The isotropic molecular polarizabilities of single methyl-branched alkanes in the terahertz range

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A B S T R A C T

Additive models for molecular parameters have a long history, and remain important for the rapid prediction of molecular properties. To test the validity of an additive approach, we study the polarizabilities of methyl branched alkanes in the terahertz spectral range, and compare these to the polarizabilities of their straight chain counterparts. A single branched methyl group increases the isotropic polarizability by a fixed amount, regardless of the carbon backbone chain length or the methyl branch’s position. These results, which are also compared to DFT calculations, establish the validity of an empirical additive approach for these prototype non-polar and non-hydrogen-bonding liquids.

The additive properties of molecular subunits, such as atoms, bonds, and groups, have been recognized as a useful tool to predict the properties of molecules for more than a century [1]. The additivity of bond and group polarizabilities, in particular, was first demonstrated in the 1940s. Even today, more complex variants of the early empirical and theoretical additive models still prove to be relevant in computational physical chemistry [2–8], largely due to a decreased computational cost compared to pure ab initio methods. Typically, experimental verification of a theoretical model of molecular polarizability relies on the measurement of a material’s index of refraction in the visible spectral range. Terahertz time-domain spectroscopy (THz-TDS) presents an interesting and sometimes advantageous alternative to these methods. With THz-TDS both the amplitude and phase of a broadband THz pulse are measured and, from comparison with a reference pulse, a material’s indices of refraction and absorption coefficients can be easily extracted [9,10]. In particular, the n-alkanes, a homologous series of saturated hydrocarbons with the general formula CnH2n+2, are a prototypical set of molecules for which the THz frequency range is an ideal window on the additive behavior of their mean molecular polarizabilities. They exhibit very low absorption (<1 cm−1), with no measurable resonant absorption features below a few THz. As a result, the dielectric behavior is essentially dispersionless, allowing for the accurate determination of their mean, isotropic, molecular polarizabilities [10].

Here, we describe a study of the mean molecular polarizability of both linear and branched liquid alkanes. The effects of adding a branched methyl group to a linear carbon chain are measured using THz-TDS and characterized using a simple additive model for the polarizability. This permits us to independently measure the polarizabilities of methyl, methanediyl, and methanetriyl. We compare these measured polarizabilities to density functional theory (DFT) calculations.

The refractive indices and absorption coefficients of single methyl branched alkanes and their linear counterparts, for carbon chain lengths from 9 to 16 carbons, were measured using a conventional THz time domain spectroscopy setup configured in reflection geometry. The liquid samples, obtained from commercial vendors with >99% purity, were used without further purification. Liquids were injected into a custom-designed stainless steel sample cell with a single 6 mm-thick high resistivity Si window and a micrometer adjustable inner (rear) stainless steel wall. The THz pulse transmits through the window and sample, reflects off of the adjustable rear wall and then back through the sample and window; this configuration is equivalent to a double-pass transmission measurement. The reflection geometry and custom sample cell allows the sample path length to be varied without requiring a different window thickness or the removal of the sample cell from the setup between measurements. Taking the ratio of the sample’s Fourier transformed THz waveform to an empty cell’s Fourier transformed reference waveform (or, alternatively, using the first reflection off of the air–Si window interface as a reference) permits the determination of the sample’s index of refraction and absorption coefficient by using the complex transmission function [11,12]. In this analysis, corrections for the Fresnel reflections at each interface are included; however, the most important aspect is the complex exponential term which represents the propagation through the sample itself. Each sample was measured over a minimum of five different path lengths, ranging from 5 to 25 mm, and the absorption

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and refraction spectra were averaged to produce the final results. The sample temperatures were controlled to within 0.1 °C using a water circulator and were monitored using a probe inserted directly into the liquid sample. All the n-alkanes measured in this experiment remain liquid over the measured temperature range from 20 to 60 °C.

Figure 1 illustrates typical results. This shows the mean indices of refraction, $n(\nu)$, and absorption coefficients, $\alpha(\nu)$, respectively for two of the linear n-alkanes (nonane and tridecane) as well as their single methyl branched counterparts (2-methylnonane and 2-methyltridecane), measured at 20 °C. The corresponding molecular structures are overlaid above the index spectra in Figure 1a. Each pair of molecules shares the same 'backbone' carbon chain structure, i.e. the number of carbon atoms in the linear carbon chain segment, $N_b$, are equivalent. The branched structures simply have another methyl group branching from one of their internal (non-end) carbons. Like the straight chain alkanes, the methyl branched alkanes' indices are approximately dispersionless within the measured frequency range. We observe an increase in $n(\nu)$ for the branched species relative to their straight chain counterparts. Despite the change in $n(\nu)$, the absorption coefficients $\alpha(\nu)$ for all the measured alkanes and branched alkanes are indistinguishable from each other, within the repeatability of the measurement. In all cases, their absorption coefficients increase with frequency smoothly and monotonically.

