six oscillators were needed to capture the complex shape of the charge transfer band. Selected lines guide the eye.

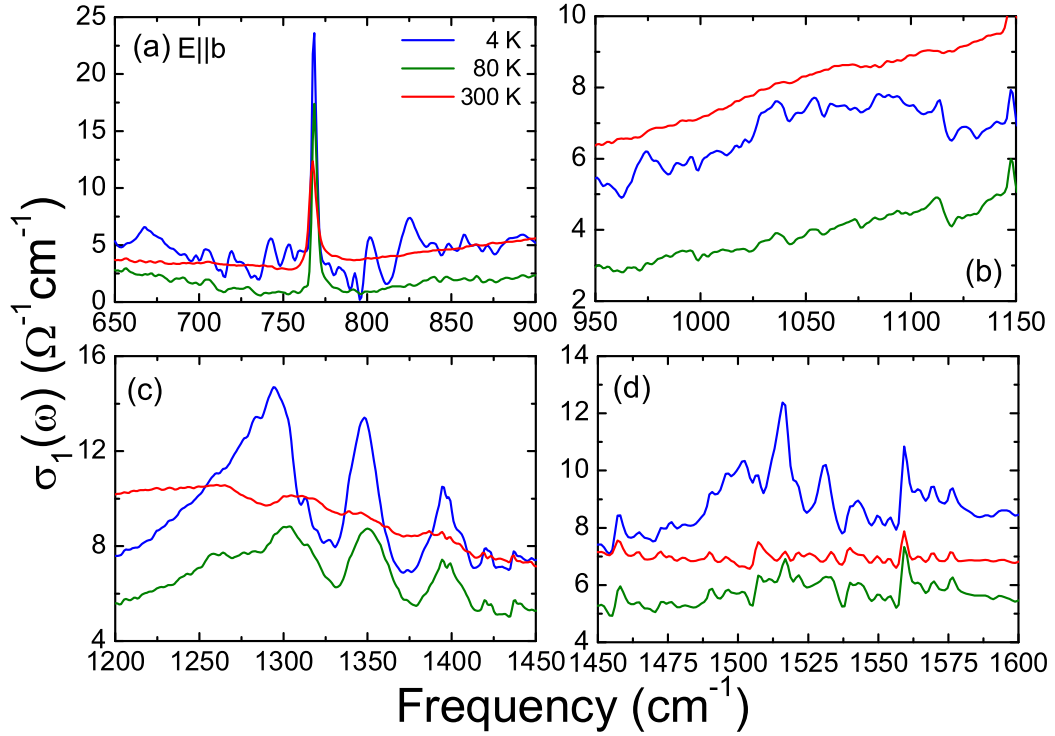


Figure 4.17: Optical conductivity of selected vibrational modes of (DT-TTF)₂Au(mnt)₂ polarized along the b direction at 300, 80, and 4 K. (a) A_g mode (C–S stretching motion of DT-TTF), (b) A_g mode (C–C; C–S stretching motion of DT-TTF), (c) A_g mode (C–C stretching motion of DT-TTF), (d) A_g mode (C=C stretching motion of DT-TTF).

ble 4.2). These vibrational modes show clear low-temperature symmetry breaking; the splitting patterns are summarized in Table 4.2. Of these various features, the $\sim 1 : 20$ (one peak splits into twenty) low-temperature splitting of the 780 cm^{-1} mode is the most striking (Fig. 4.17(a)). Above 70 K, there is only one main peak, but below the transition temperature the central peak is accompanied by numerous side peaks. The other modes in Fig. 4.17 show similar trends, with the main changes occurring at the 70 K transition. We attribute a portion of low-temperature peak splitting to perturbations of the molecular motion resulting from site symmetry breaking. At the same time, X-ray scattering and μ^+ SR measurements have

shown that there are chain breaks that limit the effective length of the ladder in $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ at low temperature [5, 70–73]. These chain breaks, combined with symmetry breaking at the molecular site, can explain the observed vibrational splitting. Note that the b -polarized modes do not show any significant changes at the 220 K transition.

Variable Temperature Response Along the c Axis

Figure 4.18 displays the optical conductivity of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ in the c direction (along the rungs of the proposed spin ladder) at 4 and 300 K. The spectra exhibit dramatic changes with temperature, with an explosion of new peaks below 220 K. A close-up view of this massive symmetry breaking is shown in Fig. 4.19.

