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Temperature-Dependent Terahertz Spectroscopy of Liquid *n*-alkanes

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Abstract We describe measurements of the terahertz dielectric properties of normal alkanes. We study all of the liquid alkanes from pentane (C_5) to hexadecane (C_{16}) over the temperature range from 20–80°C, and obtain the absorption coefficients and refractive indices in the spectral range from 0.1 to 2.5 THz (3–83 cm^{-1}). The mean molecular polarizability is found to vary linearly with chain length at all temperatures, indicating that an additive model for polarizability, with distinct contributions from the methylene groups and the methyl end groups, provides an accurate description. The absorption coefficients of these non-polar liquids, arising from transient induced dipoles, are essentially featureless in this spectral range, with an almost linear dependence on frequency and negligible temperature dependence. These results provide a baseline for far infrared spectroscopic studies of inter-molecular interactions in non-polar hydrocarbons.

Keywords Alkane · Terahertz

The normal alkanes have been the subject of a great deal of study over the years. These molecules are prototypical non-polar non-hydrogen-bonding linear chains, with the generic chemical formula C_nH_{2n+2} (generally abbreviated as C_n, where n = carbon number). Beyond their obvious technological importance in the petrochemicals industry, these materials represent a model system in the study of non-polar non-hydrogen-bonding liquids. It has long been recognized that *n*-alkanes, despite their simple structure, exhibit a rich variety of behaviors, including the manifestation of various solid-solid phase transitions [1–3], and the unusual phenomenon of surface freezing [4, 5]. The general properties of alkyl chains are also significant in the understanding of the morphology and growth of polymers [6] and the phase behavior of lipid membranes [7]. Numerous analytical techniques have been brought to bear on this problem, including traditional thermodynamic measurements such as calorimetry and dilatometry [8, 9] and spectroscopic

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techniques such as x-ray scattering [2, 10], Raman scattering [6, 11], and infrared absorption spectroscopy [12].

Despite this extensive body of literature, there is still very little information on the far infrared (terahertz) properties of *n*-alkanes, in the spectral region from 1–100 cm^{-1} (0.03–3 terahertz), particularly for longer chains. The significance of terahertz spectroscopy as a tool for understanding intermolecular dynamics was recognized almost 40 years ago [13]. This is in contrast to more conventional mid-infrared absorption signatures, which arise due to intramolecular modes (e.g., C-C stretch, CH_2 deformation modes), and therefore provide only indirect information about intermolecular motions. Throughout the 1970's and 1980's, this early work inspired a few subsequent studies of alkanes [14–18], although these reports did not include the refractive index of the samples, only the absorption coefficient.

More recently, the advent of new techniques for generation and detection of terahertz radiation based on time-domain spectroscopy has revolutionized the field, dramatically simplifying the operation of spectrometers covering the entire THz range [19]. As a result, a few additional studies of non-polar liquids [20] and in particular alkanes [21–23] and mixtures [24–26] have been described. In these experiments, typically both the absorption and refractive index of the liquid samples were obtained, over a wide bandwidth extending beyond 1 THz. This additional information, which can be extracted because of the phase-sensitive nature of the detection process, can be extremely valuable for a full understanding of material properties [20]. Despite this advantage, these more recent studies have also been limited in their scope. None have involved chains longer than decane (C_{10}), and none have reported temperature-dependent spectra. Perhaps most strikingly, the more recent studies have failed to exploit one of the key advantages of the *n*-alkanes: the number of carbon atoms can be used as a control parameter. The *n*-alkanes form a homologous series, so that one may regard the chain length as an experimental variable, providing a useful window on structure-dependent properties. Moreover, for chain lengths ranging from $n=5$ to 16 carbons, these materials remain liquid at room temperature. Thus there is a wide range of parameter space for exploration of liquid properties (e.g., more than a factor of three in molecular weight).

In this paper, we report a complete characterization of the terahertz spectroscopic properties of the entire series of liquid alkanes from C_5 to C_{16}. Using terahertz time-domain spectroscopy, we determine the absorption coefficients and refractive indices of these liquids from 0.1 to 2.5 THz (3–83 cm^{-1}), over a wide temperature range from 20°C to 80°C. The samples are obtained from a commercial vendor, at a specified purity of better than 99.5%, and are used without further purification. The measurements are performed in a transmission geometry, using a temperature-controlled stainless steel sample cell with z-cut quartz windows for high terahertz transparency and thermal conductivity. Typical path lengths range from a few millimeters to a few centimeters. The temperature of the sample is monitored with a thermocouple inserted directly into the liquid, with an accuracy of 0.1°C.

