

The complex permittivity of six n-alkanes; measurements in the far infrared

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Abstract. The optical absorption of six n-alkanes (n-pentane to n-decane) has been measured in the far infrared using the Grubb–Parsons Mark III interferometer. The results are related to low frequency permittivity, microwave loss, and refractive index measurements using the Kramers–Krönig relation.

1. Introduction

Measurements have been made of the optical absorption coefficient α (neper cm^{-1}) for the series n-pentane to n-decane, at a temperature of 20 °C. These are discussed in terms of the complex permittivity $\epsilon(\omega) = \epsilon' - i\epsilon''$. The loss component ϵ'' can be written in terms of α , c the velocity of light and n , the real part of the refractive index as for instance (Hill *et al* 1969)

$$\epsilon'' = n c \alpha / \omega. \quad (1)$$

Data on low frequency values of permittivity ϵ_s are available from dielectric measurements (Scaife and Lyons 1980). Measurements of refractive index in the visible region can be used to estimate the permittivity at very high frequencies ϵ_∞ . The behaviour of ϵ' and ϵ'' can then be related by means of the Kramers–Krönig relation (Frölich 1958) which leads to

$$\epsilon_s - \epsilon_\infty = \Delta\epsilon = (2/\pi) \int_0^\infty \epsilon''(\omega) d \ln \omega. \quad (2)$$

Optical frequencies can substitute for infinite frequency provided the loss ϵ'' at the upper, limiting, frequency is negligible. The integral in equation (2) can be evaluated as the sum of several integrals each covering a portion of the frequency spectrum. Each contributes to $\Delta\epsilon$ as follows

$$\Delta\epsilon = \Delta\epsilon_m + \Delta\epsilon_{\text{FIR}} + \Delta\epsilon_{\text{IR}} \quad (3)$$

In this $\Delta\epsilon_m$ covers frequencies from the lowest to the microwave region, 0–0.1 THz approximately. Similarly $\Delta\epsilon_{\text{FIR}}$ covers the far infrared region from 0.1 to 10 THz approximately. Finally the remaining region, the infrared, covers 10 to 150 THz and is related to $\Delta\epsilon_{\text{IR}}$. At frequencies below 1 GHz, no absorption is evident. Microwave measurements, for example Dagg and Reesor (1972, 1974) and Göttmann and Stumper (1973),

show a peak in the region 20–40 GHz. There is a gap in the spectrum from 40 GHz to 600 GHz where our far infrared measurements begin. Although infrared spectra are readily available for all six liquids, these are not available as absolute measurements of α , but rather as relative '% transmittance' values.

2. Experimental details

The samples used were supplied by Fluka and were *purissimus* grade in all cases. No extra purification or treatment was attempted. A Grubb-Parsons Mark III interferometer was used with a path length of 5 mm. The absorption coefficient was measured as the average of three separate runs for wave numbers between $\bar{\nu} = 20$ and 200 cm^{-1} (0.6 to 6.6 THz). It is estimated that a precision $\pm 2\%$ was achieved except at the extremes of the frequency range.

3. Results

All six liquids show similar behaviour, see figures 1(a) and (b). The absorption coefficient

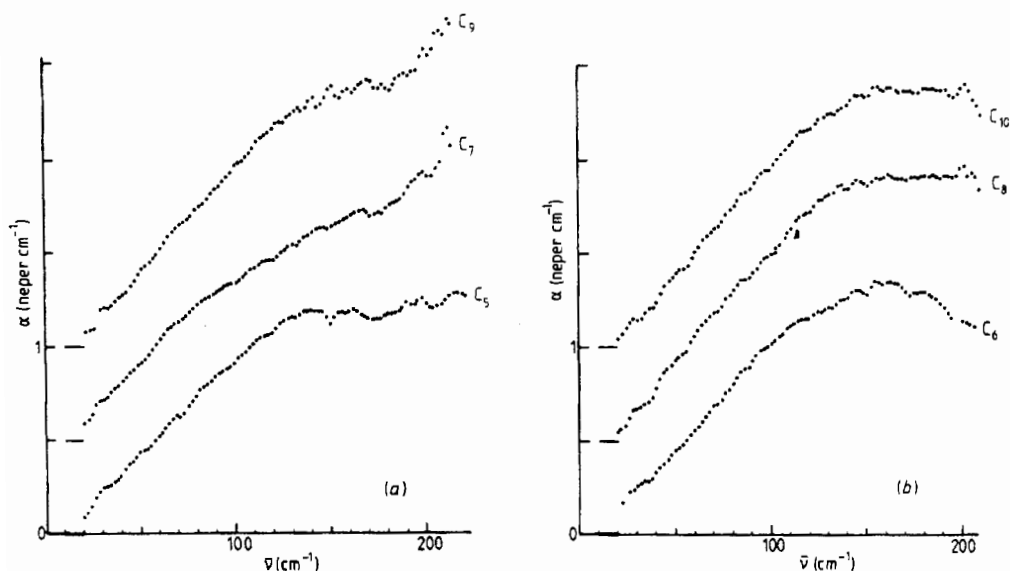


Figure 1. Optical absorption α (neper cm^{-1}) for wavenumbers between 20 and 200 cm^{-1} at 20°C . Data for each liquid is stepped vertically by an amount equal to $0.5 \text{ neper cm}^{-1}$. (a) n-pentane C_5 , n-heptane C_7 , n-nonane C_9 ; (b) n-hexane C_6 , n-octane C_8 , n-decane C_{10} .