The increase in the index of refraction with the addition of a methyl branch can be seen more clearly in Figure 2a, which shows the indices of refraction at a representative frequency of 1 THz and at 20 °C, for both the linear carbon chain structures and the branched structures, plotted vs. $N_b$, the number of carbons in their linear carbon chain backbones. Plotting the results in this manner facilitates the direct comparison of two related molecules with equivalent carbon chain structures. For nonane ($N_b = 9$), we measured multiple different species, with the methyl group branching from the 2nd, 3rd or 4th carbon atoms in the linear chain. For completeness (Figure 2b), we also show the absorption coefficients vs. $N_b$ for both the branched and linear structured alkanes at the same representative frequency (1 THz). These have no measurable dependence on the number of carbons in the linear chain backbones. Since the absorption coefficients have no measurable chain length dependence and considering $n(\nu) \approx \alpha(\nu)c/(4\pi\nu)$ for all the samples, the absorption coefficients are negligible and can be ignored for the subsequent calculations.

The mean molecular polarizability of each sample is calculated using the Lorentz–Lorenz equation [13] (Eq. (1)), which is used to
relate the macroscopic index of refraction to the microscopic mean molecular polarizability, according to:

\[
\frac{n(v)^2 - 1}{n(v)^2 + 2} = \frac{4\pi N_a \rho(T)}{3 M} \chi_i(v)
\]

(1)

We use tabulated values of each species' temperature-dependent liquid density \(\rho(T)\) [14], the molecular mass \(M\), and Avogadro's number \(N_a\). Figure 3 shows the mean molecular polarizabilities determined in this fashion vs. \(N_a\) at 20 °C and at a representative frequency of 1 THz. For this calculation, only the real components of their complex refractive indices are used since the complex components, i.e. their absorption coefficients, are negligible. For both the straight chain alkanes and their single methyl branched counterparts, \(\chi_i\) increases linearly with \(N_a\). In all cases, an additional methyl group, branched from the linear chain, results in an increase in \(\chi_i\). Plotted in the inset are the differences in polarizability, \(\Delta\chi_i\), between the methyl branched structure and linear structure. We observe no measurable dependence of \(\Delta\chi_i\) on the number of carbons in the linear chain, indicating that the addition of a single branch increases the molecular polarizability by a fixed amount, independent of chain length. In addition, we note that the mean polarizabilities of 2, 3, and 4-methylnonane (\(N_a = 9\), each of which exhibited slightly different refractive indices (Figure 2a), become indistinguishable once their densities are taken into account (Eq. (1)). Hence, \(\Delta\chi_i\) does not depend on the position of the methyl branch or on the length of the carbon chain backbone.

These experimental results suggest that a simple bond additive model can be used to predict the values of the polarizability of these species. In this approach, a molecule's individual bonds are assumed to be the additive subunit with constant and non-interacting polarizabilities. We obtain the polarizabilities of individual bonds, parallel and perpendicular to the bonds' axes, from the work of Amos and Crispin [15]: (\(C_2\) = 0.719, \(CC_i\) = 0.381, \(CH_i\) = 0.868, \(CH_2\) = 0.488 \(\times 10^{-26}\) cm\(^3\)); in that earlier work, the individual bond component contributions were calculated for the case of the shortest carbon chain \(n\)-alkane, ethane (\(C_2H_6\)). The bond axis is the line connecting the two atoms. Then, the polarizability of a molecule in any given direction, \(\chi_i\), is given by a sum over the \(n\) bonds in the molecule:

\[
\chi_i = \sum_n \chi_{ni} \cos^2 \theta_{ni} + \chi_{zi} \sin^2 \theta_{ni}
\]

(2)

where \(i = x, y, z\), \(\theta_{ni}\) is the angle between the bond axis and the direction \(i\), and \(\chi_{zi}\) and \(\chi_{ni}\) are the individual bond's polarizabilities perpendicular and parallel to the bond axis, respectively [16]. The total isotropic mean molecular polarizability, \(\chi_i\), of the molecule is the mean value of the polarizabilities in all three orthogonal directions, i.e. \(\chi_i = (\chi_{xi} + \chi_{yi} + \chi_{zi})/3\). We compute the molecular polarizabilities using this approach, under the assumption that the chains are in their fully extended trans conformation with fixed tetrahedral bond angles. This assumption may seem non-physical for molecules in an inherently disordered liquid phase at room temperature. However, with this approach different conformations, including bending and kinking of the linear carbon chain, have no effect on the computed value of the mean molecular polarizabilities. This is a direct consequence of two main aspects of this simple approach; the bonds do not interact and, with changes in a bond's orientation, its individual contributions simply vary between the 3 orthogonal axes. Thus, regardless of the true molecular configuration, its predicted mean molecular polarizability remains constant.

