

# Application of Infrared Spectroscopy in Solid State Physics problems

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A range of applications of Infrared Spectroscopic techniques to the study of solid state problems is discussed along with study of thin films using Fourier Transform Infrared Spectroscopy, accompanied by a brief comparison with other spectroscopic techniques. A specific case of infrared transmission through a superconducting film is put forth - a formulation utilizing the introduction of a complex conductivity in the superconducting state in order to attempt energy gap interpretations of such transmission is reviewed. Use of Near Infrared (NIR) spectroscopy for solid state characterization and analysis, and Far Infrared (FIR) spectroscopy for the study of high  $T_c$  superconductor are also discussed.

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## I. INTRODUCTION

Infrared spectroscopy encompasses a range of techniques, most commonly absorption spectroscopy, used to study the interaction of matter with infrared radiation (which is the part of the electromagnetic spectrum longer in wavelength than visible light and is defined within the wavelength range of 700 nm — 1 mm). Infrared radiation is commonly categorized into three sub-regions, namely, Near-Infrared (0.78–3  $\mu\text{m}$ ), Mid-Infrared (3–50  $\mu\text{m}$ ) and Far-Infrared (50–1000  $\mu\text{m}$ ).

Fourier Transform Infrared (FTIR) Spectroscopy is one of the most widely used infrared spectroscopic techniques - an Interferometer generates an interferogram (consisting of a combination of frequencies) which is passed through the sample and the distribution of infrared light is controlled by a moving mirror. The output interferogram after absorption from the sample is recorded and is turned into the spectrum through data-processing using the Fourier transform technique. The output is usually expressed in terms of wavenumbers. Since, this kind of spectroscopy provides information regarding the vibrational and rotational energy levels, FTIR is an excellent tool for characterization and study of solid state samples, as well as in gaining an understanding of the physics of novel materials such as superconductors with high and low transition temperature  $T_c$ .

In case of these superconductors, another type of Infrared study employed is Far Infrared (FIR) spectroscopy which can be used to determine the energy gap in high  $T_c$  superconductors as well as shed light on the electron-phonon coupling mechanism in such systems. For superconducting materials, existence of a complex and frequency dependent admittance results in a complex conductivity, which simplifies the interpretation of infrared transmission observations through the superconducting film, using the Kramers-Kronig relations.

Near-infrared spectroscopy (NIR) is an effective technique for chemical and physical analysis of solid state samples. It can be utilized in quantification of amorphous material, to monitor phase transformation, determine moisture content and in specialized applications such as identification of polymorphic drug forms in pharmaceuticals.

## II. FOURIER TRANSFORM INFRARED SPECTROSCOPY

Fourier-Transform Infrared Spectroscopy is a routinely used spectroscopic technique that records the absorption or emission of a sample in the form of a high-resolution spectral data over a given range of wavenumbers. A mathematical transform known as the Fourier transform is performed on the collected data to transform the interferogram obtained into a spectrum. Depending upon the

required resolution in the final spectrum, the distance over which path length of the interferometer mirror is varied can be changed.

### A. Working Principle of FTIR spectrometers : absorption measurements

The basic components of a Fourier Transform Infrared Spectrometer consist of a radiation source, an interferometer and a detector. The working component of any FTIR spectrometer consists of the Michelson interferometer — consisting of a beamsplitter, a pair of mirrors and a compensating plate. The mechanical scan of the position of one of the mirrors is used to achieve the difference in path length between the two interferometer arms. In such a way, the interferogram may be generated which is a temporal variation in the transmitted intensity of light. If the incident light is monochromatic then the interferogram is of sinusoidal nature as a function of mirror position. For broadband sources, the interferogram is a superposition of an infinite number of sine waves with different periodicity but a common central maximum.

