Temperature dependence of the dielectric function of \( \text{C}_6\text{H}_6(\text{l}) \) and \( \text{C}_6\text{H}_5\text{CH}_3(\text{l}) \) measured with THz spectroscopy

Cecilie Rønne and Kasper Jensby
Department of Chemistry, Aarhus University Langelandsgade 140, DK-8000 Århus C, Denmark

Brian J. Loughnane and John Fourkas
Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

O. Fauskøv Nielsen
Department of Chemistry, University of Copenhagen, 5-Universitetssparken, DK-2100 Copenhagen, Denmark

Søren R. Keiding\(^a\)
Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark

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We report on an experimental investigation of the temperature dependence of the intermolecular dynamics in liquid benzene and toluene. With the use of THz time domain spectroscopy we measured the complex dielectric function \((0.2–3.3 \text{ THz})\) of the liquids, at temperatures between \(-6{^\circ}\text{C}\) and \(75{^\circ}\text{C}\). By analyzing the dielectric loss (as opposed to the absorption coefficient) we found three contributions to the dielectric function for toluene and two for benzene. In the dipolar liquid toluene we observed a contribution from rotational diffusion at lower frequencies in addition to the two high-frequency librations also observed in benzene. The temperature and density dependence were different for the two librational bands, probably due to the different effect of three-body interactions for the two processes. Furthermore, we present measurements of the low-frequency depolarized Raman spectra as a function of temperature for benzene and toluene. These have been compared with the dielectric loss at similar temperatures. Moreover, for benzene a similar comparison is made between the dielectric loss and the reduced Raman susceptibility obtained by optical Kerr effect spectroscopy. Libration of the symmetric top axis is found in all spectra. © 2000 American Institute of Physics. [S0021-9606(00)51433-0]

I. INTRODUCTION

Liquid benzene has been among the most used nondipolar aromatic solvents in organic chemistry for many decades. Nowadays, toluene has replaced benzene to a great extent because toluene has nearly the same solvent properties and is less carcinogenic. In spite of this, there is still surprisingly little known about the actual molecular and intermolecular modes that facilitate the chemical reactions in both toluene and benzene.

It has been known since the beginning of the 20th century that reorientation of dipolar molecules in the condensed phase can be studied through the dielectric response of the liquid. Most theories regarding the molecular mechanism of the dielectric response are concerned with dipolar liquids and start out by the generalized Langevin equation,\(^1\) in the form of either the Debye model\(^2\) or the Mori formalism.\(^3\) A more recent formalism, extended irreversible thermodynamics,\(^4\) accounts for dielectric relaxation at low frequencies, libration at far-infrared frequencies, and the coupling between the two. Most experimental dielectric curves can be fitted to one of or a combination of the above models. However, the parameters obtained from such an analysis describe the behavior of the macroscopic time correlation functions (TCF) and do not, correspondingly, often give very much insight into the underlying molecular motion.

The main experimental issue is that the complex dielectric function typically is needed between approximately 0–6 THz, i.e., at both microwave and far-infrared (FIR) frequencies in order to observe all intermolecular modes. However, in many cases there are gaps between microwave data and reliable FIR data. For instance, in a study of the dielectric function of toluene at various temperatures it has been suggested that toluene exhibits two Debye relaxation processes.\(^5\) Yet, the second relaxation process has been predicted without experimental data at the position of the suggested dielectric loss peak. The FIR absorption coefficient of toluene at room temperature has later on been measured in this frequency range,\(^7\) but no comparison has been made between the two studies. In the present study we have obtained the dielectric function of toluene in the missing region with the use of THz time domain spectroscopy\(^8\) (THz-TDS). This technique allows us to measure both the real (\(\varepsilon\)) and imaginary part (\(\varepsilon^\prime\)) of the complex dielectric function, \(\varepsilon(\nu)\), so that the dielectric loss can be directly patched on to the microwave measurements and compared to the predicted Debye model.

