Dielectric Measurements in the Submillimeter Region and a Suggested Interpretation of the Poley Absorption

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***Abstract*—Modern activity in the field of extra-high-frequency dielectric measurements on polar liquids is briefly reviewed and the means for carrying them out briefly described. It is now possible to determine the complex permittivity (and hence the complex refractive index) over the range 10^8–10^{13} Hz to an absolute precision of 1 percent and it is therefore worthwhile to reexamine the "liquid-lattice" theory which was put forward some time ago as an explanation for the additional Poley absorption. This theory is found to give a good account of the absorption spectrum of liquid chlorobenzene in the microwave, millimeter, and submillimeter regions.**

INTRODUCTION

THE anomalous dispersion of polar liquids in the radiofrequency and microwave regions was considered theoretically by Debye in 1913 long before any accurate measurements were possible [1]. The topic arose from Debye's attempts to extend his own theory of static polarizability (which he had obtained by adapting the Langevin theory of paramagnetism to the electric case) to the situation where the applied field is varying in time. The whole problem of treating the frequency-dependent complex polarizability of an ensemble of interacting dipoles was (and still is!) intractable, but Debye with the characteristic courage of a great mind cut through the Gordian knots of the theoretical sticking points and came up with a simple theory which gave, in restricted frequency regions, a reasonable account of the dispersion. Debye's theory was in a strict sense, inapplicable at both low and high frequencies, but the low-frequency difficulties could be sidestepped by introducing the static permittivity as a parameter rather than as a determined quantity. From the late thirties onwards, when measurements became possible this Debye equation [2]

$$\frac{\hat{\varepsilon}(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau} \tag{1}$$

where $\hat{\varepsilon}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ is the complex relative permittivity, ε_s and ε_∞ are its values at zero and infinite frequency, and τ is a characteristic relaxation time, was extensively used to give some insight into the microdynamics of polar liquids. One consequence of this equation is that, since it may be written [3]

$$\left[\varepsilon' - \left(\frac{\varepsilon_s + \varepsilon_\infty}{2}\right)\right]^2 + [\varepsilon'']^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2 \tag{2}$$

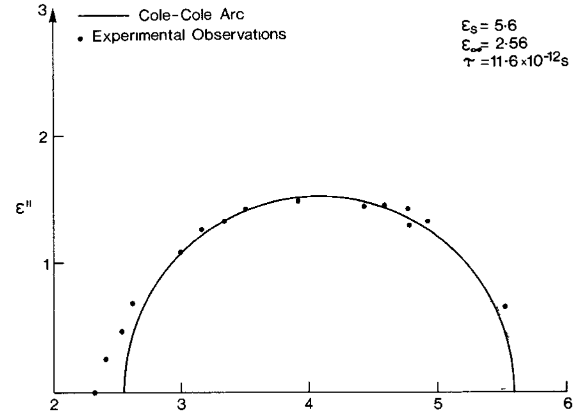

Fig. 1. Cole–Cole arc for liquid chlorobenzene at 25°C.

a plot of ε'' versus ε' should be a semicircle and such plots (often called Cole–Cole plots) feature strongly in the literature. The Cole–Cole plot for chlorobenzene is shown, as an example, in Fig. 1.

Debye was very careful to point out that his approximate equation should not be used at frequencies ω greater than τ^{-1}, for in that region inertial effects would become significant and these are expressly excluded in the derivation of the equation. The departure of the high-frequency points (towards the left of the diagram) from a strictly semicircular arc is quite evident for chlorobenzene in Fig. 1. Another illustration of the same point is that (1) taken as it stands leads (via the relationship $\alpha \approx \varepsilon''/c(\varepsilon')^{1/2}$) to a limiting high-frequency absorption coefficient α_∞ given by $\alpha_\infty = (\varepsilon_s - \varepsilon_\infty)/c\tau\varepsilon_\infty^{1/2}$. This implies that all polar liquids would be opaque throughout the infrared and optical regions in conflict, of course, with observation. Numerous theoretical attempts to overcome this difficulty have been made from time to time, but these were given a boost by the experimental determinations of submillimeter spectra which began at the National Physical Laboratory (NPL) in the middle sixties [4]. These spectra showed, for the first time, the broad additional absorption ("Poley" absorption) now known to be characteristic of the liquid state. Experimental results for chlorobenzene are shown in Fig. 2 along with the "plateau" extrapolation of the Debye equation.