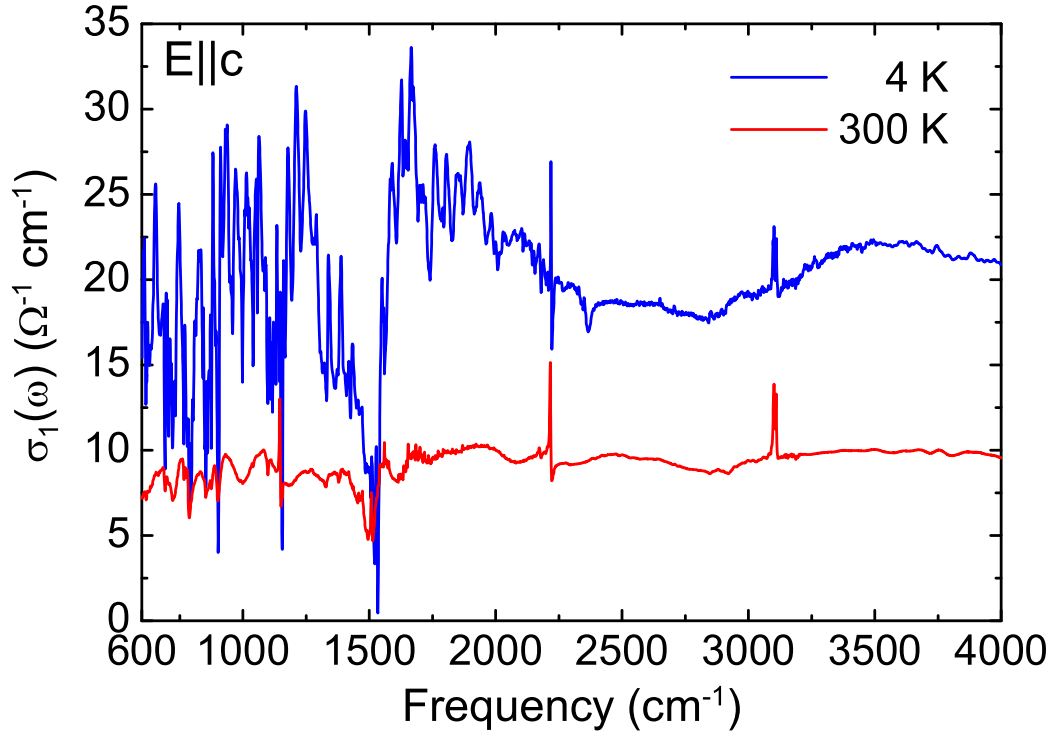


Figure 4.18: Optical conductivity of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ polarized along the c direction at 300 and 4 K.

