[30] A. S. Prokhorov and E. G. Rudashevski, "Exchange amplification and magnetic impurity oscillation quenching in antiferromagnets," *JETP Lett.*, vol. 22, p. 99, 1975.
[31] U. Dür and K. J. Button, "Temperature dependence of the localized magnon mode in MnF_2:Co^{2+}," *Solid State Commun.*, vol. 16, p. 695, 1975.
[32] Yu. M. Gufan, K. N. Kocharyan, A. S. Prokhorov, and E. G. Rudashevski, "Dependence of the resonant frequencies of antiferromagnets on the magnetic field and antiferromagnetic resonance in CoF_2," *Sov. Phys. JETP*, vol. 39, p. 565, 1975.
[33] C. R. Becker, Ph. Lau, R. Geick, and V. Wagner, "Antiferromagnetic resonance in NiO:Co^{2+} and NiO:Fe^{2+}," *Phys. Status Solidi*, (b), vol. 67, p. 653, 1975.
[34] A. R. Fert *et al.*, "Ferromagnetic resonance in $FeCl_2$ and $FeBr_2$," *Solid State Commun.*, vol. 18, p. 327, 1976.
[35] R. J. Grill, U. Dürr, and R. Weber, "FMR investigations on the one-dimensional ferromagnet $CsNiF_3$," in *Proc. Int. Conf. Magnetism* (Amsterdam, 1976), to be published.
[36] G. Geis, R. Geick, C. R. Becker, and V. Wagner, "Antiferromagnetic resonance in CoO/NiO mixed crystals," in *Proc. Int. Conf. Magnetism* (Amsterdam 1976), to be published.
[37] W. Ghidalia, J. Tuchendler, and J. Magarino, "Antiferromagnetic, spin flop and paramagnetic resonances of hexahydrated cobalt chloride at very low temperatures," in *Proc. Int. Conf. Magnetism* (Amsterdam 1976), to be published.
[38] W. Lehmann and R. Weber, "Optical investigation of the magnon spectra of pure and Ni^{2+} doped K_2MnF_4," *J. Phys. C*, to be published.
[39] B. G. Kukharenko, "Antiferromagnetic resonance in transition-metal fluorides," *Sov. Phys. JETP*, vol. 42, p. 321, 1976.

Dispersive Fourier Transform Spectrometry with Variable-Thickness Variable-Temperature Liquid Cells

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***Abstract*—Dispersive Fourier transform spectrometry (DFTS) of liquids with variable-thickness variable-temperature cells is described. Different evaluative and computational methods are discussed and comparisons with the free layer method are shown with the aid of experimental results. Data for germanium and liquid chlorobenzene are presented.**

INTRODUCTION

DISPERSIVE Fourier transform spectrometry (DFTS) of liquids [1] in the millimeter and submillimeter-wave region has been extended to include precise measurement of the complex refractive index $\hat{n}$ or the complex relative permittivity $\hat{\varepsilon}$ of medium loss as well as high-loss volatile liquids over a wide temperature range (-80 to 80 °C) by the use of a variable-thickness windowed cell in one active arm of the Michelson-type two-beam interferometer. In the past these measurements were restricted to liquids of relatively low vapor pressure because of the necessity to use a free layer of liquid. An excess of liquid vapor absorbs radiation and gives its own characteristic spectrum [2]. The free layer method and subtraction [3], [4] and double subtraction [5] procedures enabled investigation of liquids of absorption coefficient α up to 250 Np/cm. But as the absorption increases it becomes more and more difficult to produce a sufficiently thin plane parallel layer held freely under gravity. However, for very absorbing liquids, like water, reflection DFTS [5], [6] has been successfully used in which accurate determination of the phase shift and an extremely stable interferometric system are essential.