BASIC THEORY

Attempts to understand the overall high-frequency absorption spectrum of polar liquids must include an

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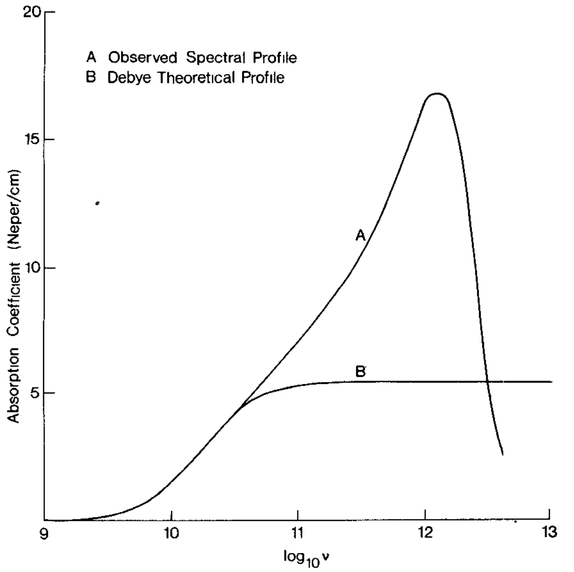

Fig. 2. Observed high-frequency spectrum of liquid chlorobenzene.

account of the recovery of transparency at sufficiently high frequency and an explanation of the Poley absorption whose absorption maximum lies far above the Debye asymptote. The first point is usually treated by the introduction of inertial terms into Debye's fundamental equations of motion. With the moment of inertia I not zero, the dipoles cannot respond instantaneously to changes in the field and at a sufficiently high frequency they will begin to lag and the absorption will start to fall. In other words there will be an "inertial rolloff." This approach came basically from Sack [5] with earlier input from Rocard [6] and Gross [7]. These authors worked in the frequency domain and the differential equations were solved by the Laplace-transform method leading to continued fraction solutions, of which the type

$$\frac{\hat{\varepsilon} - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = 1 - i\omega\tau\gamma/i\omega\tau\gamma + \gamma/1 + i\omega\tau\gamma + 2\gamma/2 + i\omega\tau\gamma + \cdots \quad (3)$$

where $\gamma = I/\tau^2 kT$ is typical. It will be seen that the various truncations (i.e., the convergents) of this continued fraction give successively some familiar results. Thus one has

$$\frac{\hat{\varepsilon} - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = 1, \frac{1}{1 + i\omega\tau}, \frac{1}{(1 + i\omega\tau)(1 + i\omega\tau\gamma)}, \cdots. \quad (4)$$

The absorption coefficient calculated from the higher truncations does go to zero at sufficiently high frequency and one has the desired recovery of transparency, but this approach does not explain the additional Poley absorption, an explanation for which has to lie in terms of intermolecular interactions. At the moment, opinions are divided on the question of how far the semiclassical approach can be pushed before quantum ideas have to be introduced.

An alternative approach, favored by many modern authors, is to work in the time domain and to derive the spectral consequences of a time-dependent model by taking a half-range Fourier transform. This involves the use of formalisms based on the correlation function, the memory function, etc. The recovery of transparency is ensured absolutely if the correlation function is chosen to be an even function of time, though in practice it seems to be necessary merely to have no linear term in the series expansion. This approach is very flexible and a wide range of spectral profiles can be produced. Lassier and Brot [8], for example, have shown that some simple models can give theoretical spectra which look remarkably similar to those observed. One can, therefore, encompass both the Poley and the Debye absorption into a single entity [9]. More abstract formalisms based on the same general approach and associated with the names of Kubo [10] and Mori [11] use general mathematical-physical concepts to constrain the theory and thus produce usable relations. Once again the solution of the equations is a continued fraction and its truncations are known by various titles "M-diffusion," "J-diffusion," etc. The method is very attractive, but of its nature there are some problems of interpretation.

EXPERIMENTAL METHODS

The most modern approach is to sidetrack these interpretational difficulties by reversing the process and calculating the correlation function by direct Fourier transformation of the observed submillimeter and radio-frequency spectrum [12]. However, for this approach to give meaningful answers the original spectral data have to be of very high quality. The efforts of the experimentalists is therefore being directed towards improving precision and eliminating sources of systematic error [13]. The submillimeter spectra are obtained from the Fourier transformation of the output of a Michelson interferometer used in either the conventional mode or else in the asymmetric (i.e., the dispersive) mode [14]. Since their introduction by Gebbie and his colleagues in the late fifties, these interferometers have been steadily improved and modern interferometers feature temperature stabilization, constant-current stabilized sources, phase modulation, high-grade mechanical construction, and last but by no means least cryogenically cooled low-noise solid-state detectors. These advanced interferometers, coupled with the radically new designs of specimen cell which are emerging, are opening up new realms of precision. Computational techniques are likewise being refined to the point where all the potential sources of error—even the most subtle—have to all intents and purposes been eliminated. The present situation is that the experimentalists can guarantee *absolute* precision of ±1 percent in α and ±0.1 percent in n, and it now remains to be seen whether these levels of accuracy are sufficient for the theoreticians to extract meaningful information or whether still more accuracy will be required.