The underlying molecular motions for the dielectric function are perhaps most easily visualized in the time domain as the TCF for the macroscopic dipole moment, which

\(^{a}\)Electronic mail: keiding@kemi.aau.dk
is intimately related to the dielectric loss by a Fourier transformation. Interaction-induced dipoles also contribute to the TCF and thereby to the dielectric loss. Naturally, this was first realized in the case of nondipolar liquids. For instance, in 1950 it was observed that various nondipolar liquids including benzene\textsuperscript{10} gave rise to absorption at microwave frequencies, even after water and other polar impurities were removed. Since then the absorption of liquid benzene at far-infrared and microwave frequencies has been widely studied.\textsuperscript{11–13} The development and use of molecular dynamics (MD) simulations to generate the TCF of liquids has made it possible to divide the TCF into components that can give a better understanding of the molecular origin of the dielectric loss. Various ways of decomposing the simulated TCF for liquid benzene into positive and negative contributions have been employed. For instance, the TCF of benzene has been divided into a positive single (or self) part and a negative distinct (or self) part.\textsuperscript{18,19} Alternatively, the TCF has been divided into contributions from two-, three-, and four-body interactions, where the contribution of the three-body interactions as a whole is negative and thereby cancel part of the absorption from the two- and four-body interactions.\textsuperscript{19} The cancellation effects will probably make the shape of the TCF, or equivalently of the dielectric function, sensitive to changes in density and temperature in a way that is more complex than what is observed for single molecule motion, e.g., Debye relaxation of a polar liquid.

In this work we report measurements of the temperature and density dependence of the transverse dielectric function of benzene and toluene between 0.2 and 3.3 THz (6.7 and 110 cm\textsuperscript{-1}) with the use of transmission mode THz-TDS. In previous studies only the absorption coefficient could be found in this frequency range. Our aim is to compare the molecular dynamics of the nondipolar liquid benzene with the chemically similar dioplar ($\mu = 0.375$ D in the gas phase)\textsuperscript{20} liquid toluene in order to determine the importance of absorption due to interaction-induced dipoles. Moreover, we want to explore the nature of the underlying molecular mechanism by comparing the temperature and density dependence of the dielectric function of the two liquids.

The intermolecular dynamics in liquids can also be studied by other techniques that reflect the time dynamics in of the macroscopic polarizability, as, for example, low-frequency depolarized Raman spectroscopy (DRS)\textsuperscript{21–24} or optical Kerr effect (OKE) spectroscopy.\textsuperscript{25–28} In this paper we present measurements of the DRS spectra as a function of temperature for benzene and toluene. These have been compared with the dielectric loss at similar temperatures. Furthermore, for benzene a similar comparison is made between the dielectric loss and the reduced Raman susceptibility obtained by OKE spectroscopy.\textsuperscript{28}

\section*{II. THEORETICAL BACKGROUND}

In the most previous studies of the FIR response of molecular liquids, the interpretation of the measurements has been based on the frequency-dependent absorption coefficient, $\alpha(\nu)$, whose relation to the dielectric loss is given\textsuperscript{9} in Eq. (1).

$$\alpha(\nu) = \varepsilon''(\nu) \nu / [n(\nu)c].$$  

This has a historical origin because it is difficult to measure the refractive index in conventional FIR spectroscopy. The THz-TDS technique allows direct measurement of both the index of refraction and absorption coefficient, and for the interpretation we can accordingly use the imaginary part of the dielectric function as the natural representation for low-frequency studies. Since the dispersion is only about 1% between 0.2 and 3 THz for both liquids in the present study at all temperatures there should not \textit{a priori} be any physical difference between the conclusions drawn from an analysis of the absorption coefficient and the dielectric loss. However, since the absorption coefficient is scaled with the frequency compared with the dielectric loss, the high-frequency components have a much higher weight than do the low-frequency components. This may hide low-frequency contours in what appears to be broad and featureless FIR-absorption profile.

New insight can be gained by comparing the dielectric loss with the imaginary part of the low-frequency Raman susceptibility. Below we briefly outline the theoretical expressions for the experimental signals obtained using the three different techniques, THz-TDS, OKE spectroscopy, and DRS.