In order to overcome these difficulties, two liquid cells with windows have been constructed, one at the University of Leiden, The Netherlands, and the other at the University of Nancy, Nancy, France, in cooperation with the National Physical Laboratory (NPL), United Kingdom. These cells were used at the NPL with an improved Michelson-type interferometric system. Different evaluation methods [7]–[13] can be used with these cell techniques. Knowledge of the complex refractive index of the window $\hat{n}_w$ is required in all evaluation methods except the two thicknesses method. $\hat{n}_w$ is evaluated directly from the same set of measurements [7], [8], [14].

EXPERIMENTAL

The ray diagram of the interferometer and the cell arrangement is shown in Fig. 1. The fixed mirror arm is mounted vertically upwards. The mirror can be moved up and down above the window to produce different thicknesses. The interferometer can be readily interchanged to either the dielectric beam splitter mode or the polarization mode [5]. The interferometer in the polarization mode with free standing wire grid beam splitters covers the frequency range between 3 and 250 cm^{-1} while the dielectric mode has been normally used between 100 and 600 cm^{-1}. The scanning mirror arm is bent at 90° with the use of a half-cube. This half-cube accommodates the phase modulator assembly.

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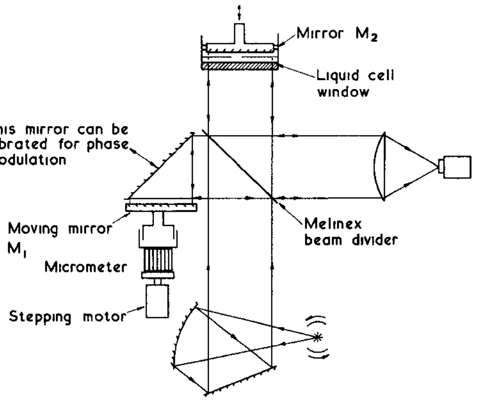

Fig. 1. Ray diagram of the Michelson interferometer with the liquid cell in the dielectric beam splitter mode.

Extreme care has been taken for thermal stabilization of the interferometer by circulating thermostated liquid in its different parts.

The Leiden cell [7], [8] comprises a 40-mm-diam window (crystal quartz or hyperpure silicon) of thickness 2.5 mm. The gold-plated mirror is mounted under a cylinder which moves in another cylinder by difference in pressure. Thermal isolation is maintained by evacuating the space between the cylinders and the outer jacket. The displacement of the mirror can be measured with an accuracy of 0.1 μm by the use of slip gauges positioned in between a fixed rigid table and the rod mounted with the inner cylinder. A liquid thickness of 10 μm to 5 mm can be used.

A germanium or a TPX (poly 4-methyl pentene-1) window of 75-mm diameter and 5-mm thickness has been used with the Nancy cell [9]–[11]. The front surface of a piston is polished and gold plated and acts as a mirror. This is mounted on a micrometer which allows displacement up to 10 mm, thereby permitting liquid thickness between 10 μm and 10 mm. The displacement is measured using precision transducers. Thermal isolation is maintained by the use of nylon spacers.

Both transmission DTFS ($\tau 0-$) and reflection DFTS ($\theta 0-$) methods for the determination of complex refractive index $\hat{n}(\tilde{\nu})$ of liquids can be employed in these cell techniques ($\tilde{\nu}$ indicates the wave number). In addition, a full interferogram method ($\lambda 0-$) can also be used in which all the recorded information is used. A recorded interferogram is the sum of several interference signatures; Fig. 2 shows a typical empty cell interferogram. The signature R_1 is the reflection signature from the front surface (vacuum–window interface) of the window. R_2 is the reflection signature from the back surface (window–dry air interface) of the window and R_3 is the mirror reflected (dry air–mirror interface) signature. The signatures $R_4,R_5,R_6,R_7,\cdots,R_M$ are multiply reflected signatures. For recording an empty cell background interferogram, the mirror M_2 can be positioned at a sufficient distance from the window that all signatures are separated. This permits editing of signatures which are then Fourier transformed (independently) to give complex spectra. Complex refractive indices of the window $\hat{n}_w(\tilde{\nu})$ are determined from the ratio of the complex spectra of R_1 and R_2 signatures. In the $\tau 0-$ method for a medium-loss liquid, a filled cell dry air–mirror interface reflection signature (R_3) is normally compared with an empty cell–mirror reflected signature. The reflection losses at window–air and window–liquid interfaces are corrected using the known values of $\hat{n}_w(\tilde{\nu})$, together with initial $\hat{n}(\tilde{\nu})$ values of the liquid (computed without loss corrections) and an iterative procedure. The liquid thickness is determined from the difference of the positions of the zero paths of the empty cell R_2 and R_3 signatures combined with slip gauge or transducer readings and the phase shift on reflection at the window–dry air interface (determined using complex refractive indices of the window).