THE LIQUID-LATTICE THEORY

Crystalline chlorobenzene at low temperature shows a strong-sharp line spectrum in the 20–70-cm^{-1} region [15] and Chantry and Gebbie [4], noticing that its integrated intensity was roughly equal to that of the Poley absorption in liquid chlorobenzene, suggested that the latter arose from vibrations of the liquid lattice. There is, of course, only the most local order in a liquid and the strong disorder over a few repeat units leads to heavy damping of the optical phonons and, therefore, to considerable width for the liquid-lattice lines. In quantitative terms, if the liquid-lattice theory is to be useful, one would expect to synthesize the Poley profile from the sum of a small number of broadened Lorentz profiles whose center frequencies and intensities bore some resemblance to the lattice lines in the crystalline spectrum and all of which showed the same broadening parameter. In other words, one would write

$$\alpha_{\text{res}} = \sum_{1}^{N} \frac{C_{1n}}{C_2 + \left(\dfrac{C_{3n}^{2}}{\nu} - \nu\right)^2}$$

where N is a small number and the subscript res denotes resonant. The total profile would then be given by

$$\alpha = \alpha_{\text{rel}} + \alpha_{\text{res}}$$

where α_{rel} is a relaxational component made up of the Debye absorption modified by inertial rolloff. A tentative decomposition of the observed spectral profile for liquid chlorobenzene is shown in Fig. 3.

TABLE I

$\bar{\nu}$ Wavenumber (cm^{-1})	α_{res}(calculated)	α(observed)
5	3.26	8.3
10	8.76	10.75
15	12.37	12.6
20	14.16	14.0
25	15.13	15.1
30	15.94	16.0
35	16.70	16.7
40	17.17	17.1
45	17.14	17.0
50	16.70	16.8
55	16.01	16.3
60	15.14	15.3
65	14.06	14.0
70	12.78	12.8
75	11.37	11.5
80	9.98	10.2
85	8.71	9.0
90	7.62	7.8
95	6.69	6.7
100	5.92	6.0
105	5.27	5.3
110	4.73	4.7
115	4.27	4.1
120	3.87	3.6
125	3.53	3.2

Note: Term with overbar appears bold face in text.

The agreement between the observed and the calculated profiles is seen to be excellent and, in fact, is so good that the residual discrepancies are not readily illustrated in the figure, and these calculated and observed ordinates are therefore listed in Table I for ease of comparison. It seems established then that one can explain all the absorption above 20 cm^{-1} by a combination of just four liquid-lattice lines. These have center wavenumbers $C_{31} = 20$ cm^{-1}, $C_{32} = 44$ cm^{-1}, $C_{33} = 60$ cm^{-1}, and $C_{34} = 70$ cm^{-1}; amplitudes $C_{11} = 24015$ cm^{-3}, $C_{21} = 14629$ cm^{-3}, $C_{31} = 5450$ cm^{-3}, and $C_{41} = 5364$ cm^{-3}, and all have the same width parameter $C_2 = 2000$ cm^{-2}. It should be stressed that these parameters have been derived using a simple iterative routine on a hand-held programmable calculator, and it is not suggested that they are truly optimized. It is also not established whether this particular resolution is the only one possible within the experimental error. The agreement becomes less good at wavenumbers above 100 cm^{-1}, where experimentally the liquid is regaining transparency at a faster rate than the Lorentz combinations permit. This is, however, a well-known phenomenon and most observed line shapes fall away more like a Gaussian than like a Lorentzian at sufficient displacement from the line center. This can be built into the theory by using the so called "Voight" line shape (a convolution of a Gaussian with a Lorentzian), but since there is no analytical expression for the Voight profile this is probably not worthwhile in the present case. Crystalline chlorobenzene at liquid-nitrogen temperature [15] shows five lattice bands at 37, 55, 70, 94, and 124 cm^{-1}, but of these only the first three are intense and of these three the 37 cm^{-1} band is the most and the 70 cm^{-1} the least intense. The comparison with the liquid-lattice theory is quite good since one would expect considerable shifts to lower wavenumbers on going from liquid nitrogen to room temperature and also in going from the more dense crystal to the less dense liquid. At the moment, however, a good explanation cannot be offered for the 60, 70-cm^{-1} doublet for the liquid when only a singlet is observed for the crystal.