THz-TDS: The imaginary part of the complex dielectric constant is related to the dipole moment TCF,\textsuperscript{9,29}

$$\varepsilon''(\nu) = \frac{4\pi^2}{3\hbar V} \left[ 1 - \exp \left( -\frac{\hbar \nu}{kT} \right) \right] \frac{1}{2\pi} \times \int_{-\infty}^{\infty} dt \exp(-i2\pi\nu t) \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle,$$

where $V$ is the volume of the sample. The absorption of far-infrared radiation is thus a direct consequence of the fluctuations of the total dipole moment, $\mathbf{M}$, of the liquid sample. $\mathbf{M}$ can be expressed by a sum of the permanent single molecule dipole moments and the additional dipole moments induced by the intermolecular interactions. The main contribution to the induced dipole moment on the $j$th molecule, is determined by the local electrical field and the polarizability of the molecule as described by Eq. (3) for pair interaction, where the local electrical field arises from the electrostatic distribution of molecule $j$.\textsuperscript{29}

$$\mu_{ij} = \alpha_j(t) E_{ij}(t).$$  

In a nondipolar liquid, the lowest-order electrostatic contribution to the induced dipole moment is the quadrupole-polarizability term.\textsuperscript{30}

DRS and OKE spectroscopy: Both techniques can be used to obtain the imaginary part of the anisotropic Raman susceptibility,\textsuperscript{31} $\chi''_{R}(\nu)$. In the case of DRS, $\chi''_{R}(\nu)$ can be found\textsuperscript{32–24} using Eq. (4).

$$\chi''_{R}(\nu) \propto (\nu_L - \nu)^4 \left[ 1 - \exp \left( -\frac{\hbar \nu}{kT} \right) \right] I_{\text{DRS}}(\nu),$$

where $\nu_L$ is the laser frequency of the incident laser light and $I_{\text{DRS}}(\nu)$ is the Fourier transform of the TCF of the anisotropic part of the total polarizability tensor of the sample.\textsuperscript{33}
The exponential term in the parentheses in Eq. (4), often referred to as the Bose factor, arise from the averaging over the thermally populated quantum levels in the liquid. This factor plays a key role when comparing to the different Raman techniques. The OKE signal is a time-dependent measurement of induced birefringence and the imaginary part of the Fourier transform of the OKE signal divided by the Fourier transform of the intensity autocorrelation function is directly comparable to the $\chi''(\nu)$ found by DRS.\textsuperscript{31,25}

**III. EXPERIMENTAL SECTION**

**A. THz-TDS**

The THz time domain technique is described in detail elsewhere.\textsuperscript{8,14,34} The fs-laser pulses used in this experiment have a center wavelength of $\lambda=800$ nm, a pulse energy $\sim 0.5$ nJ, and a pulse width of 40 fs. The pulse train is split in two by a beamsplitter. One part of the beam is used for generating the THz radiation and the other is sent through a variable delay line and used for the gated detection of the THz pulse. For the measurements of the temperature dependence a sample cell consisting of two identical cylindrical chambers with a thickness of 5.95 mm and a diameter of 10 mm enclosed by two polished, plane-parallel, and high resistivity silicon windows was constructed. The temperature was held constant to within 0.1 °C by a Peltier element controlled by a feedback loop. At each temperature ten independent measurements of the THz pulses transmitted through the sample (containing 0.5 ml of the liquid) and through the reference chamber (containing dry air), respectively, were performed. Fourier transformed, analyzed using the Fresnel relations for the involved interfaces, and, in turn, averaged to give the dielectric functions presented in this paper. The dielectric functions have been smoothed to avoid small interference oscillations from a small after-pulse in the time domain. At each scan 1024 data points, separated by 0.04 ps, were collected with a time constant of 30 ms. The home built experimental setup used for these measurements is shown in Fig. 1. Note that the THz beam is focused into the small sample volume. The beam waist of the Gaussian THz beam is approximately 2 mm for frequencies higher than 0.3 THz. In order to minimize scattering of the THz pulse from the metal window frames it was ensured that the THz beam was centered on both the back and front window of the sample cell.

The liquid solvents were of the highest spectroscopic purity obtainable purchased from Aldrich. They were used without further purification. The measurements were performed without degassing the liquids because test measurements where the liquid was exposed to N$_2$(g) and O$_2$(g), respectively, showed no change in the absorption.

**B. DRS**

Raman spectra in an Ivh-scattering configuration were recorded on a DILOR Z24 spectrometer. A home build cryostat was used to obtain spectra at $-2$ °C, 20.4 °C, 49.9 °C, and 69.7 °C with an accuracy greater than 0.1 °C. The exciting source was the 532 nm line from a Spectra Physics Millennia II laser. In order to assure that the effect of stray light was of no importance, spectra were obtained at different laser powers and spectral slit width. The imaginary part of the Raman susceptibility has been calculated according to Eq. (4).