For measurements of absorbing and very absorbing liquids, a very thin layer of liquid is used. The signatures R_2 and R_3, the reflection signatures at window-liquid and liquid–mirror interfaces, overlap. (Multiple signatures are absent for very absorbing liquid and overlap for absorbing liquid.) The R_2 signature appears to be the strongest, and recording of a third interferogram with a (very) thick layer of liquid is necessary to employ the subtraction procedure. The R_2 signature (window–liquid) of the third interferogram is identical to the R_2 signature of the thin layer interferogram, and is then subtracted from the overlapped R_2,R_3 signatures. Like the free layer case, a two-thicknesses method [5] can also be employed for a medium absorbing liquid in which a thin and a thick layer of a liquid are compared.

For very absorbing and opaque liquids, the $\tau 0-$ methods become inaccurate due to the necessity of producing an impracticably thin layer of liquid; $\theta 0-$ methods are then most suitable. Two $\theta 0-$ methods can be employed. In the first the empty-cell window–dry air interface reflection signature (R_2) acts as a reference or background against filled cell signature R_2. In the second the empty cell signature (R_3) acts as a reference. The parallelism of the mirror and the window surface is most critical in the second method in order to avoid any phase shift error. The use of the zero path difference of the R_1 signature as reference starting point has reduced the phase shift error in the methods described earlier [5], [6].

In the full interferogram method ($\lambda 0-$) the empty cell R_3 signature is compared with filled cell $R_2,R_3,R_4,\cdots,R_M$ signatures to evaluate $\hat{n}(\tilde{\nu})$. The method is only employed if the loss of accuracy in $\hat{n}(\tilde{\nu})$ exceeds the gain due to editing or subtraction of R_2 signature in a filled cell case.

DISCUSSION

The liquid cell methods have been successfully applied to the measurements of liquid bromoform, chlorobenzene, methanol, methanol–water mixtures, pure water [16], iso-octane, benzonitrile, and critical mixtures of benzonitrile and iso-octane [17]. In addition, power absorption coefficients $\alpha_w(\tilde{\nu})$ and refractive index $n_w(\tilde{\nu})$ spectra of window materials: germanium, TPX (poly 4-methyl pentene-1) silicon, and crystal quartz [14] were also determined. Complex $\hat{n}_w(\tilde{\nu})$ of germanium are shown in Fig. 3. The resistivity of the sample was about 50 Ω-cm. The phonon

