

Terahertz vibrational modes induced by heterogeneous nucleation in *n*-alkanes

Jonathan P. Laib, Daniel V. Nickel, Daniel M. Mittleman*

Rice University, Department of Electrical and Computer Engineering, MS-366 6100 Main St., Houston, TX 77005, USA

ARTICLE INFO

Article history:

Received 12 April 2010

In final form 24 May 2010

Available online 27 May 2010

ABSTRACT

We describe the observation of a broad and strongly temperature-dependent peak in the terahertz absorption spectrum of several linear *n*-alkanes. On cooling from the liquid into the rotator phase, the absorption is enhanced within a very narrow temperature range at the temperature of the first-order phase transition. This peak is associated with an enhancement in the vibrational density of states, induced by the heterogeneous nucleation of the rotator phase from the liquid. This is similar to the well-known Boson peak in glassy solids, and provides a new experimental tool for the characterization of nucleation dynamics in non-polar molecular liquids.

© 2010 Elsevier B.V. All rights reserved.

Crystal nucleation from a melt is one of the most thoroughly studied types of phase transition. Recently, the nucleation of linear normal-alkanes (C_nH_{2n+2} , abbreviated C_n) has been the focus of much attention [1–4]. These transitions exhibit several unusual features including the existence of intermediate rotator phases between the liquid and crystalline solid phases [2], and the phenomenon of surface freezing where a crystalline monolayer forms at the surface of the liquid prior to solidification [1]. Because alkanes serve as a model system for polymers, surfactants, and biomembranes, the unique aspects of this phase transition have wide implications, and new experimental tools for probing these dynamics are of compelling interest.

In many phase transitions, the key dynamical questions involve the vibrational modes of the system, as characterized by the vibrational density of states (VDOS). It is well-known that a peak in the low-frequency VDOS can be induced by molecular-scale disorder. This so-called Boson peak has been observed in many different glassy solids and has been studied using a variety of experimental techniques [5–9]. These studies can provide information on the length scale for vibrational correlations [5]. However, the Boson peak is typically observed over a broad temperature range, and has not previously been associated with a strongly temperature-dependent phenomenon such as a liquid–solid phase transition.

In this study, we report observations of a peak in the absorption spectra of *n*-alkanes in the terahertz spectral range ($1\text{--}100\text{ cm}^{-1}$). The peak only appears within a very narrow temperature range on cooling through the liquid-to-rotator (L–R) transition temperature. This suggests that it arises as a result of dipole correlations which are associated with the heterogeneous nucleation of the rotator phase from the melt. These correlations are indicative of induced dipoles resulting from correlated vibrational motion,

providing a new experimental tool for the study of nucleation phenomena and their effect on vibrational dynamics.

We have used terahertz time-domain spectroscopy (THz TDS) [10] to measure the temperature-dependent absorption spectra of four *n*-alkanes, with carbon numbers $n = 23\text{--}26$. The samples are obtained from a commercial vendor, at a specified purity of better than 99.5%, and are used without further purification. These specific chain lengths have been the focus of both experimental [3,11–14] and theoretical [15,16] study, and the phase diagrams are well characterized. In particular, all of these samples crystallize via one or more intermediate rotator phases, and the liquid-to-rotator transitions are known to be first-order phase transitions [15].

For our transmission measurements, the samples are held in a temperature-controlled stainless steel cell with quartz windows for high thermal conductivity and terahertz transparency. This provides the best combination of optical throughput and temperature uniformity throughout the sample volume. Typical path lengths are a few millimeters to a few centimeters. The sample temperature is controlled using a circulating water heat exchanger, with a temperature resolution of $0.1\text{ }^\circ\text{C}$ and a typical cooling rate below $0.01\text{ }^\circ\text{C}/\text{min}$. Such low cooling rates are required to reliably form the rotator phases [2,12]. A thermocouple is inserted into the sample to monitor the temperature. After each temperature step of $0.1\text{ }^\circ\text{C}$, the sample and sample holder are permitted to equilibrate for 1 h to ensure temperature uniformity throughout the sample volume.