The intensity of the observation points can be recorded through the use of a computer generated Fourier transform of the interferogram to generate a rapid-scan FTIR spectrum. The use of Fourier Transform Infrared spectrometers over dispersive ones is aided by the " Fellgett advantage" (the data for all wavelengths are recorded simultaneously giving a higher signal-to-noise ratio for a given time range of scans proportional to the square root of the number of scans), the "Jacquinot advantage" (an aperture regulates incoming light for a given set of resolution and wavelength, through modulation at different frequencies as the path difference changes allowing for greater signal-to-noise ratio), and a greater accuracy for recording at specific frequencies (known as Connes' advantage). FTIR spectrometers also offer lesser sensitivity to stray light (which is the appearance of one wavelength at a different wavelength in the spectrum), improving quality of signal.

### B. FTIR absorption spectroscopy of very thin films — FTIR Absorption measurements on $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-y}$ superconducting thin film

When prepared at temperatures above  $900^\circ\text{C}$   $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-y}$  thin films exhibit metallic behavior from ambient temperature range to the beginning of the superconducting temperature range with regard to the temperature variation of their resistivities. For these samples, the critical temperature at which resistivity is zero is 95-112 K, with 110-120K being the temperature at which onset of superconducting behavior takes place (separate report by Ihara *et al.* [9] places the superconducting transition temperature at 126K). The preparation of the thin films was carried out at

temperatures 1193 K, 1188 K, 1183 K and 1178 K. Due to the synthesis at high temperatures, there is partial deficiency of  $\text{O}_3$  in some of the sites in the charge reservoir layer  $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{O}_{4-\delta}$ . Taking an FTIR absorption measurement this can be observed by noting that the 464-474  $\text{cm}^{-1}$  band representing apical oxygen has a relative intensity that is enhanced (Figure 1). The  $\text{O}_3$  mode vibration is observed at 800-940  $\text{cm}^{-1}$ [3].

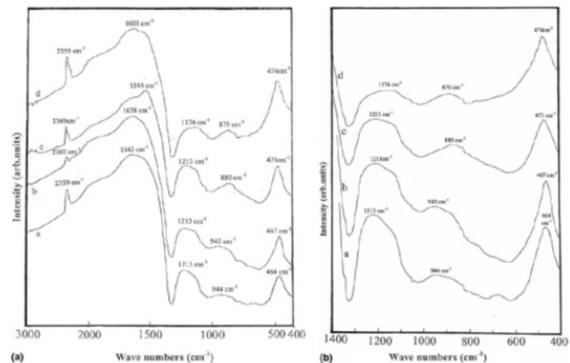


FIG. 1. (a) FTIR absorption spectra of  $\text{Cu}_{1-x}\text{Tl}_x$ -1234 samples prepared above  $900^\circ\text{C}$  before annealing (b) Extended FTIR absorption spectra of  $\text{Cu}_{1-x}\text{Tl}_x$ -1234 samples prepared above  $900^\circ\text{C}$  before annealing [3]

For preparation of  $\text{Cu}_{1-x}\text{Tl}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{12-y}$  thin films below  $900^\circ\text{C}$ , the variation of resistivity from ambient to superconducting temperature shows metallic behavior — in this case, superconductivity onsets at 120K and the resistivity is zero at 110K. Figure 2 shows the infrared measurement on the sample prepared at  $895^\circ\text{C}$  for wavenumber range 400-4000  $\text{cm}^{-1}$ . The spectrum shows bands at  $\sim 450$ -475, 800-1000 and 1300  $\text{cm}^{-1}$  with the band above 400  $\text{cm}^{-1}$  supposed to be attributed to lighter oxygen atom vibrations, with the 454  $\text{cm}^{-1}$  mode ascribed to apical oxygen and  $\text{O}_3$  vibration modes at 914  $\text{cm}^{-1}$ . Additionally, absorption band at 1300  $\text{cm}^{-1}$  is ascribed to C-O vibrational mode, as Carbon can be included during synthesis since some of the primary materials used for synthesis are compounds containing carbon.