rises almost linearly from just below $\bar{\nu} = 20 \text{ cm}^{-1}$ as far as $110\text{--}130 \text{ cm}^{-1}$. It then levels off, with the exception of n-heptane and n-nonane. If values for α for each liquid are examined at fixed frequencies between 80 and 160 cm^{-1} , we find a regular pattern in which the magnitude of α becomes alternately larger then smaller on passing from n-pentane through the series to n-decane, see figure 2.

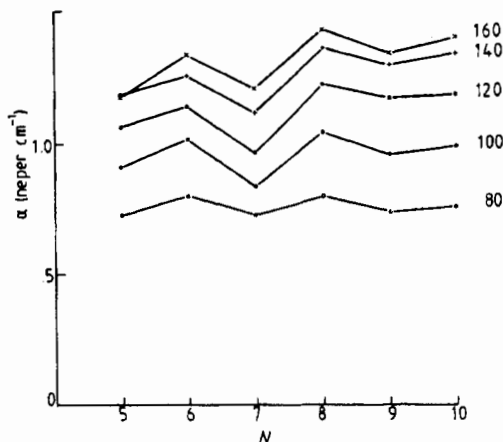


Figure 2. Optical absorption α (neper cm^{-1}) at 20°C plotted against carbon number N at wave numbers from 80 to 160 cm^{-1} .

The same information is presented in a slightly different form in figures 3(a) and (b) as plots of ϵ'' against logarithm of frequency. These plots show a peak in the region between 2 and 4 THz. The significance of the variability on the low frequency side which is discernible in the first three members of the series is not clear. This part of the data corresponds to the smallest values of α , which are therefore the least certain values.

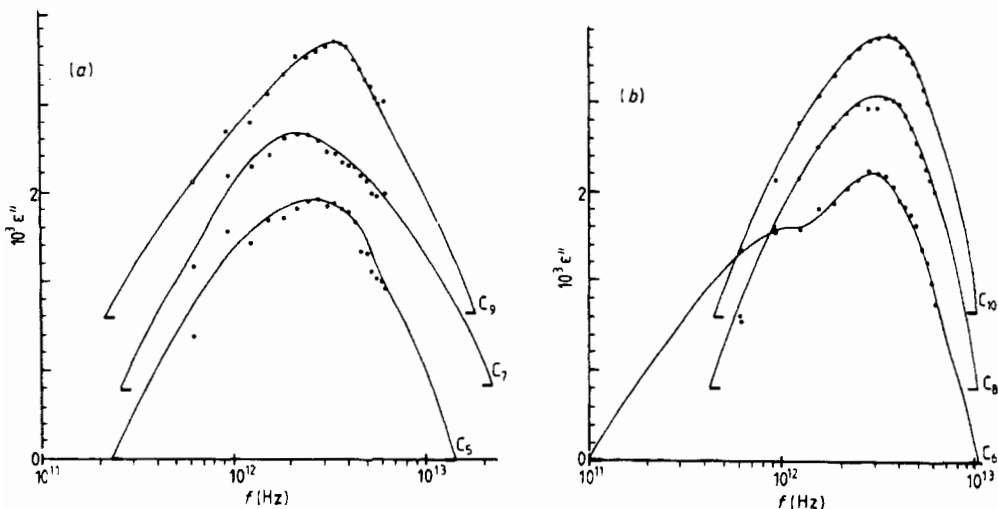


Figure 3. Loss component of relative permittivity ϵ'' as a function of frequency (THz) in the far infrared region. Curves for each liquid have been stepped vertically by an amount equal to 8×10^{-4} . (a) *n*-pentane C_5 , *n*-heptane C_7 , *n*-nonane C_9 ; (b) *n*-hexane C_6 , *n*-octane C_8 , *n*-decane C_{10} .

4. Discussion

Unlike the plots of α versus logarithm of frequency for other nonpolar liquids, the *n*-alkanes show little or no fall-away of absorption coefficient between 100 and 200 cm^{-1} .

