

DISPERSIVE FOURIER TRANSFORM MEASUREMENTS ON OPAQUE SOLIDS FROM 5 TO 350 cm^{-1}

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Abstract—A two beam interferometer for use in ambient temperature dispersive Fourier transform measurements on opaque and highly reflecting solids is described. The spectral range between 5 and 350 cm^{-1} has been covered and the performance illustrated with the first reported direct measurements of the complex reflectivity and complex relative permittivity of potassium dihydrogen phosphate and ammonium dihydrogen phosphate.

INTRODUCTION

In a conventional broad band far i.r. Fourier transform experiment a specimen is introduced into the exit beam of a two beam interferometer in such a way that its power transmission or reflection is measured. The loss of phase shift information in such a measurement means that the full complex refractive index $\hat{n} = n - ik$ can only be obtained approximately from the measured quantity. In particular with power reflection measurements on opaque and highly reflecting solids the phase can be constructed from a Kramers-Kronig analysis but the use of a truncated integral and intensity uncertainties in regions of low reflectivity can lead to substantial errors. These problems are avoided with dispersive Fourier transform techniques where the specimen is introduced into one of the arms of the interferometer to give an asymmetric interferogram which contains both the amplitude attenuation and the phase shift information.

The basis of the technique for opaque solids is to measure the full complex reflectivity, $\hat{r} = \hat{n} - 1/\hat{n} + 1$, of a plane vacuum-specimen interface at normal incidence from which \hat{n} can be calculated as the inverse of the above expression i.e. $\hat{n} = 1 + \hat{r}/1 - \hat{r}$. In the measurement \hat{r} is found from a comparison of the modulus and phase of the complex transforms of the voltage interferograms from a symmetric interferometer and from the same interferometer with its fixed mirror exactly replaced by the plane specimen surface. If this interchange of specimen and reference reflector is not exact then systematic phase errors that are linear in frequency result. The major experimental problem is the construction of an interferometer that is sufficiently stable to avoid these systematic errors. This has recently been realised for opaque solids¹⁻⁴ although dispersive techniques for transparent materials are well established due to the more relaxed stability requirements.⁵⁻⁷

EXPERIMENTAL

The interferometer used in these measurements is based on the modular cube in use at NPL⁸ and its principle of operation is illustrated in Fig. 1. It uses collimated radiation from a quartz encapsulated mercury vapour arc, thin film dielectric beam dividers and a variety of radiation detectors to cover the 5-350 cm^{-1} spectral region. The fixed mirror arm is mounted vertically upwards and terminates at a horizontal plane defined by the tops of three equilaterally spaced and rigidly mounted balls of 0.75 mm radius. These define the reflecting plane of this arm and the specimen and reference reflector rest on them in turn during measurements to give the normal incidence configuration. They are lifted off by cradles which are not in contact during measurements and which are operated manually from outside the vacuum chamber.

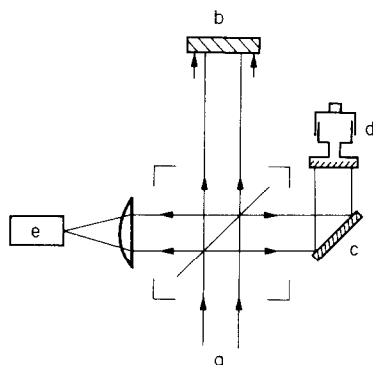


Fig. 1. Schematic representation of the dispersive interferometer. (a) collimated radiation from mercury lamp source (b) specimen or reference reflector on three point support (c) 45° mirror that can be vibrated for phase modulation (d) moving mirror on motor driven micrometer (e) detector.

This avoids disturbing the vacuum system during a series of measurements as substantial displacements of the interferogram on its sampling comb were found to occur if the pressure was let up to atmospheric and then taken down again.

A major cause of systematic errors was the sinkage of soft specimens onto the reference supports under the action of their own weight. This was minimised by additionally supporting the reflectors in use on three extra arms that were free to move in vertical arcs and counterbalanced to take almost all of the specimen weight. The net downward force on the fixed supports was therefore small and sinkage avoided. Using this system of fixed reference points it was found that the reproducibility of the specimen and reference reflector location was always better than $\pm 0.1 \mu\text{m}$ and was not a significant cause of systematic errors. The major problem arises from backlash in the moving mirror micrometer drive which can give rise to displacement errors between successive interferograms of as much as $0.5\text{--}1.0 \mu\text{m}$. Future developments will overcome this by the use of optical monitoring of the mirror position.

Initial measurements were made using amplitude modulation and partial stabilisation of the interferometer using mains water cooling of the large exposed areas of the interferometer. These gave a phase reproducibility of about ± 0.03 rad below 200 cm^{-1} increasing to about twice this at 350 cm^{-1} due to a lack of high frequency energy.³ The temperature of the interferometer is now stabilised at a few degrees below ambient to $\pm 0.25^\circ\text{C}$ over 2–3 hr by the use of a temperature controlled bath in the cooling circuit and this together with phase modulation⁹ gives phase stabilities of better than ± 0.007 rad ($\sim 0.5^\circ$) over most of the spectral range of the interferometer.