Fig. 1 shows measured absorption spectra for C_{26} in the liquid and rotator phases as well as at the L–R transition. The absorption is notably larger in the rotator phase than in the liquid, probably due in part to scattering from grain boundaries in these polycrystalline samples. However, over a very narrow range of temperatures close to the L–R transition temperature, the absorption is even higher. This enhanced absorption is clearly related to the for-

* Corresponding author.

E-mail address: daniel@rice.edu (D.M. Mittleman).

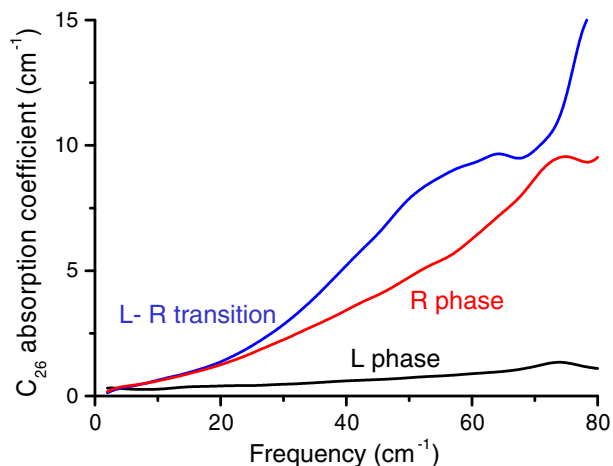


Fig. 1. Absorption spectra of the linear alkane C_{26} at three different temperatures, corresponding to the liquid phase (black), the liquid-to-rotator transition temperature (blue), and the rotator phase (red). The excess absorption induced by the first-order phase transition is evident. This excess absorption appears only over a very narrow range of temperatures close to the L-R transition. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

mation of the rotator phase, and it is not observed, e.g., when the sample is cooled too rapidly. Fig. 2 shows the measured absorption coefficient for all four alkane chain lengths as a function of temperature at one particular frequency, near the point where the excess absorption is largest. In all cases, we observe this excess within a narrow range near the L-R transition temperature. Since this enhanced absorption is only observed very close to the phase transition (e.g., within 0.3 °C or less), it seems likely that it is associated with the heterogeneous nucleation of the solid. When the sample is cooled further, the entire sample crystallizes into the rotator phase and the excess THz absorption disappears.

One possible origin for this apparent absorption feature is light scattering, arising from the heterogeneous microstructure formed during nucleation. However, we can rule out this possibility based on our measurements of the refractive index of the sample. As is well established, THz TDS provides a direct measurement, not only of the sample's absorption coefficient $\alpha(\omega)$, but also its refractive index $n(\omega)$ [10]. Fig. 3 shows the measured temperature dependence of the refractive index at one particular frequency for all four alkanes studied.

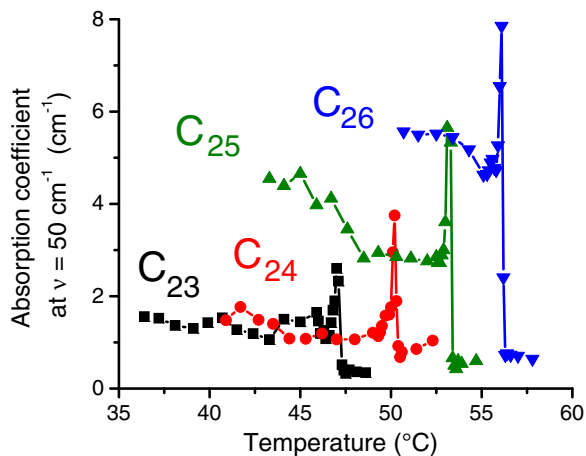


Fig. 2. Absorption coefficient at a particular frequency (50 cm^{-1}) plotted as a function of temperature, for all four alkanes studied. The enhanced absorption is observed at the L-R transition in all four samples. The temperatures of the phase transitions match well with literature values for the phase diagrams of these materials [12].