Of course, this extremely simple model neglects any quantum effects. We can benchmark the additive model by comparing to the results of quantum mechanical DFT simulations. For this purpose, the polarizabilities of the \(n\)-alkanes and 2-methylalkanes were computed at 1 THz in gas phase and solution on fully optimized geometries at the LC-oPBE/6-31+G(d) [17,18] and oB97XD/6-31+G(d) [19] levels of theory. Unless otherwise indicated, all calculations reported here were carried out in the Gaussian [20] suite of programs using default parameters. For the liquid phase simulations, the polarizable continuum model (PCM) [21,22] was used where a single molecule is embedded in a continuous dielectric medium. Due to the unavailability of PCM solvent parameters for the 2-methylalkanes, experimental data and parameters from analogous \(n\)-alkanes were utilized for these calculations (vide infra).

Figure 4 shows the isotropic polarizabilities of both the linear (Figure 4a) and the branched (Figure 4b) species, determined from both the simple bond additive approach and the DFT simulations, along with the experimentally determined values for reference. The bond additive approach underestimates the molecular polarizabilities for both the branched and linear chains, almost certainly due to neglecting intra-molecular interactions. We note that the DFT calculations also underestimate the measured polarizabilities if the molecule's local environment is ignored; the average percent errors for the gas phase calculations of alkane are \(-10.8\%\) and \(-7.3\%\) for LC-oPBE and oB97XD, respectively. To accurately reproduce the measured polarizability of the liquid phase \(n\)-alkanes, the molecule must be embedded in a polarizable dielectric continuum and the effects of dielectric dispersion must be included. Of course, in order to include these effects, dielectric constants, both optical and static, must be used as input parameters in order to define the dielectric continuum in which the single molecule is embedded. For the branched alkanes studied here, neither \(\varepsilon_0\) nor \(\varepsilon_{\infty}\) are available in the literature. Therefore, for the branched alkanes the THz dielectric constants, determined from their measured indices of refraction, were used as the static dielectric constants. In addition, their optical dielectric constants were approximated by those of their linear structural analogs. It must be stressed that the dielectric constants are only used as parameters to define the polarizable dielectric continuum. Hence, the computed polarizabilities are still the result of full quantum mechanical simulations of the single molecules. With this method, oB97XD yields less than 1.3% error for both the linear and branched \(n\)-alkanes up to \(N_a = 16\). Likewise, the error in LC-oPBE

![Figure 3](image-url)

**Figure 3.** The mean molecular polarizabilities of both the branched (red circles) and linear (black squares) alkanes plotted vs. \(N_a\). The red and black lines are their respective linear fits with \(R^2 > 0.999\). Inset: the difference in polarizability, \(\Delta\chi_i\), between the branched and the bare linear structure, plotted vs. \(N_a\). There is no measurable dependence of \(\Delta\chi_i\) on the position of the methyl branch or on the carbon chain length. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
is reduced to about 3.5%. The larger error of LC-oPBE as compared to oB97XD is probably due to the fact that the former functional does not include empirical dispersion corrections [23], which could be expected to be important for describing these hydrocarbon chains. Also plotted in Figure 4b (inset) are the values of Δαp for the two theoretical approaches compared to the experimentally determined values. The bond additive approach slightly overestimates the change in polarizability while the DFT–PCM results accurately reproduce the measured changes in polarizability.

Since Δαp is approximately constant for all backbone chain lengths and methyl branch positions, and since αp is a nearly perfectly linear function of Nb, the use of an additive empirical relation to describe the behavior of the branched alkanes’ mean molecular polarizabilities is a reasonable approach. Based on this idea, it is possible to write the overall polarizability as a sum of contributions from the two methyl end groups and the Nb – 2 internal methanediyl groups, according to:

$$\alpha_p^{\text{linear}} = 2\alpha_3 + (N_b - 2)\alpha_2$$

Equation (3)

Since, in this case, the molecules consist of only the linear carbon chain, Nb is equivalent to the total number of carbon atoms in the molecule. By fitting Eq. (3) to the experimental results for the linear n-alkanes, the values for α3 (the polarizability of a methyl group) and α2 (the polarizability of a methanediyl group) can be extracted. The results of this analysis give α3 = 2.25 ± 0.06 × 10⁻²⁴ cm³ and α2 = 1.81 ± 0.04 × 10⁻²⁴ cm³. These results are consistent with values from previous reports [10,24]. Given that αp also increases linearly with Nb for the branched alkanes, it follows that a similar empirical relation will also provide an accurate description of these species. To compare the branched structures to their branchless counterparts, Eq. (3) can be modified by adding a third contribution (i.e. the branch), and replacing a single methanediyl group with that of a methanetriyl:

$$\alpha_p^{\text{branched}} = 3\alpha_3 + (N_b - 3)\alpha_2 + \alpha_1$$

Equation (4)