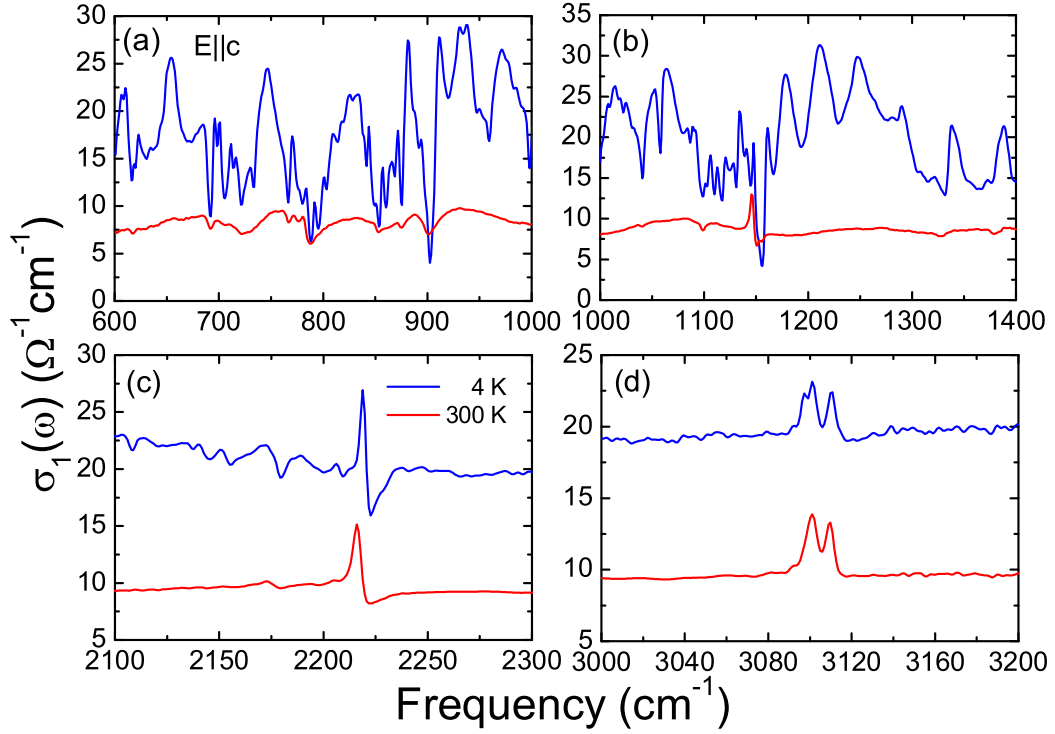


Figure 4.19: Optical conductivity of selected vibrational modes of (DT-TTF)₂Au(mnt)₂ polarized along the c direction at 300 K and 4 K. (a) B_{1u} , B_{2u} , and B_{3u} modes (various C–C; C=C; C–S motions of DT-TTF and Au(mnt)₂), (b) B_{1u} and B_{2u} modes (various C–C; C=C; C–S motions of DT-TTF and Au(mnt)₂), (c) B_{1u} mode (C–N stretching motion of Au(mnt)₂), (d) B_{1u} mode (C–H stretching motion of Au(mnt)₂).

Between 600 and 1400 cm^{-1} , the symmetry breaking involving the C–C, C–S, and C=C motion is extraordinarily strong (with typically 1:2 or 1:4 peak splitting at 220 K, see Table 4.2), whereas the splitting of the C–H stretch (1:4) at 3110 cm^{-1} is very weak, showing that most symmetry breaking takes place at the heart of the DT-TTF molecule. Note that all of the vibrational features in this polarization have B_{1u} , B_{2u} , or B_{3u} symmetry and correspond to normally infrared active modes, assigned as molecular motions of both DT-TTF and Au(mnt)₂ building block molecules (Table 4.2). There are no qualitative changes in the c -polarized spectrum of (DT-

TTF)₂Au(mnt)₂ at the 70 K transition.

It is interesting that there are several *c*-polarized vibrational modes that are completely insensitive to the two low-temperature phase transitions in (DT-TTF)₂Au(mnt)₂. One of these features is at 2214 cm⁻¹ (Fig. 4.19(c)) corresponding to C–N stretching motion of Au(mnt)₂; this mode has *B*_{1u} symmetry. The insensitivity of the 2214 cm⁻¹ C–N stretching mode to temperature suggests that the outer portion of the Au(mnt)₂ building block molecule is not involved in either the 220 K or 70 K transitions (examination of the low-temperature splitting data in Table 4.2 shows that the majority of the modes that do not display low-temperature symmetry breaking are related to the motion of Au(mnt)₂). This observation, combined with the aforementioned symmetry breaking of DT-TF-related modes, indicates that the 220 K transition is driven by a local distortion at the core of the Au(mnt)₂ building block molecule, combined with an extensive distortion of the DT-TTF stack.

The 70 and 220 K Phase Transitions in (DT-TTF)₂Au(mnt)₂

The vibrational properties of (DT-TTF)₂Au(mnt)₂ provide microscopic information on the low temperature phase transitions in this material. Along the *b* direction, changes in the infrared spectrum only appear at 70 K. In contrast, only the *c* polarized vibrational modes are sensitive to the 220 K transition. Thus the 70 and 220 K transitions are mutually independent. Note that the deformation along *c* involves both DT-TTF and Au(mnt)₂ molecules, whereas changes in the *b* direction take place only within DT-TTF. Further, our dynamic simulations provide detailed information on the most important modes in each case. These results are summarized in Table 4.2. Combining our results with previous *dc* resistivity and magnetic susceptibility data [5, 70–73], we propose that the high temperature transition at 220 K is a structural distortion that localizes charge along the *c* direction, whereas the 70 K transition is driven by a coupling between the magnetic system and vi-

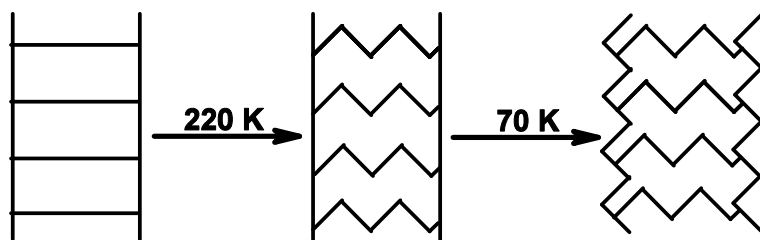


Figure 4.20: Schematic view of the two low-temperature transitions of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$, illustrating the symmetry breaking along the rungs (220 K) and rails (70 K) of the proposed spin ladder.

brational modes along b . This magnetoelastic coupling acts to distort the lattice. A diagram of these processes is shown in Fig. 4.20. Presumably, a similar scenario can explain the low-temperature transitions observed in other members of the $(\text{DT-TTF})_2M(\text{mnt})_2$ family ($M = \text{Pt}, \text{Ni}, \text{Cu}$).