**C. OKE spectroscopy**

Details about the sample preparation, the experimental setup and the analysis of the exponential parts of the OKE signal can be found in Ref. 28.

**IV. RESULTS**

**THz-TDS**

In Fig. 2 and Fig. 3 are shown the measurements of the dielectric function at four temperatures between $-4$ °C and 65 °C for benzene (Fig. 2) and $-6$ °C and 75 °C for toluene (Fig. 3). The precision of the measurements is indicated by the standard deviations (error bars) obtained from the average of the ten measurements for benzene at $-4$ °C and for toluene at 48 °C. The larger noise at the low- and high-frequency part of the measurements reflect the smaller spectral amplitude of the THz pulse at these frequencies.

The real parts of the dielectric functions are shown in the lower panels of Figs. 2 and 3. The accuracy of the curve shape is determined predominantly by the stability of the laser during a scan, and we find this to be very reproducible. $\varepsilon'(\nu)$ has a similar shape at all temperatures for benzene and toluene, respectively. Each curve is smoothly decreasing with approximately 2% from the low- to the high-frequency end of our frequency range. The absolute value of the curves decreases linearly with increasing temperature. A linear fit to points at 1.5 THz as a function of $T(\text{°C})$ gives $\varepsilon'=-2.285-0.001 62T$ for toluene and $\varepsilon'=-2.300-0.001 94T$ for benzene. For benzene the gradient compares well with that of the static dielectric constant ($-0.002 \text{ °C}^{-1}$).\textsuperscript{20} In contrast, the temperature gradient at 1.5 THz of toluene is smaller than that of the static dielectric constant ($-0.00243 \text{ °C}^{-1}$).\textsuperscript{20} The static dielectric constant will include contributions from every degree of freedom that gives rise to a macroscopic dipole moment. Accordingly, since the gradient of the static dielectric constant of benzene is very close to that of $\varepsilon'(1.5 \text{ THz})$ we may conclude that there are no further low-frequency processes in benzene. On the other hand, in toluene since the gradient of the static dielectric...
The dielectric constant is greater than that at 1.5 THz \((-0.00162\, ^\circ\text{C}^{-1})\), there has to be at least one process at lower frequencies.

The absolute value of the curves for the real part of the dielectric function is mainly determined by the alignment of the sample cell. We have observed that it is important for the accuracy of the dielectric loss to center the THz beam both on the back and front window of the sample cell. Unfortunately, this may lead to small deviations from normal incidence, which will alter the optical path in the cell, and give rise to a translation of the \(\varepsilon'(\nu)\) curve toward higher values. Santarelli et al. have measured the temperature-dependent dielectric function of toluene at frequencies between 32 and 118 GHz, and in Fig. 4(a) we have shown that our \(\varepsilon'(\nu)\) at 21 °C extrapolate well with the Santarelli et al. low-frequency data. Accordingly, the absolute value of \(\varepsilon'(\nu)\) for toluene is in agreement with previous data. This is not the case for benzene. The static dielectric constant for benzene at 21 °C has been found to be 2.282, a value that is lower than the low-frequency part of our curve. Since any given process will tend to lower the value of \(\varepsilon'(\nu)\) with increasing frequency (except very close to a resonance) it is probable that our curve is obtained at a small angle compared to normal incidence, and accordingly translated to higher values than the true value. Because we obtained the temperature dependence of the dielectric function at a fixed cell position for each liquid, the temperature gradient of \(\varepsilon'(\nu)\) will not be affected by a common translation of the \(\varepsilon'(\nu)\) curves.

The imaginary parts of the dielectric functions are shown in the upper panel of Figs. 2 and 3. The dielectric loss decreases with increasing temperature for both liquids at frequencies between 1.3 and 3.3 THz. Furthermore, when the experimental uncertainty and the temperature of the measurements are taken into account the dielectric losses are nearly equal at frequencies above 1.3 THz for the two liquids. At frequencies below 1.3 THz there is no observable temperature dependence for the dielectric loss of benzene. In this frequency range the dielectric loss of toluene increases moderately with increasing temperature. In Fig. 4(b) we have shown that our \(\varepsilon'(\nu)\) for toluene at 21 °C extrapolate well to the Santarelli et al. low-frequency data when the higher uncertainty of our data at low frequencies is taken into account.

