THz Time-Domain Spectroscopy of Nonpolar Liquids

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Abstract—Using a newly developed terahertz time-domain spectrometer based on photoconductive dipole antennas driven by femtosecond laser pulses, we have measured the absorption and index of refraction for benzene, carbon tetrachloride and cyclohexane in the far infrared. The spectra cover the region from 3–66 cm⁻¹, where the dielectric response of the nonpolar liquids is dominated by collision induced dipole moments. With terahertz time-domain spectroscopy, information on both the real and imaginary part of the frequency response is obtained in a range difficult to access by standard techniques.

I. INTRODUCTION

The far-infrared (FIR) absorption behavior of liquids is different in nature for polar and nonpolar molecules. Absorption in polar molecules is due to interaction with the permanent dipole moments of the individual molecules. The electric field tends to align the dipoles, and the subsequent collision induced relaxation (Debye-relaxation) of the oriented dipoles has a time constant in the picosecond range giving rise to strong absorption in the far infrared. For nonpolar molecules the much smaller absorption originates in the transient dipole moments induced via collisions in the liquid. Several experimental techniques such as dielectric relaxation spectroscopy, depolarized Rayleigh-wing scattering, NMR and FIR absorption have been applied to gain insight in these complex, but very fundamental dynamic processes. In this paper, we show how the newly developed technique of terahertz (THz) time-domain spectroscopy can be applied to liquids to yield very accurate data for both the real and imaginary part of the dielectric constant, or, equivalently, give both absorption coefficient and index of refraction of the liquids.

II. TERAHERTZ TIME-DOMAIN SPECTROSCOPY

During the last four years the technique of time-domain spectroscopy with subpicosecond pulses of THz radiation [1] has proved a very powerful experimental technique in obtaining spectroscopic information on gasses [2], [3], dielectrics [4], [5], semiconductors [4], [6], and superconductors [7]. Using THz beams as a source of FIR radiation has several advantages over traditional techniques. First of all, the bandwidth covers a broad spectral region from approximately 100 GHz to 2.5 THz, difficult to access with conventional sources. Second, the spectrometer operates at room temperature, thus avoiding the complications associated with cryogenic detectors. Also, the recorded data include information on both the amplitude and phase of the THz radiation thereby allowing for a simple, simultaneous measurement of both the real and imaginary parts of the dielectric constant. Finally, a very high signal to noise ratio of around 10⁴ allows for relatively short averaging times in each sampling point. This translates into fast scanning of the spectrometer and hence greater overall stability of the setup during an experimental run.

III. EXPERIMENTAL CONFIGURATION

The THz spectrometer, shown in Fig. 1, is similar to the setup described in [4]. The emitting dipole antenna consists of two 10 μm metal lines separated by 50 μm on a seminsulating GaAs substrate. It was fabricated by standard lithographical techniques, using a mixture of Au–Ge–Ni for the metal lines. Subpicosecond THz pulses are generated by biasing the antenna with a 27 V battery and focussing a 50 fs laser pulse on the inside of the positively biased line. The resulting photocurrent with subpicosecond risetime acts as source for the THz pulses. Focussing the laser on the outer side of the positive line gives an identical signal, except for a phase change of π, due to a sign change of the driving field. Only a very weak signal could be generated near the negative line. This agrees with the mechanism suggested in [8]. The focal spot was roughly 10 μm. The time dependent photocurrent radiates into the substrate and is collimated by a hyperhemispherical lens made of high resistivity silicon (> 10 kΩ·cm). A 90° off-axis paraboloidal mirror collimates the THz radiation into a parallel beam of roughly 30 mm diameter. A second paraboloidal mirror focuses the THz radiation onto the detector. The THz detector is similar to the emitter, except that it is fabricated on an ion-implanted silicon-on-sapphire (SOS) substrate. The unbiased detector is gated by the delayed pulses from the femtosecond laser, and the sampled photocurrent is proportional to the electric field strength of the THz pulse. To facilitate alignment of the THz spectrometer, the gate pulse delay is modulated at around 40 Hz, with a simple electromagnetic vibrator. This allows the THz pulse to be monitored real time on a digital oscilloscope. The amplitude of the THz pulse is roughly 10 nA. Apart from a length of 10 mm, the entire path of the THz beam is enclosed in an air tight container filled with...
nitrogen gas at atmospheric pressure. This is done to avoid the ubiquitous absorption due to water vapor.

The femtosecond laser is a standard seven mirror cavity CPM-laser [9] pumped by a small Ar-ion laser. The center wavelength lies around 620 nm, and pulses shorter than 60 fs are routinely generated with an average power of 20 mW in each of the two beams. This relatively high output power is obtained with a modest pump power of 3 W (all lines). The pulses maintain their stability, duration and power for up to six weeks after preparation of the dyes (as compared to typically 2-3 weeks). We believe that at least three factors are responsible for the excellent performance of this laser. 1) The ethylene glycol solvent is dried by boiling before mixing the dyes, 2) the laser and dye-pumps are purged with dry air, and 3) the output coupler in the CPM laser has a high transmission of 3.5%. The first two limit the degradation of the organic dyes caused by water.