Figure 1 shows THz waveforms, measured in transmission, on a sample of tridecane (C_{13}) at several different temperatures, representing typical experimental results. For these time-domain data, the sample is held in a cell with a fixed path length of 4.4 millimeters. The shift of the THz peak to smaller time delays with increasing temperature reflects the temperature dependence of the refractive index $n(\omega)$. In order to extract quantitative values for $n(\omega)$ and the absorption coefficient $\alpha(\omega)$, we compare these time-domain waveforms to a reference measurement (made with an empty cell), and account for the Fresnel reflection losses at the window interfaces. Figure 2 shows the results for the refractive index as a function of frequency, for each of the liquids studied, at a temperature of 25°C. Evidently, these materials exhibit almost no spectral dispersion within this frequency range.

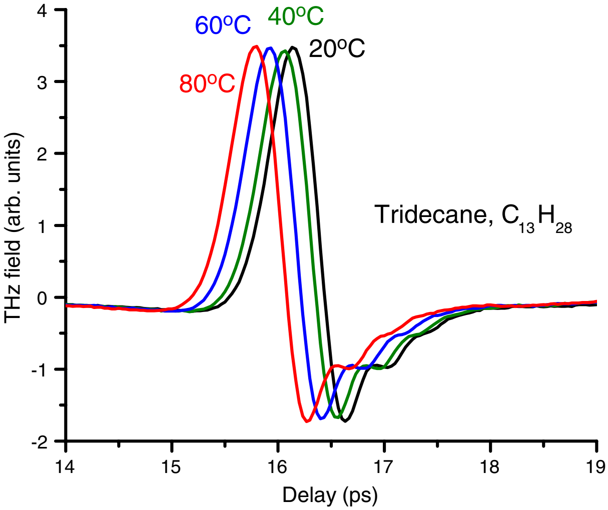


Fig. 1 Several THz time-domain waveforms, measured in transmission through a cell containing *n*-tridecane ($C_{13}H_{28}$), at four different temperatures. The cell path length was fixed at 4.4 millimeters. The shift in the transit time of the THz pulse arises from the temperature dependence of the liquid's refractive index.

Figure 3 shows the value of the refractive index at one particular frequency as a function of chain length, at a few selected temperatures. These results can be understood by using the well-known Lorentz-Lorenz formula, which relates the refractive index of a liquid to its density:

$$\frac{n^2-1}{n^2+2}=\frac{N_A\rho}{3M}\alpha_P \tag{1}$$

where N_A is Avogadro's number, ρ is the liquid density, M is the molecular weight, and α_P is the mean molecular polarizability. Using the measured values for $n(\omega)$ at a representative value of 1 THz (a reasonable approach since $n(\omega)$ is nearly frequency-independent), as well as tabulated values for the liquid densities at 20°C, we extract the mean (orientation-averaged) polarizability as a function of chain length. This result is shown in Fig. 4, along with a linear fit.

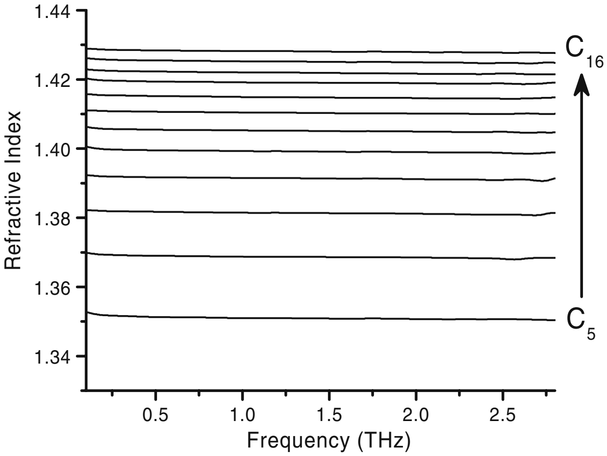
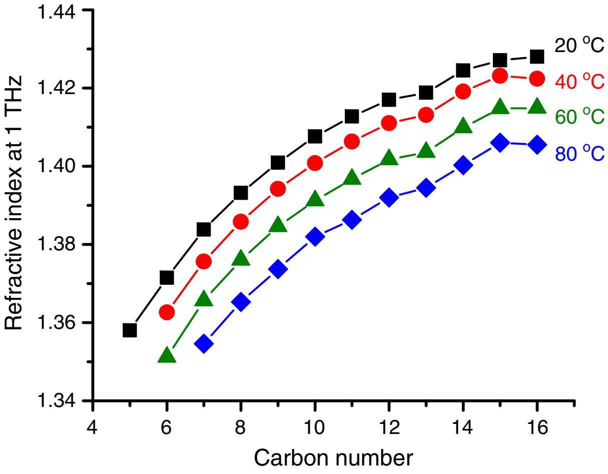


Fig. 2 Refractive index *vs.* frequency for each of the 12 liquids studied at a temperature of 25°C, extracted from time-domain measurements. The indices show a monotonic increase with increasing chain length, and are nearly frequency-independent within the accessible spectral range.