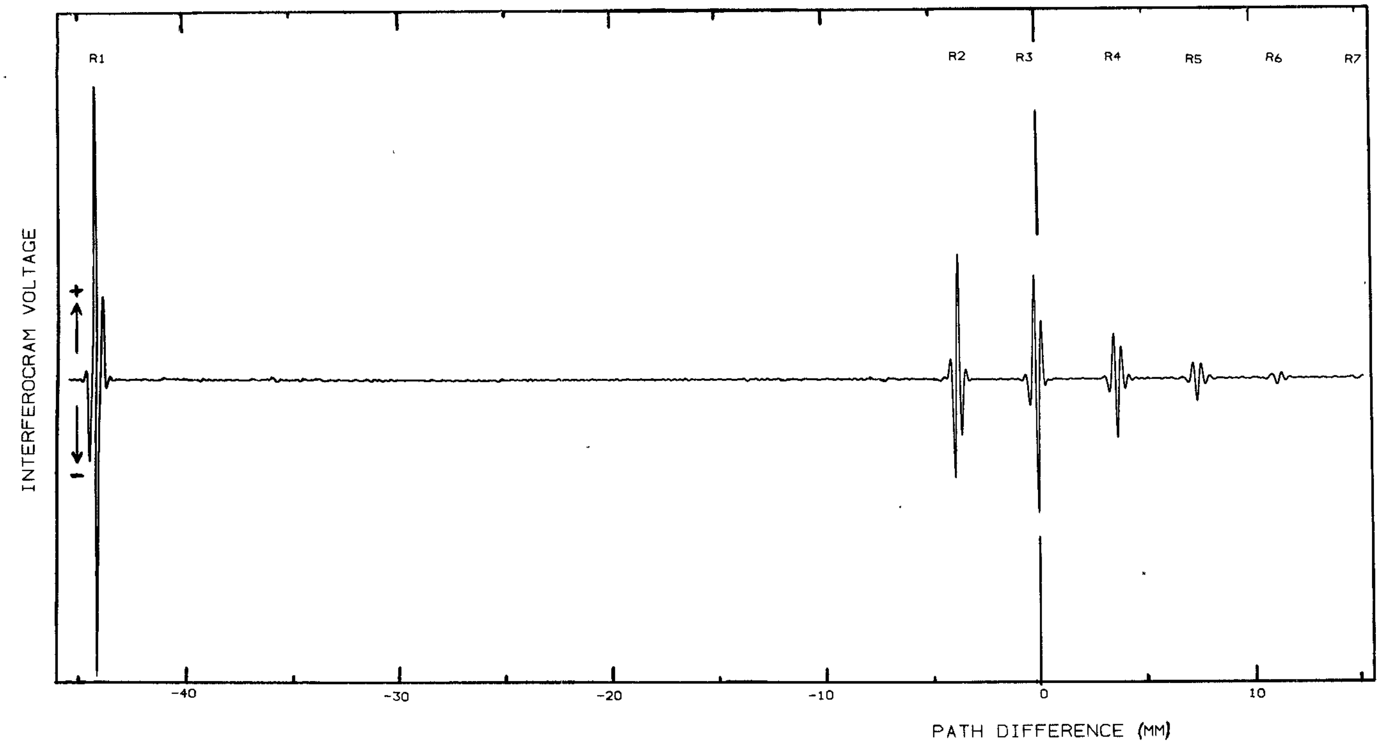

Fig. 2. Empty cell interferogram recorded using phase modulation, polarization mode, Rollin detector, and the germanium window of thickness about 5 mm. The mirror M_2 is at a distance about 1.9 mm from the window.

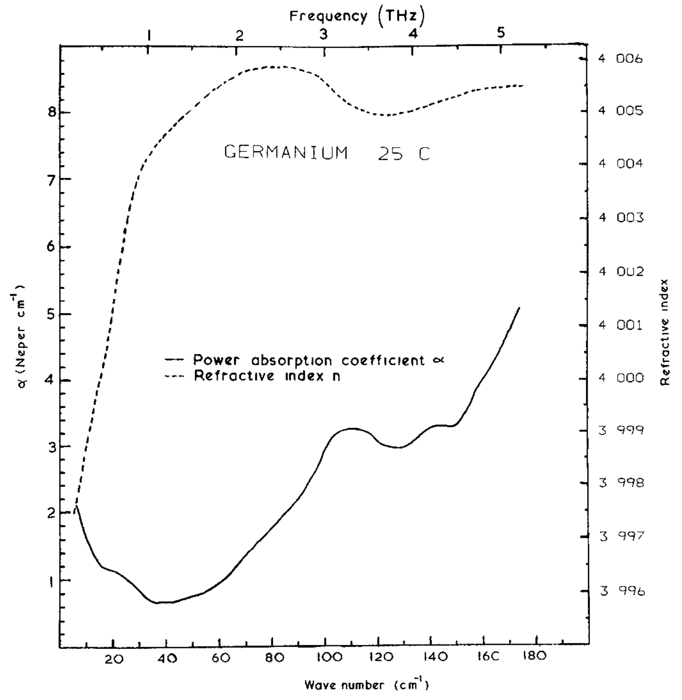

Fig. 3. Power absorption coefficient and refraction spectra of germanium at 25°C measured with the interferometer in the polarization mode with a Rollin detector between 5 and 40 cm^{-1} (0.15–1.2 THz) and a Golay cell between 20 and 190 cm^{-1} (0.6–5.7 THz).