Here α1 is the contribution from the methanetriyl; that is, the carbon bonding the added methyl group branch to the linear carbon backbone. This group only has one hydrogen–carbon bond or, alternatively, is a tertiary carbon (3 carbon–carbon single bonds). As a consistency check of the proceeding analysis, we note that the methanediyl contributions (or equivalently the slopes of both the branched and linear alkane results) agree to within 1%. Using Eq.

![Figure 4. The theoretical results for the (a) linear and (b) branched alkanes plotted vs. N_b for both the bond additive approach (gray diamonds) and the oB97XD/6-31+G(d) PCM simulations done in Gaussian (blue circles; missing points reflect unavailability of PCM solvent parameters). For reference the experimentally measured values are also shown (black squares in (a) and red circles in (b)). Inset: Comparison of Δαp for the bond additive approach and the DFT–PCM simulations plotted with the experimentally determined values (black squares). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.]

![Figure 5. (a) The computed (blue circles and gray diamonds) and measured (black squares) contributions of the methyl α3, methanediyl α2, and methanetriyl α1 to the mean molecular polarizability of the branched and linear alkanes at T = 20 °C, extracted using Eqs. (3) and (4). The Gaussian calculations use the PCM model at the oB97XD/6-31+G(d) level. (b) The experimentally determined values of the group contributions vs. temperature, showing no measurable temperature dependence. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)]
(4) and the previously determined values of \( \alpha_2 \) and \( \alpha_3 \), the value of \( \alpha_1 \) can be determined from the intercept of the upper line in Figure 3: \( \alpha_1 = 1.44 \pm 0.14 \times 10^{-24} \text{cm}^3 \). In Figure 5a, we plot the contributions from all three carbon groups. In the same figure, we also show the computed values for these same quantities, extracted using the same linear regression approach from the two different predictions shown in Figure 4. We observe that the bond additive approach slightly underestimates the values of the methyl and methanediyl group contribution but their ratios are approximately reproduced, with \( \alpha_2/\alpha_3 \approx 5/4 \). However, it predicts \( \alpha_2 \approx \alpha_3 \), which is not the case experimentally. On the other hand, DFT–PCM underestimates \( \alpha_3 \) and overestimates \( \alpha_1 \); however it still reproduces the decreasing trend in polarizability contributions from the methyl to tertiary groups. In Figure 5b, we show the measured group polarizabilities versus temperature. The group contributions to \( \alpha_\text{p} \), including the methanetriyl group, exhibit significant temperature dependence.

Finally, we can assess the effectiveness of the empirical additive approach on predicting the polarizabilities of two cyclic hydrocarbon structures. For cyclohexane, as it is comprised of simply 6 methanediyl groups in a ring, the additive approach predicts a mean molecular polarizability of \( \alpha_2 = 6 \alpha_2 = 10.86 \times 10^{-24} \text{cm}^3 \). The measured mean molecular polarizability of liquid cyclohexane, from earlier work of Pedersen and Keiding [9], is \( 10.868 \times 10^{-24} \text{cm}^3 \) at 1 THz, almost perfect agreement. However, benzene, with the same number of carbon groups in its structure, has an \( \alpha_2 \) of \( 10.433 \times 10^{-24} \text{cm}^3 \). The additive approach cannot be applied to benzene using only the 3 group contributions extracted in this Letter since it contains double bonds.

THz-TDS provides a unique alternative to traditional optical polarizability measurements. From the experimental results, the modified empirical relation (Eq. [4]) describes the mean molecular polarizabilities of the single methyl branched alkanes up to \( N_0 = 16 \). The extracted group contributions from the methyl and methanediyl groups agree with previous works; moreover, we determine the contribution from the tertiary carbon group, \( \alpha_1 \), for the first time. Of course, the inherent drawback of the empirical approach is that the individual contributions from each molecular subunit must be determined experimentally. However, these measured contributions inherently include the effects of dispersion and the molecule’s local environment, parameters which may not be readily available in the literature, and which must be used as inputs for more sophisticated quantum simulations. Of course, a large number of interacting molecules could be modeled in a molecular dynamics simulation for a true \textit{ab initio} result; however the computational cost of such a simulation may be extremely high or unfeasible. Nevertheless, while much more sophisticated techniques exist to describe the polarizabilities of the \( n \)-alkanes, a simple linear empirical relation still effectively characterizes their mean molecular polarizabilities in the THz range, even with a variation in their structure.

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