The data from Fig. 3 are replotted in Fig. 4, where the conventional "dielectric" abscissa of $\log_{10} \nu$ is employed. This brings out much better the nature of the relaxational component. The Rocard–Powles dispersion formula [the third truncation in (4)] gives an absorption coefficient α which has (with the usual approximations) the functional form $x^2[1 + x^2]^{-1}[1 + x^2\gamma^2]^{-1}$, where $x = \omega\tau$. The absorption coefficient, therefore, peaks at $x = \gamma^{-1/2}$, and the peak value is $\alpha_\infty/[1 + \gamma]^2$ where α_∞ is the Debye asymptote. Taking the largest moment of inertia for chlorobenzene (namely 6.64×10^{-45} kg-m^2) one calculates γ to

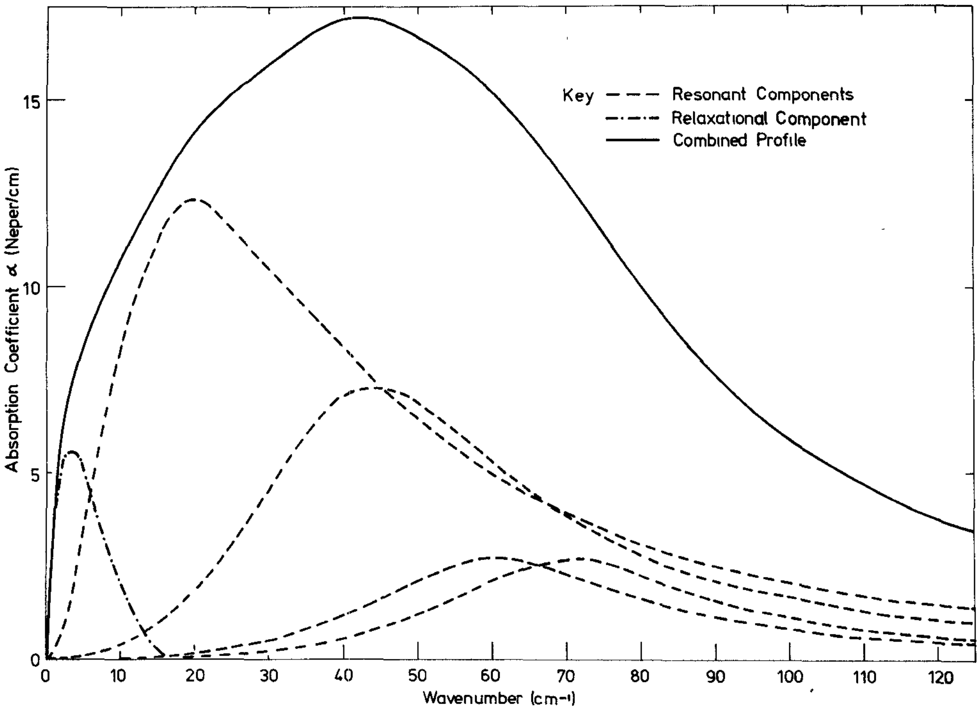

Fig. 3. Synthesis of the observed submillimeter spectrum of liquid chlorobenzene from the combination of four liquid-lattice lines and a relaxational band.