### III. INFRARED TRANSMISSION IN SUPERCONDUCTING FILMS : ENERGY GAP INTERPRETATION

Using the complex admittance per square of a film, which is thin in comparison to the skin depth and large in its transverse dimension in comparison to wavelength, the reflectance and transmission properties can be completely worked out. For a film with admittance  $M$  that is laid on a substrate having refractive index  $\mu$ , taking a ratio of the power transmission when the film is present to that when the film is absent can be written as, [2]

$$T = |1 + Z_0 M / (\mu + 1)|^{-2} \quad (3.1)$$

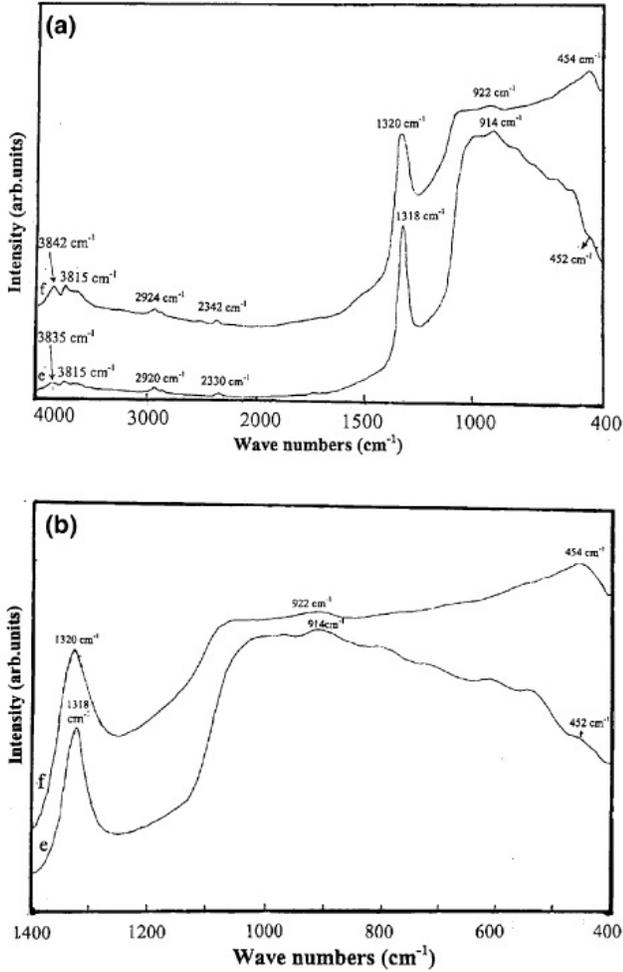


FIG. 2. (a) FTIR absorption spectra of  $\text{Cu}_{1-x}\text{Tl}_x\text{-1234}$  samples prepared below  $900^\circ\text{C}$  before annealing (b) Extended FTIR absorption spectra of  $\text{Cu}_{1-x}\text{Tl}_x\text{-1234}$  samples prepared below  $900^\circ\text{C}$  before annealing [3]

where,  $Z_0 = \text{impedance of free space}$ . For metals,  $M$  is  $1/R_N$ , where  $R_N$  is the dc resistance per square for film.

For these films, regardless of the value of  $\omega$ , transmission is only about one-fourth even though the skin depth is dependent on  $\omega$ . For superconducting state,  $M$  is a complex, frequency-dependent quantity. Using Eq.(3.1) the ratio of the power transmission in the superconducting state  $T_S$  to that of the normal state  $T_N$ , is

$$\frac{T_S}{T_N} = [ \{ \sqrt{T_N} + (1 - \sqrt{T_N}) \frac{\sigma_1}{\sigma_N} \}^2 + \{ (1 - \sqrt{T_N}) \frac{\sigma_2}{\sigma_N} \}^2 ]^{-1}$$

where  $\sigma$  is used to denote conductivity and for the superconducting state, the complex conductivity is introduced using the expression  $\sigma_1(\omega) = \sigma_1(\omega) = \sigma_N R_N Y(\omega)$