Comparison with Other Semiconducting Organic Charge Transfer Salts

The low-temperature vibrational properties of $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ are exceptionally rich, due to the striking mode splitting observed at the 220 and 70 K transitions. To illustrate how this kind of symmetry breaking is unusual for semiconducting organic charge transfer salts, we compare our $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ data with results for the three other representative materials. Mode splitting in $(\text{TMTSF})_2\text{BF}_4$ is driven by anion ordering [102], low-temperature doublet splitting in $\text{NPrQn}(\text{TCNQ})_2$ is due to a change in the charge distribution within the tetramer [103], and the new low-temperature vibrational mode in $\beta'-(\text{ET})_2\text{CF}_3\text{CF}_2\text{SO}_3$ is related to a spin-Peierls transition [104]. Although the nature of the mode splitting is entirely different in these model compounds, symmetry breaking generally splits vibrational features into doublets or triplets. Thus, the symmetry breaking in $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ is rather extraordinary.

Chapter 5

Summary

We have studied three representative complex molecular solids, using optical spectroscopy as a our primary technique for investigation the nature of these materials. Optical spectroscopy gives knowledge about local macroscopic behavior from low energy intramolecular excitations to high energy electronic transitions. Our experiments, supported by other research and theoretical calculations, can contribute to very important issues, and lead us to valuable conclusions.

Vibronically-activated totally symmetric modes are well known to be some of the most sensitive spectral features available, making them ideal for investigating microscopic aspects of the magnetically-driven superconducting to normal state transition in organic molecular solids. This fact helped us focus our research on these materials. We completed the 4.2 K magneto-infrared reflectance experiments of two quasi-isostructural organic solids: κ -(ET)₂Cu[N(CN)₂]Br and κ -(ET)₂Cu[N(CN)₂]Cl, and compared our results with already existent similar report on κ -(ET)₂Cu(SCN)₂ [90]. In the two superconducting materials, several totally symmetric intramolecular modes change systematically with applied magnetic field. The magneto-infrared features in κ -(ET)₂Cu[N(CN)₂]Br ($T_c = 11.6$ K) are similar but noticeably larger than those in κ -(ET)₂Cu(SCN)₂ ($T_c = 10.4$ K), indicating that the strength of the effect may be correlated to T_c (although the exact relationship is probably not sim-

ple) or to the locally different (eclipsed vs. staggered) molecular distortions. On the other hand, no field-induced features were observed within our sensitivity in the quasi-isomorphous reference compound κ -(ET)₂Cu[N(CN)₂]Cl. The unusually strong magneto-infrared features in the organic superconductors are related to the important energy scales in the problem (H_{c2} and T_c) suggestively indicating that totally symmetric intramolecular modes, among other features (i.e. the lattice modes) and mechanisms, are involved in the superconducting transition in organic layered superconductors. Our results support the contributing role of electron-molecular vibrational coupling in the pairing mechanism of layered organic superconductors, and we identify the most important totally symmetric modes in κ -(ET)₂Cu[N(CN)₂]Br within the non-planar molecular building block picture.

Another molecular solid that we investigated was a molecule-based magnet. This time we explored the electronic structure and optical properties of the Fe₈Br₈ molecule using experimentally measured optical conductivity spectrum of this material, and we compare the results with an all-electron DFT formalism. The agreement is excellent. We find that interionic Fe $d \rightarrow d$ excitations dominate the spectrum in the low energy region, whereas O $p \rightarrow$ Fe d transitions dominate the high energy region. The contributions from Br p states are also significant. The observed modest optical anisotropy is well reproduced by the calculations. We suggest that the 0.4 eV peak in the optical conductivity may be attributed to the spin majority to minority HOMO-LUMO excitation, activated by inclusion of spin-orbit coupling, which mixes states of different symmetry and spin. C–N, N–H, and O–H stretching motion is present and superimposed with the low-energy electronic excitation. While the theoretical majority spin gap and the corresponding peak position (and the extrapolated gap) obtained from optical conductivity are in agreement with DFT calculations, the transport gap is larger, indicating that high energy excitations or intermolecular hopping barrier are involved in the electron transport.

Finally, we carried out the variable temperature polarized infrared measurements of the organic spin ladder candidate $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ in order to investigate the 220 and 70 K transitions. Complementary dynamic simulations allowed us to identify the most important vibrational modes associated with each distortion [81]. The 220 K transition is driven by massive symmetry breaking along the c -axis. Evidence for a new transition at 70 K is also observed and is associated with magnetoelastic coupling in the b direction. The charge transfer bands, which are connected with the localization of unpaired electrons in the interacting DT-TTF double chains, are modified at the lower transition temperature as well. It has been suggested that the magnetic interactions along the b (rail) and c (rung) directions in $(\text{DT-TTF})_2\text{Au}(\text{mnt})_2$ might be an accurate realization of the two-leg Heisenberg spin ladder. Future inelastic neutron scattering measurements should allow an unambiguous test of this hypothesis.

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