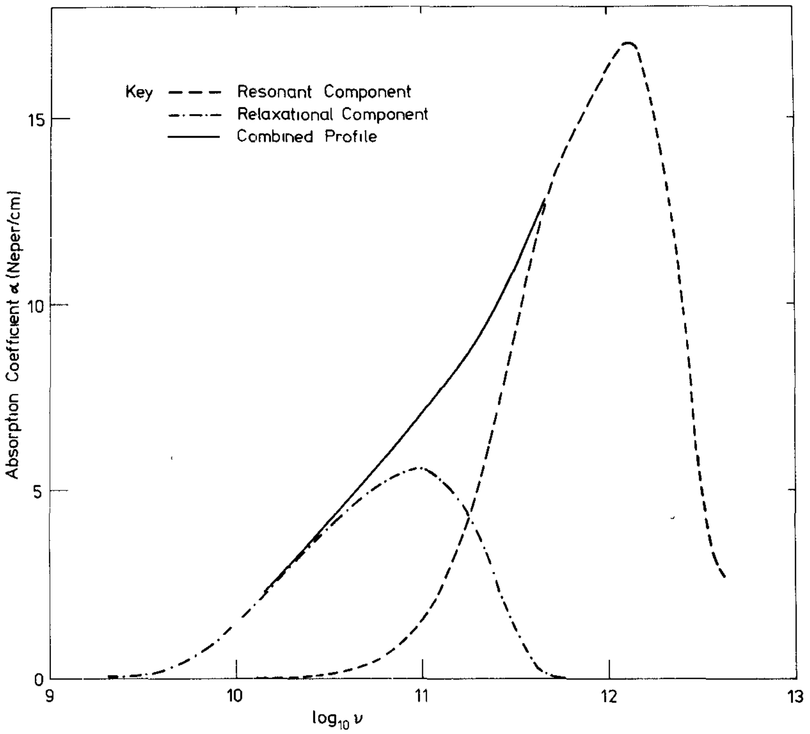

Fig. 4. Decomposition of the observed submillimeter absorption of liquid chlorobenzene into a resonant and a relaxational component.

be 1.2×10^{-2}. The "experimental" value derived from the frequency where the peak is located is 1.7×10^{-2}. The agreement is therefore fair and the small value of γ agrees with the fact that the peak height is close to the Debye asymptote. However the rolloff is much quicker than the Rocard–Powles formula predicts, since this, as does the Lorentz, goes only as ω^{-1} for large ω. Of course, the resolution into the resonant and relaxational components may not be perfect and one might be able to find a different combination with a slower rolloff, but investigations of this nature are probably best done with a series of liquids so that significant trends can be identified.

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Application of Submillimeter Spectroscopy to Magnetic Excitations

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***Abstract*—Magnetic excitations are the collective excitations of the magnetic moments in ferro- and antiferromagnets. The frequencies are mostly in the far-infrared spectral range. Their study is of current interest with respect to the properties of phase transitions, since in ordinary 3-dimensional crystals the dominating exchange interactions can be 3-dimensional (MnF_2, NiO) or may be restricted to 2 dimensions (K_2MnF_4, $CoCl_2$) or even to 1 dimension ($CsNiF_3$, $CoCl_2 \cdot 2H_2O$). In this paper, an introduction and a review is given of the results on $q = 0$ magnon modes (ferro- or antiferromagnetic resonance) which can be studied rather directly by submillimeter-wave spectroscopy. Some results about 2 magnon bands are also mentioned. Experimentally, grating monochromators, Fourier-transform interferometers, FIR laser, and microwave techniques have been employed. In the past, not only pure materials have been studied but also doped crystals where localized magnon modes can occur (MnF_2:Co^{2+}, CoF_2:MnF_2, NiO:Co^{2+}).**

I. INTRODUCTION

MAGNETIC EXCITATIONS are the collective modes of a system of spins or magnetic moments which are usually observed in the ordered ferromagnetic or antiferromagnetic state of the system. The frequencies of these excitations fall in the microwave range and in the far-infrared or submillimeter spectral region, up to 1000 cm^{-1}.

The study of magnetic excitations is of current interest since the dominating exchange interaction between the magnetic ions may be 3 dimensional or may be restricted to 2 or 1 dimensions even though the crystal in an ordinary 3-dimensional one, but with an anisotropic structure. The properties of such systems, i.e., susceptibility, excitations, specific heat, etc., are of particular interest with respect to the theory of phase transitions and critical phenomena [14], [15]. Some materials are compiled as examples in Table I. Among the great number of existing materials of each kind, those have been selected which were actually

TABLE I
EXAMPLES OF 1-, 2-, AND 3-DIMENSIONAL MAGNETIC MATERIALS

Dominating exchange interaction		
1-dimensional	2-dimensional	3-dimensional
← pure materials →		
$CsNiF_3$ /35/	K_2MnF_4 /20,29/	MnF_2 /1,4/
$CoCl_2 \cdot 2H_2O$ /9,25/	K_2NiF_4 /13,16/	NiF_2 /6,23,28/
	Rb_2MnF_4 /20/	CoF_2 /5,23,32/
	$CoCl_2$ /7,24/	$KMnF_3$ /27/
	$FeCl_2$ /7,21,34/	MnO /3,22/
	$CoCl_2 \cdot 6H_2O$ /37/	NiO /3/
		CoO /11,12/
← doped materials, mixed crystals →		
	K_2MnF_4:Ni^{2+} /19,29,38/	MnF_2:Fe^{2+} /8,10/
		MnF_2:Zn^{2+} /15,17/
		MnF_2:Co^{2+} /10,31/
		CoF_2:Mn^{2+} /18,30/
		CoO/NiO /33,36/

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