The Kramers-Kronig relations allow for a provision to have both  $\sigma_2$  and  $\sigma_1$  at a fixed frequency, if there are measured observations throughout the relevant range of

frequencies, despite the limitation of a transmitted power measurement being insufficient to have fixed values of frequency for  $\sigma_2$  and  $\sigma_1$ . [5,6]

Using the London-type conductivities  $\sigma_1^L = \frac{c^2}{8\lambda^2} \delta(\omega - 0)$ ,  $\sigma_2^L = \frac{c^2}{4\pi\omega\lambda^2}$ , the Kramers-Kronig relations can be satisfied and for the superconducting film these would be equivalent to their inductive admittance without loss. Considering these to be the only term present, complete transmission at high frequencies would lead to  $T_S = 1$ , with transmission increasing continuously with frequency. However, given that observations support at high frequencies  $T_S \rightarrow T_N$ , therefore the normal conductivity would have to be present in both states too. Such a description explains the high frequency limit but for explanation of the observed transmission peak at intermediate frequencies the following model needs to be considered.

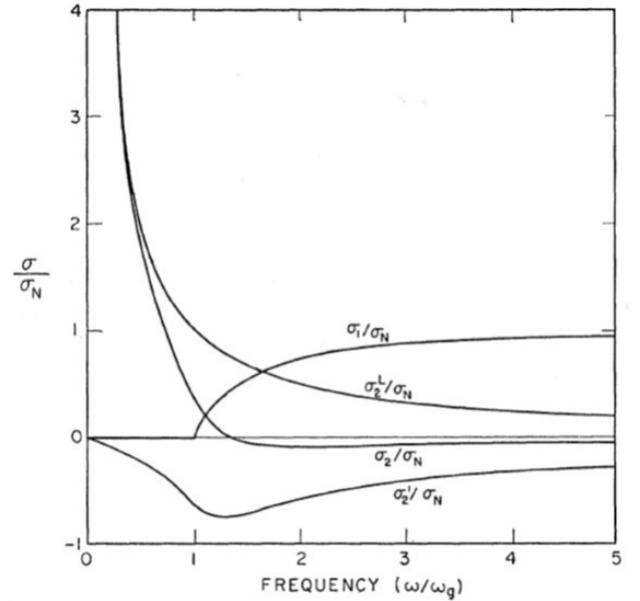


FIG. 3. Frequency dependence of conductivity for an energy-gap model at  $T=0$  under the assumption  $\frac{\sigma_1}{\sigma_N} = 1 - \frac{\omega_g^2}{\omega^2}$  and  $\frac{\sigma_2^L}{\sigma_N} = \frac{\omega_g}{\omega}$ . [2]

For the superconductor a model is considered where the energy gap is  $\hbar\omega_g \approx 3kT_c$  for one-electron energy states - this gap is chosen in accordance with specific heat data (Corak *et al.*, 1956) [10]. For energies  $\hbar\omega < \hbar\omega_g$ , the lossy conductivity  $\sigma_1$  is 0. For  $\hbar\omega > \hbar\omega_g$ , increasing  $\omega$  leads to a gradual increase in  $\sigma_1$ , since the fraction of available states for excitation with regard to the occupied state below the Fermi Level increases.

For Figure 3, considering the assumptions that  $\frac{\sigma_1}{\sigma_N} = 1 - \frac{\omega_g^2}{\omega^2}$  and  $\frac{\sigma_2^L}{\sigma_N} = \frac{\omega_g}{\omega}$ , the Kramers-Kronig relations come out to be,  $\frac{\sigma_2'}{\sigma_N} = -\left(\frac{1}{\pi}\right) \left\{ \frac{\left(1 - \frac{\omega_g^2}{\omega^2}\right) \ln|\omega_g + \omega|}{|\omega_g - \omega| + 2\frac{\omega_g}{\omega}} \right\}$ . The

sharp transmission peak can be explained by considering that both 1 and 2 are small and for  $T > 0$ , 1 will be  $> 0$ , at value greater than  $g$  too, and 1 has a gradual rise from a lower frequency leading to a lower transmission peak in calculated curve.