Fig. 3 The refractive indices of the *n*-alkanes at one particular frequency *vs*. the number of carbon atoms in the linear molecule. The chosen frequency, 1 THz, is a representative value. The decreasing index with increasing temperature is evident for all chain lengths.

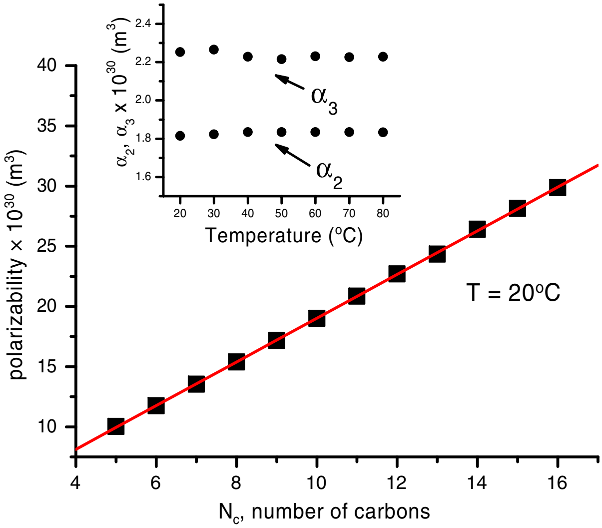


Following Scaife [27], we expect that the mean polarizability for a given chain length should contain two contributions: one part, denoted α_2, from the methylene groups, and a second contribution α_3 from the two methyl end-groups. These contributions can be expected to contribute additively to the net polarizability, so that

$$\alpha_P = 2\alpha_3 + (N_C - 2)\alpha_2 \tag{2}$$

where N_C is the number of carbons. The linearity of the data in Fig. 4 support the use of this additive model for linear polarizability, an approach dating back to at least the 1940's [28]. From the linear fit to these data, we extract numerical values of $\alpha_2 = 1.81 \times 10^{-30}$ m^3, and $\alpha_3 = 2.25 \times 10^{-30}$ m^3. These results are in excellent agreement with literature [27], showing that this simple additive model applies even to the longest chains that remain liquid at room temperature.

Fig. 4 The mean molecular polarizability α_P as a function of the carbon atom number, measured at 20°C. These are determined using the Lorentz-Lorenz formula, Eq. 1. The inset shows the polarizability α_2 of a CH_2 group and α_3 of a CH_3 end-group, extracted from the linear fit as described in the text. These polarizability parameters are temperature-independent.



We can extend this analysis to study the temperature dependence of the polarizability parameters α_2 and α_3. Our measurements indicate a decreasing refractive index with increasing temperature, for all of the liquids studied. However, the liquid density is also temperature-dependent, with a similar trend. For many organic liquids, including *n*-alkanes, the dependence of density on temperature can be described using a phenomenological equation of the form

$$\rho(T) = A \cdot B^{-(1-T/C)^p} \tag{3}$$

where A, B, C, and p are parameters that can be found in the literature for many different liquids [29]. With these tabulated values, we determine $\rho(T)$ and therefore $\alpha_2(T)$ and $\alpha_3(T)$ using the same approach described above. These results, shown in the inset to Fig. 4, indicate that neither of the two polarizability parameters show a significant temperature dependence. In other words, essentially all of the temperature dependence of the refractive index arises from the temperature dependence of $\rho(T)$. The ratio $\alpha_3/\alpha_2 \approx 5/4$ is nearly temperature-independent.

From our data, we can also extract the absorption coefficient for each of the liquids studied. These data are shown in Fig. 5. In this spectral range, the absorption spectrum does not exhibit any sharp features, but rather shows a monotonic increase with increasing frequency. As suggested by the data shown in Fig. 1, the temperature dependence of the absorption is quite weak, showing no discernable trend for any of the liquids studied here. The different chain lengths are similar in their absorption strength, although there is a weak chain-length dependence, as shown in the inset to Fig. 5. The error bar represents a typical measurement uncertainty, indicating that the trend is barely measureable above the noise.