RESULTS

The technique using amplitude modulation has already been used for measurements on potassium bromide,³ intrinsic indium antimonide¹⁰ and soda lime glass.¹¹ In the following we present amplitude modulated measurements on the ferroelectric potassium dihydrogen phosphate (KDP) and the antiferroelectric ammonium dihydrogen phosphate (ADP) at 290°K . Both materials are anisotropic so measurements were made with plane polarised radiation. The polariser consisted of aluminium strips deposited on a polyethylene substrate and orientated to coincide with the natural polarisation direction of the dielectric beam divider.

(i) KDP. The complex reflectivities of KDP for radiation polarised perpendicular to and parallel to the *c* axis at 290°K are shown in Fig. 2. In both orientations the amplitude reflectivity falls from a low frequency value of about 0.8 and exhibits considerable structure to higher wavenumbers. The real and imaginary parts of the complex relative permittivity $\hat{\epsilon} = \epsilon' - i\epsilon''$ have been calculated from these complex reflectivities using standard expressions and are shown in Figs. 3 and 4 for each orientation.

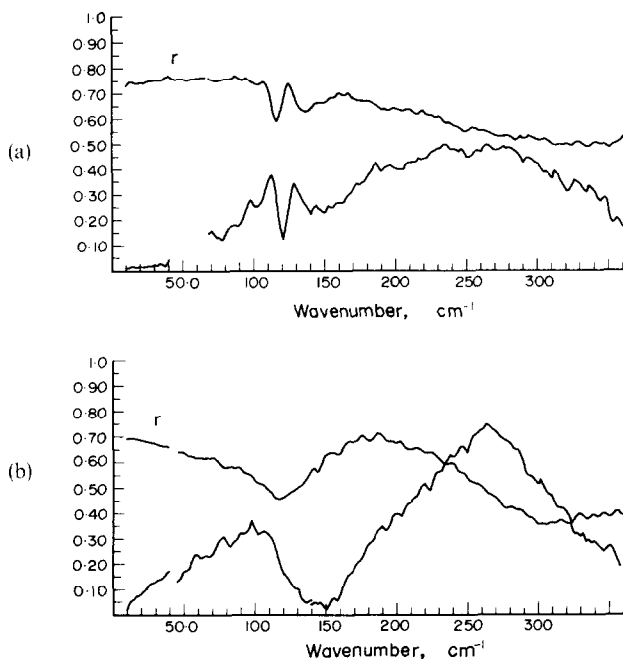


Fig. 2. The complex reflectivity of KDP for radiation polarised (a) perpendicular to, and (b) parallel to the c -axis at 290 K. In each case the amplitude reflectivity is the upper curve. The lower curve is the measured phase $\phi_r - \pi$. The ordinate is fractional reflectivity or phase in radians.

At the present time these measurements cover roughly the 15–350 cm^{-1} region with a small gap at about 50 cm^{-1} caused by the non-complete overlap of the spectral ranges of the beam dividers used. These measurements are now in process and will be reported on later. The perpendicular polarised results shows several features which have been attributed to hydrogen bond stretching modes¹² as these are known to be almost perpendicular to the c -axis and so are expected to contribute to the perpendicular

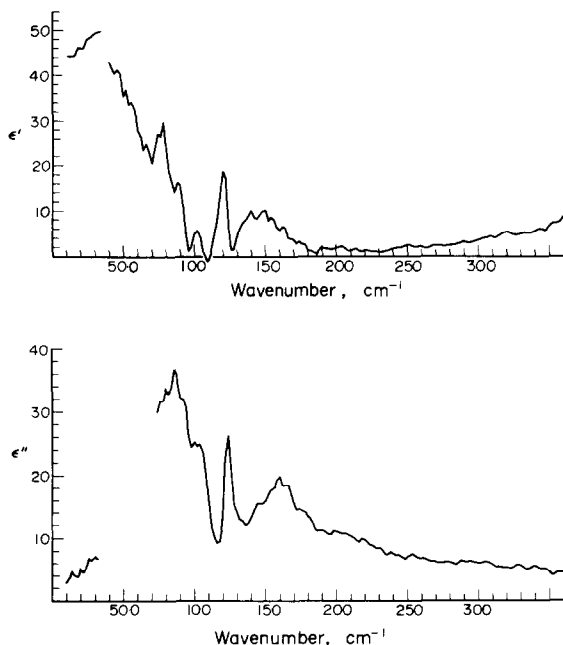


Fig. 3. The complex relative permittivity $\hat{\epsilon} = \epsilon' - \epsilon''$ of KDP at 290 K for radiation polarised perpendicular to the c -axis.

