High-Frequency Dielectric Processes in Liquids

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***Abstract*—Recent advances in dispersive Fourier spectrometry are described. The complex refractive indices of lossy materials are now directly measurable over a wide spectral range which extends from microwavelengths to the midinfrared. Some results for liquid ethanol and butanol are presented and interpretation of the spectra in terms of hydrogen bonding is offered.**

I. INTRODUCTION

THE possibility of "high-frequency" ($\sigma > 10\text{-cm}^{-1}$) absorption in dipolar and nondipolar organic liquids had been suggested by Poley [1] and Whiffen [2], respectively, following measurements by them at microwavelengths ($\lambda > 10$ mm). The first complex permittivity measurements [3] made with a HCN laser (29.7 cm^{-1}) supported the possibility and the absorption was discovered explicitly by Chantry and Gebbie [4] who used Fourier transform spectrometry (FTS) to record the absorption of liquid monohalobenzenes. The discovery of a similar but weaker absorption feature in some nondipolar liquids [5], [6] led to much work [7] which showed the feature to be typical of both polar and nondipolar molecules in the liquid state. Those organic liquids which have no appreciable hydrogen bonding exhibit a band which, in terms of power absorption coefficient $\alpha(\sigma)$, is centered in the range $\sigma = 40\text{–}80$ cm^{-1} and has a full width at half height which is of the same order as the center wavenumber. The magnitude of the absorption, which is believed to be of quasi-resonant character [8], [9], is about ten times less for nondipolar than for dipolar liquids but no single quantitative comparison of a general nature is possible because of the range of values covered by the absorption. Some typical $\alpha_{\max}$ values are given in Table I.

TABLE I
PEAK SUBMILLIMETER-WAVE POWER ABSORPTION COEFFICIENT α_{MAX} FOR SOME POLAR AND NONDIPOLAR LIQUIDS

Liquid	$\alpha_{\max}$ [Np m^{-1}]
C_6H_5CN	9400
$C_6H_5NO_2$	7900
CH_3CCl_3	3200
$\underline{o}$-ClC_6H_4Cl	1800
C_6H_5Cl	1600
$\underline{m}$-ClC_6H_4Cl	1400
C_6H_6^{a}	500
$\underline{p}$-ClC_6H_4Cl^{a}	400
CS_2^{a}	330
CCl_4^{a}	200

[a] No permanent dipole moment (i.e., nondipolar).

Note: Data taken from [7] and S. R. Jain and S. Walker, "Far infrared absorption of some organic liquids," *J. Phys. Chem.*, vol. 75, pp. 2942–2947, 1971.

Hydrogen-bonded liquids show a rather different behavior. On account of the great strength of their absorption they have been little studied until recently [10], [12]. Some new results are reported here.

II. THE REFRACTION SPECTRUM

It has been customary in infrared measurements to rely solely on transmission data, or on absorption deduced from them, for the assessment of spectra. It is true to say that this is no longer adequate. Although the absorption spectrum is extremely valuable it is not sufficient to allow the submillimeter-wave process to be fully characterized and related to lower frequency dielectric phenomena for which the complex relative permittivity $\hat{\epsilon}(\sigma) = \epsilon'(\sigma) - i\epsilon''(\sigma)$ is usually determined. Knowledge of the refractive index $n(\sigma)$ is also required to calculate $\hat{\epsilon}(\sigma)$, since $\hat{\epsilon}(\sigma)$ itself cannot be directly measured. It is also often needed to correct transmission data for nonabsorptive losses and to use in, for example, such condensed-phase corrections as the Polo–Wilson factor when attempting interpretation in terms of a simple model. While n and α (or ϵ' and ϵ'') are, of course, not independent but are related as a consequence of causality by the Kramers–Krönig relations, it is undoubtedly a great aid to interpretation to have independent experimental knowledge of both. Dispersive (or asymmetric) Fourier transform spectrometry (DFTS) has enabled $n(\sigma)$ to be measured for transmitting liquids. This paper describes how DFTS has been improved to: 1) enable lossy liquids to be studied, and 2) give spectra which extend to and overlap with discrete microwave data.