The liquids under investigation were placed in a 10 mm cell made from high density polyethylene (RIALEN-HDPE). The thickness of the windows was 3 mm and the cell diameter was 75 mm. The cell diameter should be at least twice the beam diameter, to avoid diffraction losses for the low frequencies. Although the material losses in HDPE are higher than in silicon [4], [12], the low index for HDPE (n = 1.495) as compared to Si (n = 3.4200), allows for a higher transmission through a cell made from HDPE. The spectra were obtained by first measuring a THz reference pulse transmitted through the empty cell and then measuring a sample pulse transmitted through the same cell, filled with the liquid under investigation. A second reference pulse was then taken with the cell emptied. The optical constants are next obtained by comparing the Fourier transforms of the sample and reference pulses. Comparison of the two reference pulses was used to ensure that the performance of the system was maintained during the course of the measurement. In order to avoid complications from multiple reflections in the HDPE windows of the cell, the maximum recorded delay was limited to roughly 25 ps after the main pulse. The reference pulse, in both frequency and time domain is shown in Fig. 2. The bandwidth, extending out to 2.5 THz, is presently limited by the dimensions of the receiving antenna. Using smaller antennas, this bandwidth would extend beyond 3 THz. The weak features after the pulse arise from reflections within the antenna substrates, and from absorption due to traces of water in the experimental setup. These features are compensated out when comparing with the sample spectra obtained under identical conditions. The excellent signal to noise ratio is illustrated by the low noise level in front of the THz pulse. The data points marked on the pulse represent the temporal sampling density or, equivalently, the step length of the delay line.

IV. RESULTS

The examined liquids, benzene, carbon tetrachloride, and cyclohexane (Merck, Spectroscopic grade) were used without further purification. Cells made from HDPE degrade when exposed to benzene for more than a day or two, so all spectra were obtained over a period of no more than two hours using a new cell. The cells were carefully cleaned in cyclohexane and purged with nitrogen after each run. The index and absorption data obtained this way were then checked against data obtained using a cell made of fused silica, which is resistant to benzene, but limits the bandwidth to 1.5 THz due to absorption in the cell walls. The optical constants of the pure liquids are shown in Figs. 3, 4, and 5.

A number of factors contribute to the uncertainty of the given values. The delay line was calibrated by recording a THz pulse propagating through water vapor, and comparing the frequencies of the water lines with accurately
Fig. 3. Index and absorption for benzene. The line represents the calculated absorption based on a fit to (3) with the parameters listed in Table I. The calculated index is obtained using the Kramers–Kronig relations on the calculated absorption profile.

Fig. 4. Index and absorption for carbon tetrachloride. The line represents the calculated absorption based on a fit to (3) with the parameters listed in Table I. The calculated index is obtained using the Kramers–Kronig relations on the calculated absorption profile. The stars indicate the calculated absorption from [15].

Fig. 5. Index and absorption for cyclohexane. The line represents the calculated absorption based on a fit to (3) with the parameters listed in Table I. The calculated index is obtained using the Kramers–Kronig relations on the calculated absorption profile.

THz beam within ±45 mrad. These factors mainly influence the absolute value of the index of refraction. The accuracy of that parameter is estimated to be approximately ±0.002. This figure corresponds well with the reproducibility between experimental runs. The dispersion of the indices, which depends on the smoothness of the delay line rather than its absolute position, is at least a factor of 10 more accurate.

The absorption data are more sensitive to changes in conditions during the scans, that is change in laser power, alignment, etc. The noise is constant over the bandwidth of the THz pulse, so consequently the signal to noise ratio degrades rapidly below 200 GHz and above 2 THz. The given values of the absorption coefficients represent averages over several measurements, and are in general reproducible within 0.2 cm⁻¹ for benzene and carbon tetrachloride and 0.1 cm⁻¹ for cyclohexane at the central frequencies. Again the shape of the absorption curve as a function of frequency is reproduced to a higher standard than the absolute value. The recorded absorption data are in good agreement with absorption profiles obtained using standard FT-FIR spectrometers [11]–[15].

V. DISCUSSION

The general trend in the absorption spectra can be rationalized from simple physical considerations. Carbon tetrachloride is the heaviest of the three molecules, and consequently the absorption peaks at lower frequencies, corresponding to the slower dynamics of the induced dipole moments. In benzene the absorption is an order of magnitude larger than in cyclohexane. This is due to the fact that electrons occupying π-orbitals give larger con-
tributions to the induced dipole moments than electrons occupying σ-orbitals as in cyclohexane.