V. DISCUSSION

We have performed our measurements at constant pressure as opposed to constant density and correspondingly we observe a combined effect of temperature and density. By studying the dielectric loss of benzene we can directly observe two processes with different temperature/density dependence (Fig. 2). In the case of benzene the absorption we observe is due to quadrupole-induced dipoles. This means that there is no contribution from single molecules. The simplest case of interaction-induced dipoles will arise from two-body interactions in the liquid. It is known from low-density gas phase studies that the intensity of the absorption due to two-body collisions will scale with the square of the density, \(\rho^2\). In Fig. 5 we have plotted \(\varepsilon''(\nu)/\rho^2\) as a function of temperature. Interestingly, near 1.7 THz we find a crossover area between a low-frequency region where the dielectric loss increases with increasing temperature and a high-frequency region where the dielectric loss decreases slightly with increasing temperature. The same description matches an analogous plot for toluene (not shown). This indicates that the high-frequency part of the dielectric loss is...
dominated by a two-body interaction mechanism for both benzene and toluene, and that the effect of changing the temperature is mainly that the density changes.

The FIR absorption coefficient of benzene has been suggested to be due to libration around an axis perpendicular to the top axis (out-of-plane libration)\textsuperscript{21} based on the experimental observation of the isotope shift of the frequency at the maximum absorption of C\textsubscript{6}H\textsubscript{6} and C\textsubscript{6}D\textsubscript{6}. More recently, the total absorption spectrum and the in-plane and out-of-plane librational pseudo absorption spectra have been generated with the use of MD simulation.\textsuperscript{18} It has been found that the total spectrum has contributions from in-plane and out-of-plane librations. The low-frequency part of the in-plane libration only has a minor contribution to the total spectrum because of cancellation effects. This explains why the isotope shift\textsuperscript{21} of the frequency at the maximum absorption is in agreement with an assignment to the out-of-plane libration. As shown in Fig. 2 and Fig. 5 the measurement of the dielectric loss instead of the absorption coefficient allows for the observation of two processes instead of one because the low-frequency process is not hidden by a frequency factor as described by Eq. (1). The most reasonable assignment of the two processes is that both librations are observed in the THz-TDS measurements. However, before any conclusions are drawn, the temperature and density dependence must be investigated in order to determine whether it is probable that the two librations observed via two-body interactions have different temperature dependence (Fig. 5). The two librations may be influenced differently by the local environment. There is no general consensus in the literature about the existence of a structural change in the liquid when the temperature is changed. For example, in a high-resolution stimulated Brillouin gain study\textsuperscript{37} no evidence of a structural transitions was found, as opposed to a study\textsuperscript{23} of the temperature dependence of the Rayleigh wing of benzene where a change of the temperature gradient of the normalized second moment was suggested to occur at 38 °C. However, in a more recent MD simulations and neutron diffraction study it was found that the structure around a given benzene molecule is almost isotropic at distances corresponding to the first solvation shell and changes very little with changing temperature.\textsuperscript{38} A different structural influence on the librations is thus unlikely to be the explanation for the different temperature dependence. Another and more likely explanation can be found when higher order than two-body interactions are taken into account. As described below the temperature and density dependence of both librations may be understood as a competition between positive contribution from two-body interactions and the cancellation of absorption from three-body interactions.

The MD simulations by Danten et al.\textsuperscript{18} indicate that in-plane libration is more affected by cancellation effects than is the out-of-plane libration. If the in-plane libration is affected by many-body interactions, the density dependence cannot be removed by the division of the squared temperature-dependent density. Accordingly, competing effects of temperature and density changes must be taken into account when explaining the observed changes in dielectric loss as a function of temperature. The influence of changing density at constant temperature has been investigated experimentally\textsuperscript{16} and by MD simulations.\textsuperscript{19} It has been observed that the negative three-body contributions increase more rapidly than the positive two-body contributions with increasing density. This is in agreement with that the three-body contributions will scale with the density cubed and the two-body contributions with the density squared. Furthermore, the effect of changing the temperature seems to be well described by a density change according to the high-frequency part of the curve in Fig. 5. In conclusion, the observation that the low-frequency in-plane libration seems to be unaffected by an isobaric temperature change, may be understood as the combined effects of the dielectric loss aris-
ing from two-body interactions will decrease with decreasing density,\textsuperscript{19} and that the cancellations due to three-body interactions will decrease more slowly with decreasing density than the absorption from two-body interactions.\textsuperscript{19} The temperature dependence of the contribution from three-body interactions has so far not been investigated. Currently, we are performing MD simulations at different temperatures to investigate the precise influence of changing the temperature.\textsuperscript{42}