The recent development [13] of an amplitude reflection technique for very lossy liquids (such as water) will not be discussed. DFTS results are supported by HCN and H_2O laser measurements.

Conventional FTS is well established and need not be described. In DFTS, as shown by Chamberlain *et al.* [16], [17] and Bell [14], [15], the refractive index spectrum is found by placing the specimen in one arm of the two-beam interferometer which is the basis of a Fourier transform spectrometer. This gives a shifted and distorted interferogram. If the interferogram voltages recorded with

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and without the specimen in the interferometer are $V(x)$ and $V_0(x)$, respectively, where x is the path difference, the ratio

$$\mathfrak{F}\{V(x)\}/\mathfrak{F}\{V_0(x)\}$$

of their full Fourier transforms $\mathfrak{F}\{\ \}$ gives the complex insertion loss $\hat{\mathfrak{L}}(\sigma)$. The form of the relation between $\hat{\mathfrak{L}}(\sigma)$ and the complex refractive index depends on both the nature and location of the specimen. Honijk *et al.* [18] have given a full treatment which can be applied in simplified form in most practical cases. For liquids, the technique first established by Chamberlain *et al.* [19] has been used most widely. In it, the radiation traverses twice a plane-parallel gravity-held layer of liquid which rests on the fixed mirror (held horizontal) of a Michelson-type interferometer. The interferogram is the sum

$$V(x) = V_R(x) + V_T(x) + V_M(x)$$

of a number of interference signatures representing, respectively, radiation reflected from the surface of the specimen (R), transmitted through it (T), and multiply reflected within it $2m$ times:

$$V_M(x) = \sum_{m=1}^{\infty} V_{(m)}(x).$$

The T term alone can be simply related to $n(\sigma)$ and has been isolated to enable $n(\sigma)$ to be found by editing the interferogram. For lossy liquids, the specimen thickness d has to be small and the R and T signatures overlap; because of the absorption, the M signatures are generally negligible. Editing, always of questionable justification, is not possible and so a subtraction technique which uses three interferograms has been devised [20] to isolate T. The third interferogram is recorded for a specimen so thick ($d' \gg d$) that there is only one noticeable signature $V_{R'}(x)$, identical in shape to $V_R(x)$ but located at a different center. A suitable shift $2(d' - d)$ of $V_{R'}(x)$ gives a replication of $V_R(x)$ and enables $V_T(x)$ to be calculated, when $V_M(x) \simeq 0$, from

$$\begin{aligned} V_T(x) &\simeq V(x) - V_R(x) \\ &\equiv V(x) - V_{R'}(x) * \delta(x - 2d' + 2d). \end{aligned}$$

This technique can be employed for low-loss liquids also and has been compared in the case of chlorobenzene with the simpler editing procedure and the full iterative procedures devised by Honijk and Passchier. Agreement is satisfactory and the technique has subsequently been applied to lossy liquids.

III. EXPERIMENTAL

The spectral range accessible in a single measurement is wider if a polarizing interferometer of the type devised by Martin [21] is used rather than the more usual Gebbie type of Michelson interferometer [17]. In our arrangement, two wire-grid beam dividers are employed. The transfer function of the instrument has been experimentally assessed and found to be high and virtually independent of wavenumber up to the cutoff region which, for 10-μm tungsten wire with 25-μm spacing, is near 200 cm^{-1}. The range 3–220 cm^{-1} is available with the instrument; we cover this in two measurements in which two different detectors are used (a Rollin and a Golay cell). Using Gebbie-type and Martin-type interferometers, refraction and absorption spectra of a number of primary alcohols have been recorded and are reported here. The most strongly absorbing liquid to which our technique has been applied so far is ethanol for which $n(\sigma)$ has been recorded up to 100 cm^{-1}. The refraction spectrum of methanol, which is more strongly absorbent, has been recorded up to only 30 cm^{-1}. The refraction spectrum of water has been found from its amplitude reflectivity using a variant of DFTS [13].