Several models have been suggested to account for the dielectric response of nonpolar molecules in the far infrared [15]. Transient dipole moments are induced in the nonpolar molecules as a consequence of collisions between the individual molecules. The induced dipole moments tend to create a short range transient ordering of the molecules. The ordering is described in the time-domain by a dipole correlation function \( C(t) \), linking the orientation of the induced dipole moment of molecule \( i \), \( \mathbf{\mu}_i \), at time \( t \), with the orientation of the surrounding dipole moments.

\[
C(t) = \sum_{i,j} \langle \mathbf{\mu}_i(t) \cdot \mathbf{\mu}_j(0) \rangle.
\]

(1)

The shape of the observed FIR absorption is directly related to the Fourier transform of (1) [11]. The correlation function can be represented by an equation of the form

\[
\tilde{C}(\tau) = -\int_0^\infty K(t - \tau) C(\tau) d\tau
\]

(2)

where the function \( K(t) \) is related to the dynamical coherence of the liquid. The \( K \) function is often referred to as the memory function. Equation (2) belongs to a family of generalized Langevin equations, that, depending on the form of the memory function \( K(t) \), describe the dynamics of many complex systems. The memory function can be expanded into a series of memory functions \( K_0(t), \ldots, K_n(t) \) and the Fourier transform of the dipole correlation function can then be given as a continued fraction of the Fourier transforms of the memory functions \( K_0(t), \ldots, K_n(t) \). The simplest form of the memory function \( K_0 = D\delta(t) \), gives the classical Langevin equation for Brownian motion, corresponding to a dipole correlation function of the form \( C(t) = \exp(-t/t_D) \), where \( t_D \) is the Debye relaxation time.

This model can be used to describe the dielectric behavior of liquids at low frequencies, but fails at the higher frequencies. The FIR absorption of non-polar liquids can be described by a second-order memory function of the form \( K_1(t) = K_1(0) \exp(-\gamma \cdot t) \). This assumption then leads to an absorption coefficient of the form [13],

\[
\alpha(\omega) = \frac{E\omega^2\gamma K_0(0)K_1(0)}{\omega^2 + \omega^2 - K_0(0) - K_1(0)}.
\]

(3)

The amplitude factor \( E \) is proportional to the square of the effective dipole moment of the absorbing molecule, and is defined as,

\[
E = \frac{\epsilon_i - \epsilon_{\infty}}{n(\omega) \cdot c}
\]

(4)

where \( \epsilon_i \) and \( \epsilon_{\infty} \) represent the low and high frequency limits of the model. All the absorption spectra were fitted to the expression in (3), and the fitting parameters are given in Table I. To further check the validity of the model, the absorption profile calculated from (3), with the adjusted parameters, was used to calculate the refractive index, using the Kramers–Kronig relation,

\[
n(\omega) = n(\infty) + \frac{33,356}{\pi} \int_0^\infty \frac{\alpha(\omega)}{\omega^2 - \omega_0^2} d\omega.
\]

(5)

The integration was truncated around 6 THz, where the absorption is below 1% of the peak value. The value of \( n(\infty) \) was used to normalize the calculated index with the observed index of refraction at 0.6 THz. As it is evident from Figs. 3–5, (3) can accurately reproduce the observed spectra both for index and absorption. The obtained fitting parameters differ somewhat from the fitting parameters obtained in [13] and [14], but since we use a very flexible model for the absorption with four adjustable parameters and since our spectral range only covers part of the characteristic spectrum of (3), this is not unexpected, especially for benzene and cyclohexane. However, using the fitting parameters obtained in [13] and [14] does not accurately reproduce the absorption profiles observed in this paper. Presently we are working on fabricating smaller THz detectors that will extend our bandwidth to beyond 3 THz. This will enable us to cover the characteristic spectrum of the index and absorption profiles, and consequently obtain better estimates on the memory function parameters.

It is a drawback of the memory function approach, however, that a direct link between the fitting parameters \( \gamma, K_0, K_1 \) and molecular constants, such as the multipole moments, is not straightforward to establish. For simple molecules with permanent dipole moments, \( K_0(0) \) and \( K_1(0) \) are related to the moment of inertia and the mean square torque between the molecules. For nonpolar molecules the parameters are averages over all the intermolecular interactions, including contributions from many body effects.

A different approach used for benzene and carbon tetrachloride is to calculate the absorption profile directly from the point multipole moments of the molecule. This is done for carbon tetrachloride in [17], where the calculated results are found to be somewhat lower than the corresponding experimental observations in [16]. The agreement with our observations is better as illustrated in Fig. 4, where the calculated absorption is indicated at selected frequencies. The shape of the calculated absorption is in good agreement for frequencies above 0.8 THz, but differs somewhat for the lower frequencies. The lower frequencies represent the slow response of the molecules and
consequently the response that includes many-body interactions. THz time-domain spectroscopy therefore allows for a detailed comparison with the modeling of the complicated many-body effects. Similar calculations have been performed for benzene and fluorinated benzenes [11] and compared with the integrated absorption. These calculations demonstrate a breakdown of the point multipole model and argue that a model with distributed multipoles must be used to obtain agreement with the experimental observations.

VI. CONCLUSION

We have applied the new technique of THz time-domain spectroscopy to study the collision induced far-infrared absorption spectra in nonpolar liquids. The spectra cover a region difficult to access with conventional techniques, and give valuable information on the detailed dynamical behavior of the liquids.

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