resonance absorption band around 115 cm^{-1} (3.45 THz) [18] is observed along with the corresponding dispersion in the refractive index spectrum. The refractive index rises from 3.9975 at 6 cm^{-1} (0.18 THz) to about 4.005 at 55 cm^{-1} (1.65 THz), and is almost flat between 55 and 190 cm^{-1} (1.65–5.7 THz). Fig. 4 shows the comparison of the free layer method and liquid cell method $\alpha(\tilde{\nu})$ and $n(\tilde{\nu})$ of liquid chlorobenzene. A two-thicknesses method [5] has been used for the free layer method. This also gives very accurate $\alpha(\tilde{\nu})$ and $n(\tilde{\nu})$ results [15]. The agreement is quite good over the whole range. The discrepancy in $n(\tilde{\nu})$ is less than 0.2 percent and in $\alpha(\tilde{\nu})$ is about 1 percent, and can be expected considering the fact that the measurements were carried out with different samples at different times and under different experimental conditions. Both $\alpha(\tilde{\nu})$ and $n(\tilde{\nu})$ spectra lie well within the band shown in [19].

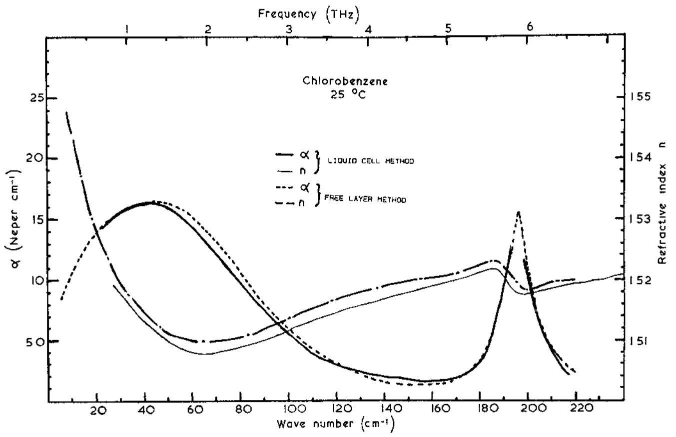

Fig. 4. Comparison of liquid cell method and free layer method $\alpha(\tilde{\nu})$ and $n(\nu)$ of liquid chlorobenzene at 25°C. The interferometer was in the polarization mode and Rollin and Golay detectors were used between 5 and 40 cm^{-1} (0.15–1.2 THz) and 20 and 240 cm^{-1} (0.6–7.2 THz), respectively.

The foregoing suggests that the liquid cell method can be applied to the measurements of complex refractive indices and subsequently complex relative permittivity of a wide variety of medium absorbing, absorbing, very absorbing, and opaque liquids and solutions over a wide temperature range with high accuracy. The method has also combined both transmission DFTS and reflection DFTS methods into one system and one interferometric setup. The problem of liquid vapor (in the free layer transmission DFTS) has totally disappeared. An extensive error analysis of the method will be discussed in [20].

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REFERENCES

[1] J. Chamberlain, J. E. Gibbs, and H. A. Gebbie, "Refractometry in the far infrared using a two-beam interferometer," *Nature* (London), vol. 198, pp. 874–875, 1963. J. Chamberlain, A. E. Costley, and H. A. Gebbie, "Submillimetre dispersion of liquid tetrabromoethane," *Spectrochimica Acta*, vol. 23A, pp. 2255–2260, 1967.