Pardoe (1970) has measured cyclohexane, cyclopentane, carbon tetrachloride, carbon disulphide and benzene. Their peak values of α range from 0.5 to around 5 neper cm^{-1} . With the exception of cyclopentane which has a peak at 140 cm^{-1} , the peaks occur around $50\text{--}70 \text{ cm}^{-1}$. Of all these, cyclopentane is the most like the n-alkanes, with a flat curve of similar strength. Plotted as ϵ'' on a log frequency scale, the n-alkane data show peaks at between 120 and 180 cm^{-1} . Two instances are given by Pardoe of strong narrow peaks which are attributed to vibrational modes, at 154 cm^{-1} in the case of 1-4 dioxan, and at 245 cm^{-1} in the case of cyclohexane. Something similar may account for the higher frequency behaviour of the n-alkanes. In order to quantify $\Delta\epsilon_{\text{FIR}}$, a somewhat arbitrary curve was drawn through the ϵ'' data for each n-alkane, and this is visible in figures 3(a) and (b). The resulting values of $\Delta\epsilon_{\text{FIR}}$ average 0.005 and there is little variation among the six n-alkanes.

Separated by a gap of just over one decade in frequency, there are also microwave data, Dagg and Reesor (1972, 1974). In the case of n-pentane, n-hexane and n-heptane, these fit a Debye curve well, but the n-nonane and n-decane curves are much broader. Notwithstanding this, the parameters for a Debye curve have been given, so that the integral of ϵ'' can be evaluated. The resulting $\Delta\epsilon_{\text{m}}$ lies between 0.003 and 0.004.

The low frequency measurements of Scaife and Lyons (1980) showed that most of the variation of ϵ_s could be accounted for by a polynomial dependence on density. However there was a small residual temperature effect at constant density. This can be expressed as $\Delta\epsilon_{\text{T}}$, that fraction of ϵ_s which is equivalent to the temperature dependence. The effect is small and close to the limit of experimental error. It averages 0.005 but it does have wide fluctuations (0.001 for n-hexane, 0.008 for n-pentane). This was attributed to a small residual dipole moment. The microwave absorption would be compatible with this suggestion, with relaxation times between 2.5 and 6 ps.

As has been mentioned, adequate data are not available to permit the calculation of $\Delta\epsilon_{\text{IR}}$ from measurements. It is however possible to establish an estimate of ϵ_{∞} at the highest infrared frequencies, at which ϵ'' is small. This can be done by using the refractive index, $n(\lambda)$, measurements quoted by Timmermans (1950). These cover six wavelengths between 4471.5 and 6678.1 \AA . The effect of the optical resonance can be taken into account by using a Cauchy expression (Böttcher 1952)

$$n(\lambda) = n_{\infty} + b/\lambda^2 + c/\lambda^4. \quad (4)$$

A polynomial fit gives n_{∞} , the refractive index at frequencies where n no longer varies with frequency. In this case $n^2(\lambda)$ reaches within 0.1% of n_{∞}^2 at 5000 cm^{-1} . Because ϵ'' is small at this wavelength, we can approximate $\epsilon_{\infty} = n_{\infty}^2$. The curve fitting causes

Table 1. Changes in the real part of complex permittivity

	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	Mean	S
ϵ_s^{\dagger}	1.8471	1.8933	1.9275	1.9541	1.9756	1.9935		0.003
n_{∞}^{\ddagger}	1.8261	1.8731	1.9054	1.9305	1.9527	1.9686		0.003
$\Delta\epsilon$	0.0211	0.0202	0.0221	0.0236	0.0229	0.0249	0.023	0.004
$\Delta\epsilon_{\text{FIR}}$	0.005	0.006	0.005	0.005	0.005	0.004	0.005	
$\Delta\epsilon_{\text{m}}^{\S}$	—	0.004	0.003	—	0.004	0.003	0.003	
$\Delta\epsilon_{\text{T}}^{\dagger}$	0.008	0.001	0.007	0.005	0.005	0.003	0.005	

\dagger 15° Scaife *et al* (1980); \ddagger 15° Timmermans (1950); \S 25° Dagg *et al* (1972); || Probable uncertainty.

some loss of certainty, which means that ϵ_{∞} has from 0.1% to 0.2% standard error. A somewhat similar precision in ϵ_s results in the estimates of $\Delta\epsilon = \epsilon_s - \epsilon_{\infty}$ having an uncertainty of ± 0.004 . The position is summarised in table 1.

5. Conclusions

The average of $\Delta\epsilon$ for the six liquids is 0.023 with little variation among them. Even allowing for all the uncertainties in $\Delta\epsilon$, and for the unknown behaviour in frequency regions where no measurements exist, it is clear that $\Delta\epsilon$ is larger, probably double the sum of $\Delta\epsilon_m$ plus $\Delta\epsilon_{\text{FIR}}$. The difference must lie in the absorption bands in the infrared region.

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