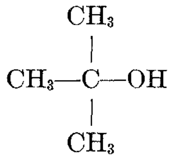
IV. DISCUSSION OF RESULTS FOR ETHANOL AND BUTANOL

The alcohols from ethanol through to octanol show similar submillimeter-wave absorption and refraction spectra from 30 up to 100 cm^{-1}. The absorption curves $\alpha(\sigma)$ have a similar featureless use; the level reducing as one moves through the series from methanol to n-octanol. The refractive index falls steadily with wavenumber without a minimum value turning point. This behavior is quite different from that of chlorobenzene which is a typical dipolar organic liquid (Fig. 1). The refractive index has a minimum near 65 cm^{-1}. This is about 1.6 times the wavenumber of peak absorption and this is typical of the behavior of a very heavily damped resonance. We have extended our earlier measurements on ethanol down to 5 cm^{-1} to meet microwave results. Good continuity is obtained for $n(\sigma)$ and $\alpha(\sigma)$, as it is also for chlorobenzene.

Conversion of n and α to ϵ' and ϵ'' reveals completely different behavior in the complex plane for ethanol and for chlorobenzene. The submillimeter-wave dielectric process is represented as a bulge at the high-frequency end of the large arc which extends from the static value ϵ_0 and depicts the lower frequency relaxational processes. Ideally, overlap with microwave data and extension of n and α measurements well into the infrared to beyond 300 or 400 cm^{-1} is required to provide an adequate basis for the interpretation of the mechanism giving the loss. Absorption measurements have been made above 100 cm^{-1} to about 350 cm^{-1} to locate the peak in $\alpha(\sigma)$; corresponding refraction measurements have been made only for butanol and these exist only to about 200 cm^{-1}. Thus many gaps remain.

Butanol is an interesting system because of its existence in the normal and tertiary forms

CH_3—CH_2—CH_2—CH_2—OH and



$$CH_3\text{—}\overset{\displaystyle CH_3 \atop |}{\underset{\displaystyle | \atop CH_3}{C}}\text{—}OH$$

and the similarity of the n form to the alkyl bromide 1-bromobutane:

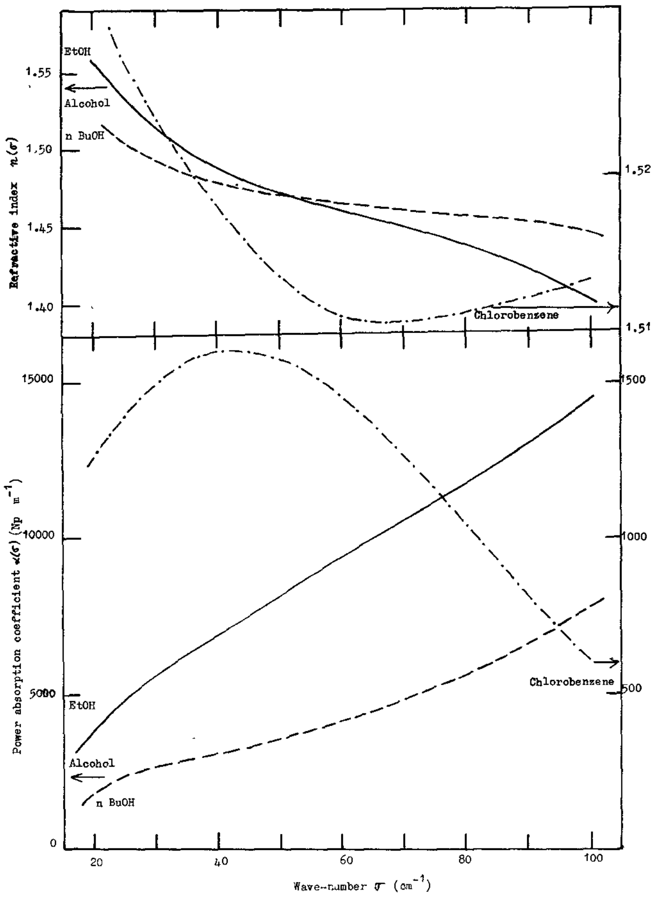


Fig. 1. Submillimeter-wave refractive index $n(\sigma)$ and power absorption coefficient $\alpha(\sigma)$ of ethanol (—), n-butanol (– – –), and chlorobenzene (•—•—•) at ambient temperature. The left ordinates refer to the alcohols, the right ordinates to the chlorobenzene.