[2] W. F. Passchier, D. D. Honijk, and M. Mandel, "The determination of complex refractive indices with Fourier transform interferometry—IV error analysis of free layer experiments," *Infrared Physics*, vol. 16, pp. 389–401, 1976.

[3] J. Chamberlain, M. N. Afsar, and J. B. Hasted, "Direct measurement of refraction spectrum of ethanol at submillimetre wavelength," *Nature Physical Science*, vol. 245, pp. 28–30, 1973.

[4] M. N. Afsar, J. Chamberlain, and J. B. Hasted, "The measurement of refraction spectrum of a lossy liquid in the far infrared region," *Infrared Physics*, vol. 16, pp. 587–599, 1976.

[5] M. N. Afsar, J. B. Hasted, and J. Chamberlain, "New techniques for dispersive Fourier transform spectrometry of liquids," *Infrared Physics*, vol. 16, pp. 301–310, Jan./Mar. 1976.

[6] J. Chamberlain, M. N. Afsar, D. K. Murray, G. D. Price, and M. S. Zafar, "Submillimetre-wave dielectric measurements on absorbing materials," *IEEE Trans. Inst. Meas.*, vol. IM-23, pp. 483–488, Dec. 1974.

[7] D. D. Honijk, W. F. Passchier, M. Mandel, and M. N. Afsar, "The determination of complex refractive index spectra of liquids in the far-infrared spectral region 5–500 cm with dispersive Fourier transform spectrometry," *Infrared Physics*, vol. 16, pp. 257–262, Jan./Mar. 1976.

[8] D. D. Honijk, W. F. Passchier, M. Mandel, and M. N. Afsar, "The determination of complex refractive indices with Fourier transform interferometry—V," *Infrared Physics*, vol. 17, pp. 9–24, Jan. 1977.

[9] J. Goulon, M. N. Afsar, and G. W. Chantry, "A simple variable temperature, variable path length, cell for dispersive Fourier transform spectroscopy of liquids," to be published.

[10] M. Hollecker, Docteur de Specialité, Thesis, University of Nancy, France, 1975.

[11] M. N. Afsar and J. Goulon, "Dispersive Fourier transform spectroscopy of liquids with a simple variable path length, variable temperature cell—Computational Methods," to be published.

[12] D. D. Honijk, W. F. Passchier, and M. Mandel, "The determination of complex refractive indices with Fourier transform interferometry—Experimentally accessible quantities," *Physica*, vol. 68, pp. 457–474, 1973.

[13] W. F. Passchier, D. D. Honijk, and M. Mandel, "The determination of complex refractive indices with Fourier transform interferometry III—Computation of the complex refractive index spectrum," *Infrared Physics*, vol. 15, pp. 95–109, 1975.

[14] W. F. Passchier, D. D. Honijk, M. Mandel, and M. N. Afsar, "A new method for the determination of complex refractive index spectra of transparent solids in the far infrared region," *J. Physics D*, to be published.

[15] M. N. Afsar, "The measurement of the power absorption coefficient of liquids and low loss solids by transmission dispersive Fourier transform spectrometry," to be published.

[16] D. D. Honijk, A. C. Houwaart, M. N. Afsar, and M. Mandel, to be published.

[17] M. Hollecker, J. Goulon, J. Brondeau, M. N. Afsar, and G. W. Chantry, "High frequency dielectric behaviour of critical binary solutions of benzonitrile-iso-octane," to be published.

[18] E. V. Loeawenstein, D. R. Smith, and R. L. Morgan, "Optical constants of far infrared materials 2: Crystalline solids," *Applied Optics*, vol. 12, pp. 398–406, Feb. 1973.

[19] M. N. Afsar, J. Chamberlain, G. W. Chantry, R. Finsy, and R. Van Loon, "An assessment of random and systematic errors in high-frequency dielectric measurements," *Proc. IEE*, to be published.

[20] W. F. Passchier, D. D. Honijk, M. Mandel, and M. N. Afsar, "The determination of complex refractive indices with Fourier transform interferometry VI—Error analysis of liquid cell experiments," *Infrared Physics*, to be published.