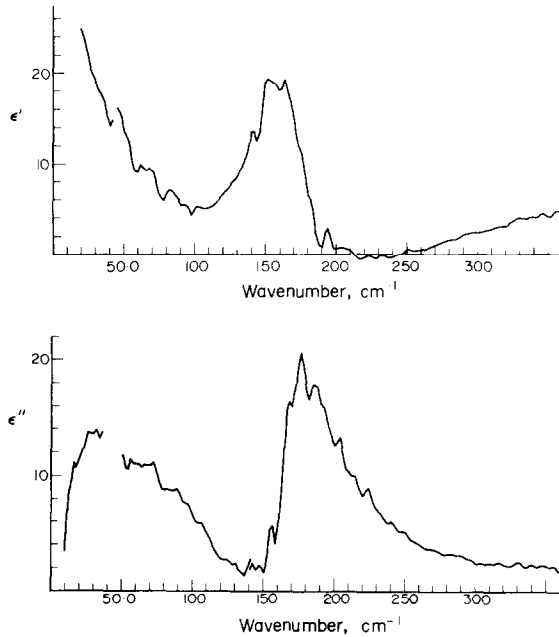


Fig. 4. The complex relative permittivity of KDP at 290 K for radiation polarised parallel to the c -axis.

spectrum. The real part of the complex permittivity for this orientation must go through a maximum in the region of 50 cm^{-1} that is not resolved in our measurements but has been seen in a Kramers–Kronig analysis of power reflectivity measurements.¹³ The static value of ϵ' for the perpendicular orientation can be extrapolated from these results as ~ 44 which agrees with the value found from the Kramers–Kronig analysis¹³ and microwave measurements. Overall, the perpendicular polarised results show good quantitative agreement with the earlier Kramers–Kronig measurements.^{12–14} The parallel polarisation results of Fig. 4 have only two broad features present with the lowest frequency one at about 50 cm^{-1} in ϵ'' associated with the ferroelectric transition. We again find overall agreement between the positions and strengths of these features and those found by Kramers–Kronig measurements with one major discrepancy. The static value of the real permittivity extrapolated from our measurements is $\sim 30/35$ which is substantially higher than the generally accepted value of 20.^{12,13} The measurements are consistent and reproducible and will be repeated on another specimen to eliminate the possibility of crystal damage.

(ii) ADP. These measurements were performed on an isotropically cut crystal i.e. c -axis perpendicular to the reflecting surface. Figure 5 shows the complex reflectivity and Fig. 6 the complex relative permittivity obtained at 290°K from these measurements.

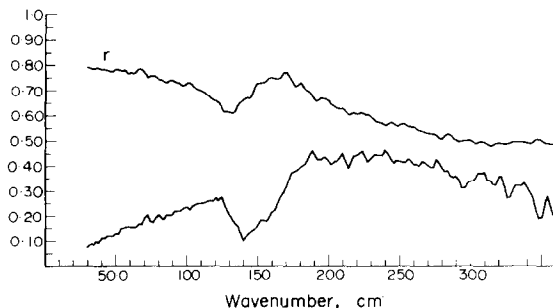


Fig. 5. The complex reflectivity of isotropically cut ADP at 290 K. The axes are as in Fig. 2.

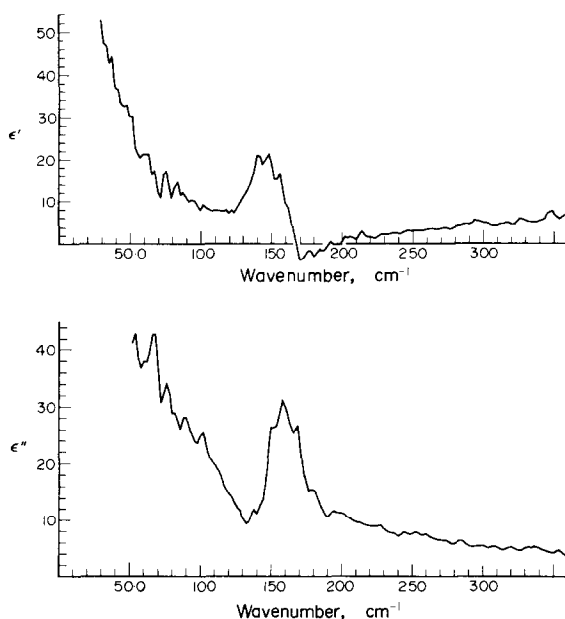


Fig. 6. The complex relative permittivity of ADP at 290 K.

The general features of the imaginary part of the permittivity spectrum are in good agreement with earlier Kramers–Kronig work using radiation polarised perpendicular to the c -axis.¹⁴ In this earlier work the low frequency ϵ'' spectrum is fully resolved into an intense low frequency band at 46 cm^{-1} .

CONCLUSIONS

A modular interferometer for use in dispersive Fourier transform measurements on opaque solids between 5 and 350 cm^{-1} has been described. By the use of phase modulation within the interferometer and careful attention to its temperature stability phase reproducibilities of about ± 0.007 rad have been achieved. Measurements made with this interferometer on KDP and ADP provide the first direct measurements of their complex reflectivities and the values of their complex relative permittivities calculated from these agree very well with previous Kramers–Kronig determinations.

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