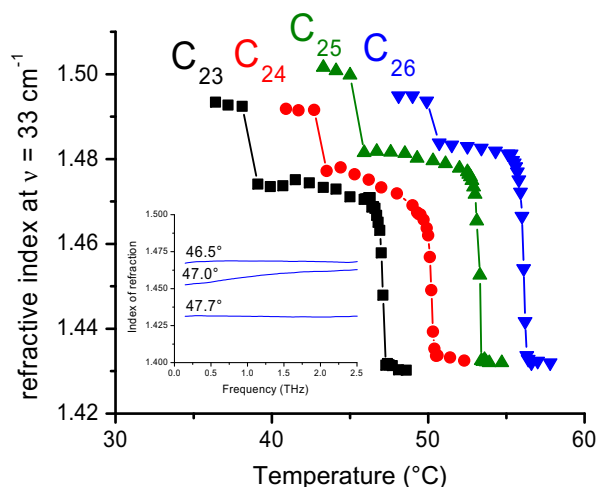


Fig. 3. Refractive index at a particular frequency (33 cm^{-1}) plotted as a function of temperature, for all four alkanes studied. The L-R transition is evident as an abrupt jump in the refractive index from ~ 1.42 to ~ 1.47 . A second smaller jump at lower temperatures corresponds to the rotator-to-crystalline phase transition. The inset shows the frequency dependence of the index, for C_{23} at three different temperatures. These typical results illustrate the fact that the measured indices are nearly dispersionless.

dence of the refractive index at one particular frequency for all four alkanes studied. In all cases, the L-R transition is clearly observed as an abrupt jump in $n(\omega)$ as the sample is cooled. The rotator-to-crystalline transition is also observed in each case, at a lower temperature. These measured transition temperatures are consistent with literature results for the phase diagrams for these materials [12]. The inset shows the frequency dependence of $n(\omega)$ for C_{23} (representing typical results for all four alkanes). This illustrates that the index is nearly dispersionless over the range of frequencies studied here, even at temperatures close to the phase transition. In our subsequent discussions, we consider $n(\omega)$ to be a dispersionless (but temperature-dependent) value.

A key result illustrated by Fig. 3 is the magnitude of the jump in the refractive index. If we imagine that, near the phase transition, the sample consists of a random collection of nucleated regions of rotator phase embedded in a liquid background, then we could possibly attribute the observed attenuation features to Mie scattering from an inhomogeneous dielectric composite. However, in the liquid phase, for all four alkanes, the refractive index is approximately 1.42, while in the rotator phase, the index is 1.47–1.48. This corresponds to a dielectric contrast $\Delta\epsilon < 0.17$, which is a fairly small value. As a point of comparison, we have previously studied the effects of scattering on broadband terahertz pulses [17]. We showed that the spectral response of an inhomogeneous dielectric medium can indeed contain strong frequency-dependent modulation. That is, scattering can give rise to signatures that can mimic absorption peaks. However, in those measurements, the scatterers were of a size comparable to the radiation wavelength, and moreover the dielectric contrast was significantly larger, $\Delta\epsilon \sim 1.2$. Based on a similar Mie scattering analysis, we conclude that the alkane samples do not exhibit sufficiently large dielectric contrast to produce the measured attenuation peaks from scattering off of a random medium.

If the excess absorption is not due to light scattering, then it must arise from dipole correlations induced in this non-polar material by the L-R transition. To obtain the spectrum of the excess absorption for each sample, we subtract the absorption spectrum in the R phase from that of the transition phase, $\Delta\alpha = \alpha_{L-R} - \alpha_{\text{rotator}}$. This procedure is similar to the treatment previously used to study collision-induced absorption in various