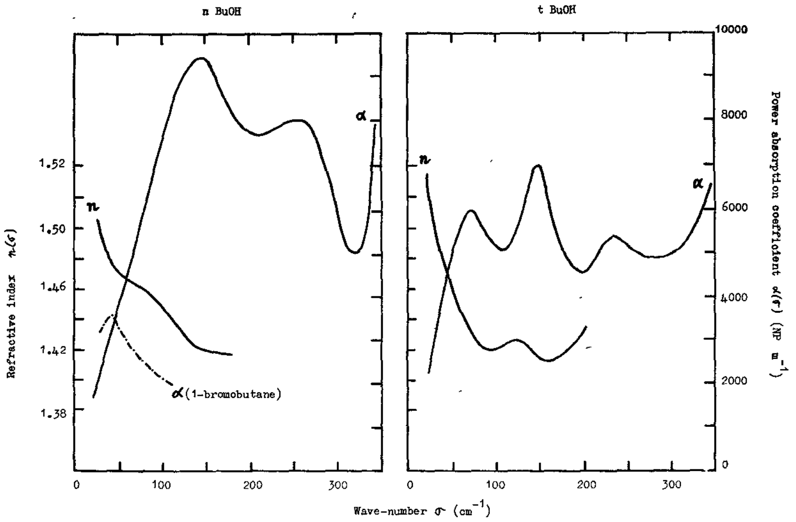


Fig. 2. Far infrared refractive index $n(\sigma)$ and power absorption coefficient $\alpha(\sigma)$ of n-butanol and t-butanol. Also shown is the power absorption coefficient of 1-bromobutane (•—•—•) as recorded by Pardoe [23].

$$CH_3—CH_2—CH_2—CH_2—Br.$$

n-butanol is strongly hydrogen bonded but t-butanol forms only dimers [22] and 1-bromobutane is not hydrogen bonded at all. Up to 100 cm^{-1}, the absorption of n-butanol is quite different from that of 1-bromobutane [23]. The latter shows a peak near 40 cm^{-1} of Poley type whereas the former has absorption rising steeply to a peak at 145 cm^{-1} with a smaller, but nevertheless strong, peak near 250 cm^{-1}. The refractive index falls steadily from 30 to 200 cm^{-1}. t-butanol has absorption which is different in form and generally of lower level than that in n-butanol (Fig. 2). There is a peak below 100 cm^{-1} at 70 cm^{-1} which

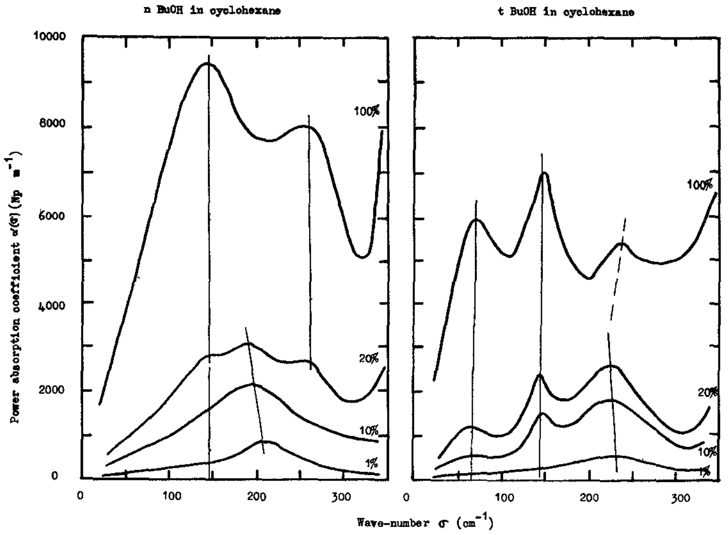


Fig. 3. Far infrared power absorption coefficient of solutions of *n*-butanol and *t*-butanol in cyclohexane at various concentrations (percent by volume). The faint straight lines indicate possible relationships between the absorption features.