For toluene, Santarelli \textit{et al.}\textsuperscript{6} have suggested a second overlapping relaxation process in addition to a Debye relaxation process of 5.56 ps at 20°C to account for the high-frequency dielectric loss. In Fig. 4 we have compared the Debye model, including one relaxation process (the solid line) and the Debye model including two relaxation processes (the dashed line) with our dielectric loss of toluene at 21°C. At frequencies below 0.3 THz and above 1.4 THz the double Debye model is found to fit the current data. However, in between 0.3 and 1.4 THz, this model predicts a value that is higher than the measured dielectric loss. At the peak position this difference is about 20%. Although it is evident that there are one or more high-frequency processes in toluene, a second relaxation process does not reproduce the detailed shape of our high-frequency dielectric response. There is, accordingly, only one true relaxation process in toluene, i.e., rotational diffusive relaxation. Note that this process can account for the difference between the gradient of the static dielectric constant and that at 1.5 THz. In order to investigate the dielectric loss of toluene besides the Debye process, in Fig. 6 we have shown the residue of the dielectric loss (filled circles) when a single Debye process has been subtracted. It is interesting to see that the shape of the resulting curve is very similar to the dielectric loss of benzene, shown in Fig. 6 as open circles. Accordingly, it is very likely that we are observing three processes in toluene: (part of) the Debye process (rotational diffusive relaxation), and the processes similar to what we observe in benzene. The similarity in amplitude of the dielectric loss for the librations in benzene and toluene implies that the librational bands in toluene mainly have an interaction-induced origin and thus that the permanent single molecule dipoles play only a minor role.

Qualitatively, it is expected that the absorption for structurally similar molecules will increase with increasing polarizability and quadrupole moment [Eq.\textsuperscript{3}]. The size of the polarizabilities and quadrupole moments for benzene and toluene, listed in Table I, is in agreement with the assumption of an interaction-induced librational band with comparable size for benzene and toluene.

In many cases Raman and IR bands give complementary information about vibrational transitions, especially for molecules of high symmetry. Likewise, information may be obtained for the intermolecular dynamics in liquids by comparing the spectra measured using light absorption and scattering. In Fig. 7 we have compared the dielectric loss with the imaginary part of the Raman susceptibility found using DRS. The $\chi''$ curves have been calculated according to Eq.\textsuperscript{3} and, since the absolute value of $\chi''$ is not known, these curves have been scaled to overlap with the high-frequency part of the dielectric loss curves.

![Figure 6](image_url)

FIG. 6. The open circles are the dielectric loss for benzene at room temperature and the filled circles are the dielectric loss for toluene, where the contribution to the Debye process has been subtracted. When the single Debye process is subtracted from our dielectric loss, we find that the resulting shape is very close to the dielectric loss of benzene.

![Figure 7](image_url)

FIG. 7. The lines are the imaginary part of the Raman susceptibility (measured using DRS with a spectral slit width of 1.5–2.0 cm\textsuperscript{-1}) and the symbols are the dielectric loss. The lines have been scaled to overlap with the high-frequency part of the dielectric loss curves.

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TABLE I. Quadrupole moments, polarizabilities, and moments of inertia for benzene and toluene calculated at the B3LYP/6-31G** level of accuracy using \textit{gaussian} 94 (Ref. 39). In toluene the $z$ axis is along the C–CH\textsubscript{3} bond and the $x$ axis perpendicular to the benzene plane.
frequency part of the dielectric losses at temperatures as close to each other as possible. We find that the shapes of the curves are in agreement at frequencies above 1.3 THz for benzene and 0.8 THz for toluene. Because of the anisotropic static polarizability of both benzene and toluene (Table I) we expect that there is a single molecule contribution to the depolarized low-frequency Raman spectrum as opposed to the dielectric spectrum that is purely interaction induced. The scattering spectra of liquids like O$_2$, $^4$S and CS$_2$, $^4$I have theoretically been shown to be influenced only little by the interaction-induced polarizability and is thus mainly caused by the permanent molecular polarizability. Assuming that the same is the case for benzene and toluene this has some interesting consequences for the selection rules of $\chi''$ that will be discussed in the following paragraphs.