non-polar liquids [18,19], as discussed below. In all cases, the temperature difference between the spectra α_{L-R} and $\alpha_{rotator}$ used to compute $\Delta\alpha$ is 0.3 °C or less. The results are shown in Fig. 4. For all four samples, we observe a broad peak in the differential spectrum $\Delta\alpha(\omega)$, lying below 80 cm^{-1} . The value of the differential absorption coefficient at its spectral peak, $\Delta\alpha_{\max}$, is in the vicinity of 1–3 cm^{-1} . This is slightly larger than the corresponding absorption strength in the liquid phase at these frequencies, but smaller than the attenuation of the fully solidified rotator phase. In other words, the excess absorption induced at the L–R transition is a relatively small peak riding on top of a larger background absorption which is observed when the entire sample volume is in the rotator phase.

We analyze the measured differential absorption spectra using a generalized Langevin formalism. Mori has described a useful route for obtaining an analytical expression for the relevant response functions, based on a truncated continued fraction expansion of a memory function that serves as a kernel for computing the dipole correlation function [19–21]. Extending the Mori kernel to second order, one can derive the absorption coefficient as [19–21]:

$$\alpha(\omega) = \frac{\epsilon_0 - \epsilon_\infty}{nc} \omega^2 \frac{\gamma K_0 K_1}{\gamma^2 (K_0 - \omega^2)^2 + \omega^2 (\omega^2 - K_0 - K_1)^2}. \quad (1)$$

In this expression, K_0 , K_1 , and γ are coefficients in the expansion of the memory function. In the case of molecules with a permanent dipole moment, these coefficients can be related to parameters such as the molecular moment of inertia and the mean square torque. For non-polar molecules, their interpretation is less clear, as they are averages over all molecular interactions. Nevertheless, we can fit our measured differential absorption spectra to Eq. (1), treating K_0 , K_1 , and γ and the dielectric dispersion ($\epsilon_0 - \epsilon_\infty$) as fit parameters. These non-linear least-squares fits are shown as solid lines in Fig. 4.

The Mori method has frequently been used to discuss dipole correlation dynamics in both polar and non-polar liquids, and for example has been the standard method for analysis of the well-known Poley absorption peak [20,21]. Because the Poley peak is typically regarded as an excess absorption, sitting atop the conventional Debye relaxational absorption, one typically subtracts off the Debye contribution prior to analysis of the Poley peak. This ap-

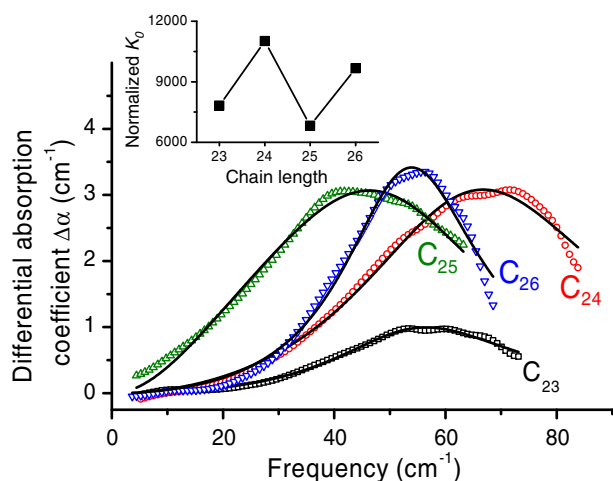


Fig. 4. Differential absorption coefficients $\Delta\alpha$ vs. frequency, for the four alkanes studied, computed as described in the text. The solid lines are optimized non-linear least-squares fits to these data using Eq. (1). From these fits we extract fit parameters including K_0 , which is the amplitude of the memory kernel used to generate the dipole correlation function [20,22]. The value of this parameter is plotted in the inset. These values are normalized to $I_C/k_B T$, where I_C is the molecular moment of inertia, and T is the L–R transition temperature. K_0 exhibits an even–odd alternation as a function of chain-length.

proach has inspired the analysis method for computing $\Delta\alpha$ described above, and should be equally valid if the absorption signature is vibrational in character, as we have proposed.