is probably the Poley absorption caused by libration of monomers and/or dimers and two other features at 145 and 230 cm^{-1}. The refractive index is of the same order as that for *n*-butanol but shows a minimum near 100 cm^{-1}, such as we would expect[1] for a Poley absorption peaking at 70 cm^{-1}, and anomalous dispersion near 150 cm^{-1} indicative of a resonance process. Since most of the associated alcohols show a peak around 150 cm^{-1} it would appear that this is related to hydrogen bonding in the liquid. Dilution studies, like those of Passchier *et al.* [12] on methanol, can shed some light on this although so far only absorption data have been obtained. The situation for *n*-butanol is less clear than that for *t*-butanol. Using cyclohexane as the solvent, we find the behavior shown (Fig. 3). For *t*-butanol there is only one band at 1-percent (by volume) concentration (at 227 cm^{-1}). At all higher concentrations, three bands are present and the 227-cm^{-1} peak shifts to lower wavenumbers. The peak heights show differing variations with concentration. That of the 70-cm^{-1} band increases linearly; that of the 145-cm^{-1} band rises rapidly at first and then more slowly at higher concentrations, tending towards the rate for the Poley absorption; and that of the 225-cm^{-1} band rises rapidly (like the 145-cm^{-1} band) at first, but the rate reduces so that ultimately, at full concentration, this band is the weakest of the three, whereas at low concentrations it is the strongest. For *n*-butanol, at concentrations up to 10 percent, only one band is clearly visible. This is similar in shape to that at ~225 cm^{-1} in *t*-butanol but it starts at 210 cm^{-1} and shifts rather rapidly to lower wavenumbers and is not discernible above 20 percent as extra bands develop on either side from 15 percent upwards. The absorption level at 145 cm^{-1} grows to exceed that at either ~210 or ~250 cm^{-1}. The level of absorption in *n*-butanol is generally greater than that of *t*-butanol as would be expected if association is responsible for the loss mechanism. As it is difficult to divide meaningfully the absorption curves into component profiles, we have considered the variation with concentration of the absorption coefficient at some key wavenumbers and compared these data with those of Passchier *et al.* [12]. We deduce that the 145-cm^{-1} band is an associative band, attributed to H-bond stretch [10] (ν_σ) and resonant in character; and that the bands near 200 cm^{-1} in *n*-butanol and near 225 cm^{-1} in *t*-butanol are, like the 210-cm^{-1} band in methanol, due to CO torsion in single molecules. This band tends to be suppressed in the pure normal liquids, but the more simply associated *t*-butanol reveals this band as an explicit feature in the pure liquid. The band which appears near 250 cm^{-1} in *n*-butanol seems to be related to molecular interactions but no detailed explanation is currently available. The generally greater level of absorption in *n*-butanol than in *t*-butanol and the absence of an explicit Poley band are consistent with a greater degree of association in the normal form.

It is evident that the submillimeter-wave properties of the alcohols are dominated by hydrogen-bonding effects which are centered above 100 cm^{-1} and are possibly resonant in character although the refraction spectrum does not clearly reveal this. Underlying relaxation effects may also be present. Liquid water has a similar but stronger spectrum [24], but the interpretation is still far from certain and is probably different in many respects from that proposed for the alcohols [24]–[26].

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A New Technique for Dispersive-Reflection Spectroscopy in the Far Infrared

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***Abstract*—A new technique is described for measuring the amplitude- and phase-reflection spectra of solids in the far infrared. The field of view in the fixed arm of a Michelson interferometer is divided by screens to allow the specimen and reference mirror to be placed side by side. Interferograms are then recorded by reflection from each in turn so that phase errors arising from the physical replacement of the reference mirror by the specimen are eliminated. The method is demonstrated with room-temperature and low-temperature measurements on a crystal of KBr.**

INTRODUCTION

During the past few years important advances have been made in the use of dispersive (or asymmetric) Fourier-transform spectroscopy for the determination of refractive-index spectra (n,k) in the far infrared from transmission measurements [1]–[3], and for obtaining the optical constants directly from measurements of amplitude- and phase-reflection spectra (r,ϕ) [4]–[6].

To make dispersive reflection measurements on solids the fixed (reference) mirror of a Michelson interferometer is replaced by the specimen and an asymmetric interferogram is obtained which can be Fourier analyzed to give a complex transform. The complex reflectivity

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