#### IV. FAR- INFRARED SPECTROSCOPY IN HIGH $T_c$ SUPERCONDUCTOR :AN EXAMPLE

Far-infrared reflectivity measurements of polycrystalline  $YBa_2Cu_3O_{7-\delta}$  samples with superconducting transition temperature in the 90K range were performed by Genzel *et al.* [4]. The Far-Infrared reflectance measurements were performed in the range  $20\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$ . Presence of phonon absorption in interference with the superconducting electron influenced reflection properties were observed noting the distinct features in the spectrum obtained. The Far infrared reflectance was measured with  $2\text{cm}^{-1}$  resolution with single reflection near normal incidence for unpolarized light. Distinct bands in the spectra at  $150\text{-}230\text{ cm}^{-1}$  region are attributed to phonon frequencies. From the generated reflection spectra, the band width could be determined taking into account the effect of electron-phonon interaction. For an approximate carrier concentration of  $10^{22}\text{ cm}^{-3}$ , a band gap energy of  $5 \times 10^{-4}\text{ eV}$  is obtained for 100K, leading to a relaxation time of  $\tau = 2 \times 10^{-15}\text{ s}$ . Also, for measurements in the  $150\text{-}350\text{ cm}^{-1}$  range, temperature dependent features due to optical phonon were observed between 10 K - 300K.

#### V. NEAR-INFRARED SPECTROSCOPY

##### A. Near-IR absorption bands : origin

The operation range for Near-Infrared spectroscopic measurements is usually  $13,300$  to  $4000\text{ cm}^{-1}$  (which corresponds to a wavelength range of  $750\text{-}2500\text{ nm}$ ). At this range, the energy of the incident photons is large enough to produce only the lowest vibrational excitations, and insufficient to induce electronic excitations. The application of Near-Infrared spectroscopy is useful since it provides advantage of being universally applicable since any molecule containing C-H, S-H, N-H or O-H bonds can be probed using this method.

To produce excitation to a higher vibrational energy level in a molecule, radiation of energy equal to the difference between two vibrational levels or of their overtones or combinations of two or more vibrations are needed. An equality between the energies of the incident photon and the vibrational levels is not sufficient, though, to cause absorption of radiation. For any molecular vibration to be infrared active, the vibrational motion must result in a net electric dipole moment within the molecule. This holds true for the fundamental mode of vibration ; for combination bands, some modes of vibration may not be

visible, however, in the mid-infrared region. The intensity of the vibrational absorption band is proportional to the change in dipole moment in the molecule and the degree of anharmonicity. For samples having bonds with hydrogen, carbon, sulfur and nitrogen atoms, this change in dipole moment as well as the degree of anharmonicity are very prominent and therefore the near-infrared absorption bands pertaining to these types of bonds are very prominent. For C-H, N-H, S-H and O-H bonds (which have significant anharmonicity) the fundamental modes occur at wavelength range of  $3000\text{-}4000\text{ nm}$ , so the overtones and combination modes of these fundamental vibrations can be seen in the near-infrared region.[7,8]

##### B. Solid State characterization

Application of Infrared techniques in the solid state characterization of materials is useful given that it is a non-destructive and non-invasive technique and especially for materials such as pharmaceutical drugs, the identification and monitoring of solid state transformation is a critical requisite in the study of changes in biopharmaceutical properties and processing behavior, both qualitatively and quantitatively.[1]

###### 1. Identification of hydration state

For pharmaceutical drugs, hydration state affects physical or chemical stability of the drug as well as its solubility and dissolution bioavailability if a change occurs in the hydration state during manufacturing or storage. It is important therefore that this be monitored.