As pointed out by several authors [20,22], the parameter K_0 in Eq. (1) is of particular interest. In the case of a linear or symmetric top molecule with a permanent dipole moment, this parameter is equal to $2k_B T/I_C$, where I_C is the moment of inertia about the symmetry axis. Davies and Evans have shown that, for non-polar molecules, the value of K_0 is larger than $2k_B T/I_C$, and moreover that it increases with increasing I_C [20]. This discussion motivates us to plot K_0 , normalized by $I_C/k_B T$, as a measure of intermolecular interaction strength (as shown in the inset of Fig. 4). These values exhibit a clear even–odd chain-length alternation. This even–odd effect is well-known in many thermodynamic properties of n -alkanes in their solid phases [3,12]. The observation of an even–odd effect suggests that end-chain packing may play an important role in mediating the observed vibration-induced dipole correlation. A detailed discussion of this point is beyond the scope of this work; however, the observation of an even–odd effect supports our interpretation of the results as being related to short-range intermolecular interactions.

The data and the high quality of the fits shown in Fig. 4 are an unambiguous indication of correlations between induced dipoles in these materials [20,21]. We now address the question of their origin. Because of the striking temperature dependence, it seems reasonable to propose that the induced dipole correlation occurs within the small regions of nucleated rotator phase, that initially form near the surface-frozen layer and ultimately grow to encompass the entire medium. The effect would be related to the vibrational modes of these nucleated regions. This resembles conventional descriptions of the origin of the Boson peak.

An explanation based on vibrational modes induced during the nucleation process has some precedent. It is known that terahertz absorption can be directly correlated with the VDOS in disordered media [8]. Further, it has been shown that an enhanced VDOS can result from structuring or heterogeneity on the nanoscale [5,23–25]. Finally, the idea that n -alkanes, upon cooling, may form locally ordered regions with enhanced VDOS has been proposed previously [26]. Notably, we do not observe any enhanced absorption or signatures of lattice vibrations once the sample is cooled enough so that the rotator phase is fully formed. With the disappearance of mesoscale phase boundaries, one would expect acoustic modes in non-polar media to be largely infrared-inactive, consistent with our observations.

In analyzing the Boson peak in glasses, one can estimate a correlation length scale from the frequency of the peak. We can apply a similar analysis here. We assume that the THz spectra are a direct reflection of the VDOS, so the peak of our measured absorption spectrum corresponds to ν_{\max} , the peak of the VDOS [8]. Then, we can estimate the vibrational correlation length scale as $D = S(V_S/\nu_{\max})$, where S is a factor of order unity depending on the shape of the correlated regions, and V_S is the sound velocity [5]. The sound velocities in n -alkanes have not previously been reported for either the crystalline or rotator phases, but the room-temperature value for high-density polyethylene, $V_S \sim 2400$ m/s, is a reasonable order-of-magnitude estimate. With this value, and using $\nu_{\max} = 1.6$ THz for C_{23} (see Fig. 2) and assuming $S = 1$, we estimate the correlation length scale to be ~ 15 Å. This is about half of the inter-layer separation in the C_{23} rotator phase; in the lamellar plane, this corresponds to roughly four times the nearest-neighbor distance [12]. This estimate further supports the conclusion that the measured peaks arise from short-range dipolar correlations induced by localized vibrations.

Our observations are consistent with previous studies of low-frequency vibrational modes in alkane crystals. For example, inelastic neutron scattering has been used to study the VDOS in

the region below 100 cm^{-1} , for chain lengths less than $n = 20$ [27]. These results indicate a significant peak in the VDOS near 70 cm^{-1} for even n , and at a somewhat lower frequency for odd n . The variation with chain-length seen in Fig. 2 is consistent with these earlier data and could result from an even–odd alternation in the sound velocity, although the lack of data on the chain-length dependence of V_S makes this speculation difficult to verify.