In contrast to the dielectric loss where the single molecule diffusion is only observed in toluene, the diffusive motions are observed in the scattering spectrum for both liquids. This has previously been studied with the use of OKE spectroscopy, where two exponential decay times have been found for the polarizability TCF with time constants of 3.19 and 0.98 ps for benzene and 5.90 and 1.88 ps for toluene. Since there is, coincidentally, different relaxational process with the same time constant (~6 ps) in both the dielectric and scattering spectrum for toluene it can be understood why these spectra are in agreement (Fig. 7) down to lower frequencies than those of benzene, where single molecule diffusion is not observed in THz-TDS.

The similar shape of $\varepsilon''$ and $\chi''$ at the high frequencies at all temperatures indicate that we observe the out-of-plane libration in both spectra. Theoretically this is certainly a possibility. First, the polarizability for both benzene and toluene is considerably bigger in the molecular plane than out of the plane, and thus will the out-of-plane libration change the time-dependent macroscopic polarizability. Second, in a quadrupolar liquid a librational motion may show up at the same frequency and with the same spectral shape in the dielectric and scattering spectra because a quadrupole and a polarizability TCF have the same rank.

The low-frequency in-plane libration is very unlikely to Raman active because the polarizability is isotropic in the molecular plane of benzene and only slightly anisotropic in toluene. Note that the in-plane libration may still be FIR active because a time-dependent change of the dipole moment described by Eq. (3) can be created by a motion that either changes the polarizability or the local electric field. The latter effect can be exemplified by the fact that FIR absorption is also observed in tetrahedral molecular liquids such as CCl$_4$. Since the polarizability for such molecules is isotropic, the time-dependent dipole moment will be caused solely by a change in the induction field felt by molecule $j$ in Eq. (3). Thus, the in-plane motion in benzene may still be observed because the direction of electric moment belonging to molecule $i$ is altered with respect to molecule $j$ thereby changing the time-dependent dipole moment. Accordingly, it is interesting to investigate the librational contribution to the low-frequency region further. For the data obtained with OKE spectroscopy the diffusional components can be removed by subtracting the two exponential decays in the time domain before Fourier transforming the data as described in Ref. 28. In Fig. 8 we have plotted the resulting reduced Raman susceptibility for benzene together with the dielectric loss. Again, we find a reasonably good agreement at frequencies above 1.8 THz as expected due to the out-of-plane libration. At lower frequencies the reduced Raman susceptibility is generally lower than the dielectric loss and has the same temperature dependence as that observed for the out-of-plane libration in the dielectric loss. These observations are in agreement with that the in-plane libration is not visible in the Raman spectrum. The in-plane librational band can, in principle, be obtained by subtracting the reduced Raman susceptibility from the dielectric loss.

VI. CONCLUSION

We have measured the complex dielectric function (0.2–3.3 THz) of liquid benzene and toluene, at temperatures between −6 °C and 75 °C with the use of THz time domain spectroscopy. We found three contributions to the dielectric function for toluene and two for benzene. In the dipolar liquid toluene we observed a contribution from rotational diffusion at lower frequencies in addition to the two high-frequency librations also observed in benzene. The temperature and density dependence were different for the low-frequency in-plane and out-of-plane interaction-induced librational bands. This is due to the different effect of three-body interactions, and thus cancellation of the positive part of the macroscopic dipole TCF. The observation that the low-frequency in-plane libration seems to be unaffected by an isobaric temperature change, may be understood as the combined effects of that the dielectric loss arising from two-body interactions will decrease with decreasing density, and that the cancellations due to three-body interactions will decrease more slowly with decreasing density than the absorption from two-body interactions. Furthermore, measurements of the DRS spectra as a function of temperature for benzene and toluene were presented. These were compared with the dielectric loss at similar temperatures. Moreover, for benzene a similar comparison was made between
the dielectric loss and the reduced Raman susceptibility obtained by OKE spectroscopy. The out-of-plane libration was found in all spectra.

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