To determine the origin of this weak trend, we use the measured absorption coefficients to derive an effective absorption cross-section σ_{abs} for each chain length, via

$$\alpha(\omega) = \sigma_{abs}(\omega) \cdot \rho N_A/M \tag{4}$$

where $\rho N_A/M$ is the number density of molecules in solution. We compute σ_{abs} using the data from the inset to Fig. 5 (i.e., the absorption coefficient at a representative frequency of 1 THz) and the value of ρ at 25°C. We then normalize this cross-section to the area of a single molecule A_M, in its fully extended conformation. To compute A_M, we use values for

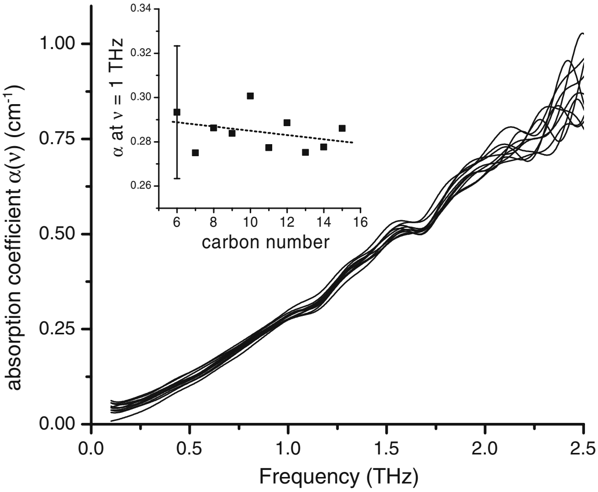


Fig. 5 Absorption coefficients $\alpha(\omega)$ for each of the 12 liquids studied, measured at 25°C. The inset shows the values at a representative frequency, as a function of chain length. There is a weak trend of decreasing absorption coefficient with increasing chain length. The error bar shows a typical measurement uncertainty.

the length and width from the literature. We assume that the length is a linear function of N_C and that the width is constant, equal to 4.15Å [30]. This relatively crude calculation neglects effects such as random molecular orientations and the many possible torsional conformations. Nevertheless, the normalized result σ_{abs}/A_M can provide some insight as it is essentially an estimate of the absorption strength per carbon atom. The results, shown in Fig. 6, indicate that the molecular cross-section is much smaller than the size of a single molecule, which is not surprising since the absorption strength is so weak for these non-polar species. Also, it is independent of chain length, indicating that the weak trend in absorption strength (inset to Fig. 5) probably results merely from a weak variation in packing density in the liquid state.

A number of authors have reported studies of the dielectric loss in *n*-alkanes in this spectral region [14, 17, 18, 31]. Based on these data, an induced dipole moment of less than 0.1 Debye has been inferred, with a weak dependence on alkane chain length. Yet, the origin of this induced dipole remains unresolved, having been attributed to various mechanisms including intramolecular vibrations, collisional effects, etc. In our results, we observe a nearly linear dependence of $\alpha(\omega)$ on frequency, and no notable temperature dependence. In particular, we observe essentially no structure at low frequencies, in contrast to several of these earlier reports. As a result, these data provide little additional insight into the dynamical mechanism responsible for the absorption. Further analysis would require the extension of these spectra to higher frequencies, where the rollover of the Debye plateau may be more evident [14].

In conclusion, we present a systematic study of the terahertz dielectric properties of all of the *n*-alkanes that remain liquid at room temperature. From the dependence of the refractive index on chain length and temperature, we show that the temperature dependence of the real part of the dielectric is almost entirely determined by the variation of the liquid density. Using an additive model, we determine the ratio of the polarizability of the CH_3 methyl end groups and the CH_2 methylene groups to be $\alpha_3/\alpha_2 \approx 5/4$, independent of temperature in the range 20–80°C. Finally, we observe that the absorption coefficient is nearly proportional to ω in the spectral range of our measurements. This result is consistent with various mechanisms for induced transient dipole formation, and a broader bandwidth is required for further studies.

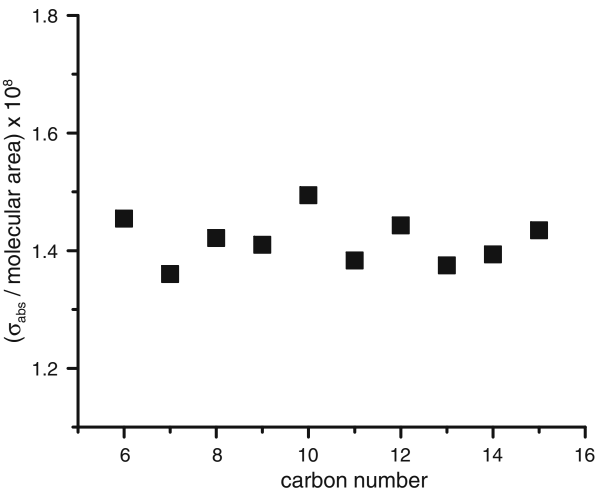


Fig. 6 The molecular cross-section, obtained from the data shown in the inset to Fig. 5, normalized to the area of a single molecule, as discussed in the text. This dimensionless ratio exhibits no significant chain-length dependence.

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