In conclusion, we present the first evidence for the formation of a Boson peak induced by a first-order phase transition. This indicates an enhancement in the vibrational density of states at the phase transition, induced by heterogeneous nucleation. The correlation length scale estimated from the measured spectra suggests that the correlations are relatively short-range. This result demonstrates a new method for characterizing the dynamics of heterogeneous nucleation in non-polar liquids.

Acknowledgements

Funding for this research has been provided by the R.A. Welch Foundation, the National Science Foundation, and by Shell International Exploration and Production, Inc.

References

- [1] X.Z. Wu, B.M. Ocko, E.B. Sirota, S.K. Sinha, M. Deutsch, B.H. Cao, M.W. Kim, *Science* 261 (1993) 1018.
- [2] E.B. Sirota, A.B. Herhold, *Science* 283 (1999) 529.
- [3] H. Kraack, E.B. Sirota, M. Deutsch, *J. Chem. Phys.* 112 (2000) 6873.
- [4] Y. Shinohara, N. Kawasaki, S. Ueno, I. Kobayashi, M. Nakajima, Y. Amemiya, *Phys. Rev. Lett.* 94 (2005) 097801.
- [5] E. Duval, A. Boukenter, B. Champagnon, *Phys. Rev. Lett.* 56 (1986) 2052.
- [6] E. Duval, A. Boukenter, T. Achibat, *J. Phys.: Condens. Matter* 2 (1990) 10227.
- [7] G.P. Johari, *J. Non-Cryst. Solids* 307–310 (2002) 114.
- [8] T.S. Grigera, V. Martin-Mayor, G. Parisi, P. Verrocchio, *Nature* 422 (2003) 289.
- [9] H. Shintani, H. Tanaka, *Nat. Mater.* 7 (2008) 870.
- [10] D. Mittleman, *Sensing with Terahertz Radiation*, Springer-Verlag, Heidelberg, 2002.
- [11] G. Ungar, *J. Phys. Chem.* 87 (1983) 689.
- [12] E.B. Sirota, J.H.E. King, D.M. Singer, H.H. Shao, *J. Chem. Phys.* 98 (1993) 5809.
- [13] K. Nozaki, M. Munekane, M. Hikosaka, T. Yamamoto, *Jpn. J. Appl. Phys.* 40 (2001) 6918.
- [14] S.L. Wang, K. Tozaki, H. Hayashi, S. Hosaka, H. Inaba, *Thermochim. Acta* 408 (2003) 31.
- [15] P.K. Mukherjee, M. Deutsch, *Phys. Rev. B* 60 (1999) 3154.
- [16] P.K. Mukherjee, *J. Chem. Phys.* 116 (2002) 10787.
- [17] J. Pearce, D.M. Mittleman, *Opt. Lett.* 26 (2001) 2002.
- [18] M.W. Evans, G.J. Davies, *J. Chem. Soc. Faraday Trans. II* 72 (1976) 1206.
- [19] G.W. Chantry, *Long-wave Optics*, Harcourt Brace Jovanovich, London, 1984.
- [20] G.J. Davies, M. Evans, *J. Chem. Soc. Faraday Trans. II* 72 (1976) 1194.
- [21] J.E. Pedersen, S.R. Keiding, *IEEE J. Quantum Electron.* 28 (1992) 2518.
- [22] R.G. Gordon, *J. Chem. Phys.* 43 (1965) 1307.
- [23] J. Boyd, A. Briskman, V. Colvin, D. Mittleman, *Phys. Rev. Lett.* 87 (2001) 147401.
- [24] J. Boyd, A. Briskman, C. Sayes, D. Mittleman, V. Colvin, *J. Phys. Chem. B* 106 (2002) 6346.
- [25] X. Zhang, R.S. Bandhu, R. Sooryakumar, B.T. Jonker, *Phys. Rev. B* 67 (2003) 075407.
- [26] L. Brambilla, G. Zerbi, *Macromolecules* 38 (2005) 3327.
- [27] J. Tomkinson, S.F. Parker, D.A. Braden, B.S. Hudson, *Phys. Chem. Chem. Phys.* 4 (2002) 716.