Abstract— Interference fringes in the far-infrared spectra of thin films are the result of the coherent adding up of waves and can influence the spectral interpretation by concealing smaller features. A number of methods have been developed in order to eliminate such oscillating features from the transmittance spectrum. The paper critically evaluates the total transmission-reflection technique and applies the method to quantify the spectra of different polymer films.

I. INTRODUCTION

Far-infrared (FIR) spectroscopy is a widely used tool to study the molecular dynamics and the intermolecular interactions in polymers from which important chemical and physical properties can be deduced. Already several decades ago this low frequency region of the electromagnetic spectrum has been exploited, for example, to render insights in the role of hydrogen bonding in biology related molecules [1], to study phase transitions and crystallinity in polymers [2] or to study ionic interactions in ion-containing polymers (ionomers) [3].

The sample preparation methods for FIR absorption measurements are as manifold as they are for mid infrared (MIR) measurements. Like for the MIR spectral range, transmittance measurements of free-standing film material seem here to be the simplest approach in order to obtain absorbance data. However, for both the spectral regions experimental conditions exist, where interference fringes can disturb or even hinder the quantitative interpretation of absorption bands.

Interference fringes are the result of a coherent adding up of waves with an optical path length difference of $2nd$ caused by multiple reflections at the internal boundaries of the free-standing film, where $d$ is the thickness and $n$ the index of refraction of the film. Constructive and destructive interference occur for path differences of an even number and an odd number of half of the wavelength, respectively. A number of methods have been developed in order to eliminate such oscillating features from the transmittance spectrum in the MIR spectral range. This includes the preparation of special samples, like wedged films or films with one rough surface, or mathematical treatments of the spectra [4].

Other methods are based on suited optical arrangements, like measuring the film transmittance under the Brewster angle with polarized light, using attenuated total reflection (ATR) spectroscopy or applying the total transmission-reflection (TTR) technique [5]. The later method is based on measuring the reflectance of a film which is placed in front of a back mirror so that the waves are passing the film twice.

This paper reviews some of the above mentioned methods and discusses their applicability to absorbance measurements of polymer films in the THz or FIR spectral range.

II. EXPERIMENTAL

PTFE polymers films of different thicknesses between 10 µm and 1 mm were obtained from Goodfellow. Nafion NR211 perfluoro-sulfonate membranes in acid form (Nafion/H+) with an equivalent weight of 1100 g/equivalent and a nominal thickness of 25 µm were obtained from Ion Power GmbH. The preparation of the Nafion alkali salts are described elsewhere [3].

Spectra are obtained with FTIR vacuum spectrometers at a...
temperature of about 300 K. Spectra in the region between 30 and 300 cm\(^{-1}\) were measured with either an DTGS detector or a liquid He-cooled 4 K-Si-bolometer using a mercury arc lamp as a radiation source. In addition for spectra below 1 THz a synchrotron light source (HZB, BESSY II, IRIS beamline [4]) was used operating at low-alpha mode. The low-alpha mode is necessary to generate stable coherent synchrotron radiation (CSR) in the very FIR which is at least 100 times more intense than usual incoherent synchrotron sources [5].

III. RESULTS

The FIR optical constants of PTFE have been modelled assuming a harmonic oscillator at 202 cm\(^{-1}\) for the strong backbone absorption in PTFE [9] and the simple transmission and the TTR absorbance spectra have been calculated for a spectral resolution of 2 cm\(^{-1}\).

The calculated TTR spectra are free of interference fringes (Fig. 1) which is not the case for the transmission spectra. However, for thicker films a distortion of the absorption band becomes apparent and the maximum shifts to higher frequencies (Fig. 2). A second but smaller maximum appears at the lower energy wing of the absorption band. The simulation with higher spectral resolution show dominant interferences caused by the back mirror and the back interface of the film and which are averaged out at coarser spectral resolution (Fig. 3).

In addition, the strength of the absorbance band in the TTR spectra of the model film does not anymore follow Beer’s law (Fig. 4) and even starts to saturate. This is due to an increasing absorbance and with it an increasing reflectance at the first surface of the film upon increasing film thickness. As a consequence a distortion-free reflectance spectrum will be obtained for films thicknesses close to bulk. These findings are supported by a series of experimental PTFE film spectra.

The TTR technique has successfully been applied to measure thin ionomer films. From the low vibrational frequencies of the acid and the alkali salt forms of Nafion an average vibrational force constant could be derived.

IV. SUMMARY

The paper shows the successful removal of interference fringes in tetrafluoroethylene (PTFE) film spectra and compares calculated and measured spectra both for simple transmission and TTR geometry. Further, it is shown that the removal of interference fringes allows the quantification of the low vibrational frequency in alkali salts of Nafion.

REFERENCES


* Deceased on March 8, 2014.