Even though, other spectroscopic techniques can be used for this purpose, Near-infrared spectroscopy has an advantage over other techniques since it shows unique absorption bands in spectral region. For a given solid state sample, a difference in environment of  $H_2O$  leads to a unique change in the near-infrared spectral region which can serve as a signature. Due to the anharmonic nature of the -OH bond of water five maxima appear at  $760, 970, 1170, 1450$  and  $1940\text{ nm}$ . Of these bands, the first overtone of -OH stretching vibration and a combination of -OH stretching and bending vibrations are assigned to  $1450$  and  $1940\text{ nm}$ , respectively. Hydrogen bonding intensity and molecular interactions further influence the band positions. These can then be used to study the water-solid interactions and to distinguish between hydrate forms of the drug.

###### 2. Quantification of change for crystalline to amorphous transformation or vice versa

The transformation of amorphous substances to crystalline form is detrimental with respect to performance and stability for various drugs, in general. Given that

such a change directly affects the critical qualities of drug products therefore, it is essential to be able to quantify the change in state of a drug from amorphous to crystalline both during development as well as production. Even though other techniques such as Inverse Gas Chromatography (IGC), FT-Raman spectroscopy, Isothermal micro-calorimetry (IMC) exist, each of these techniques is limited by certain conditions such as requirement of large sample size, lack of specificity and a prerequisite of specified experimental conditions and methodology.

Owing to intermolecular interactions (specifically hydrogen bonding) as well as conformational differences that lead to characteristic band shift and intensity difference, Near-Infrared spectra of amorphous materials are significantly different from that of their crystalline counterparts. For various drug molecules such as miokamycin, indomethacin and lactose, Near-Infrared spectroscopy can be used with appropriate chemometric tools for quantification of amorphous to crystalline ratio, with appreciable degree of accuracy. For crystalline materials, ease of processing can be affected by the crystalline to partly amorphous transformation due to mechanical or thermal stress.

### 3. Characterization in co crystallization process

In co-crystallization, a supramolecular synthesis involving formation of linkage between molecules via weak interactions takes place. Even though single crystal X-ray diffraction technique is preferred to study and confirm co crystal formation, generation of crystals suitable for x-ray diffraction studies can be difficult (especially challenging is the identification of the location of the hydrogen bond). Infrared spectroscopy can be used to detect the formation of cocrystals and to distinguish them from salts. However, due to the prerequisite of a reference set of samples representing different solid forms of drug, near infrared spectroscopy can sometimes be less preferred in the characterization of co crystals.

## VI. COMPARISON OF INFRARED SPECTROSCOPY WITH OTHER SPECTROSCOPIC TECHNIQUES

Even though Infrared spectroscopy is a very useful technique in study and characterization of various solid state samples, other spectroscopic techniques exist that can complement or improve over the results obtained for a given sample using Infrared Spectroscopy. Two of the most common and widely used spectroscopic techniques for study of relevant samples are Raman Spectroscopy and NMR spectroscopy. NMR or Nuclear Magnetic resonance Spectroscopy has the advantage of being a direct method of probing, in that it can detect changes in the connectivities between different atoms directly - providing sharp peaks for each of the species constituting

the sample, for both proton-NMR and  $^{13}\text{C}$ -NMR type of probing. Infrared spectroscopy is a good tool to identify functional groups so it can be coupled with NMR spectroscopy to obtain more precise information about the samples being analyzed.

IR spectroscopy can very efficiently identify the C=O stretching vibrational mode due to the presence of a characteristic spectral band at  $2100\text{ cm}^{-1}$ . However, one of the significant limitations in IR is the limitation of having aqueous samples since water absorbs infrared radiation giving intense bands that might mask the absorption bands for the sample under study. This limitation is absent in Raman spectroscopy, since water is a weak Raman scatterer and so aqueous samples can be easily probed. However, Infrared spectroscopy and Raman spectroscopy can be used to complement each other for analysis of observed data especially if the sample is an unknown one, and Infrared and Raman spectroscopy can be used to identify ionic and covalent character of the bonds present, respectively.

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