Charge Transport and Carrier Dynamics in Liquids Probed by THz Time-Domain Spectroscopy

E. Knoesel,[1,*] M. Bonn,[2] J. Shan,[1] and T. F. Heinz[1]
[1]*Department of Physics, Columbia University, 538 West 120th Street, New York, New York 10027*
[2]*Leiden Institute of Chemistry, P.O. Box 9502, 2300 RA Leiden, The Netherlands*
(Received 17 July 2000)

We examine the transport properties and the dynamics of free electrons in n-hexane by means of femtosecond spectroscopy using an ultraviolet pump pulse to create the electrons and a THz electromagnetic pulse as a probe. The complex dielectric response of the photogenerated electrons is determined over a broad range of frequencies, from which we infer the electron scattering time and density through the Drude model. The time evolution of the carrier density reveals nongeminate electron-ion recombination within hundreds of picoseconds at high ion concentration.

DOI: 10.1103/PhysRevLett.86.340 PACS numbers: 78.47.+p, 42.62.Fi, 72.10.–d, 72.80.–r

The nature of charge transport in condensed matter is of great fundamental and technological importance. One of the key parameters of the motion of electrons is the *scattering time*, i.e., the mean time between momentum changing collisions that act to impede the flow of current under an applied electric field. Typical scattering times range from femtoseconds to picoseconds, depending on the nature, purity, and temperature of the material. Since these times correspond to the terahertz (THz) frequency range, THz time-domain spectroscopy (THz TDS) has emerged as a powerful probe of charge carriers and their transport processes in condensed matter [1–5]. This method provides direct information on the real and imaginary parts of the dielectric constant or, equivalently, the complex conductivity. These data, when analyzed in conjunction with a description of the carrier response, as, for example, embodied in the Drude model, yield basic properties relevant in transport, such as carrier densities, plasmon frequencies, and scattering rates. The approach has been applied successfully in semiconductors [1,2] and semiconductor nanostructures [3], as well as in superconductors [4,5]. An important additional aspect of THz TDS is the possibility to probe dynamical processes with picosecond temporal resolution, as has been demonstrated in solid state materials [2,3,5,6] and liquids [6,7]. In this Letter, we report on a pump-probe THz TDS study of electrons in a model nonpolar liquid, namely, solvated electrons in n-hexane.

Solvated electrons in liquids have long been a subject of scientific interest. Since the early experimental findings of Thompson [8] and the seminal theoretical contributions of Onsager [9], the problem of solvated electrons has been addressed by a variety of techniques [10]. Attention has been focused both on the characteristics of the solvated electrons themselves and on their generation and recombination with ions. Important experimental approaches have included radiolysis measurements [11–13], in which induced currents from irradiation of the sample are recorded, and laser-based probes [14–16], in which the infrared or visible transient absorption induced by an ionization step may be followed with high time resolution. From these investigations, a two-state model of solvated electrons has emerged that is capable of describing many of the experimental observations [12,13]. In this picture, solvated electrons exist in thermal equilibrium between localized bound states and a quasifree state, with only those electrons in the quasifree state contributing significantly to the electrical conductivity of the liquid. Lacking from the studies to date, however, is direct information on the relative proportion of quasifree and bound electrons and on the basic transport properties, such as scattering time or mobility, of the quasifree electrons. These parameters have been obtained only through modeling of the temperature dependence of the average mobility [13], except in a few special systems for which measurements of both the conventional and Hall conductivity have been achieved [17]. As we demonstrate in this Letter, THz TDS complements existing approaches to the study of electron transport in liquids. Like pulsed radiolysis measurements, THz TDS is sensitive to the charge transport process itself, but provides *direct* access to the time scale of the scattering process, as well as to the density of the quasifree electrons. THz TDS further permits one to observe the evolution of the system following excitation with picosecond time resolution. As such, THz TDS complements optical pump-probe spectroscopy, which probes predominantly solvated electrons in bound, rather than in quasifree states.

The apparatus employed for THz TDS is indicated in Fig. 1. The laser for these measurements is an amplified, mode-locked Ti:sapphire system that provides 100-fs pulses at a wavelength of 810 nm with an energy of 1 mJ/pulse and a repetition rate of 1 kHz. Pulsed THz radiation is produced by optical rectification of these laser pulses in a ZnTe crystal; and the electric field of the THz pulses is detected in a second ZnTe crystal via electro-optic sampling [18]. Between the generation and detection stages, the THz beam passes through a focus of ~1-mm diameter, where the sample is introduced. The n-hexane (spectroscopic grade, Alpha Aesar) was probed both in the form of a jet and in a 1-mm-thick flow cell. The solvated electrons in the n-hexane sample were generated by a two-photon ionization process

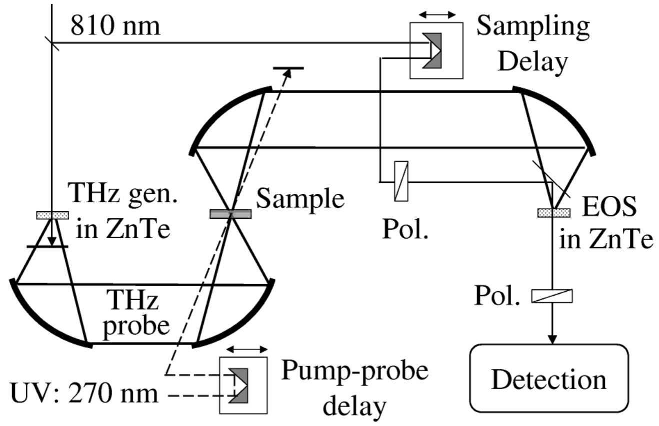

FIG. 1. Experimental setup for THz time-domain spectroscopy with an ultraviolet pump beam for photoexcitation of the liquid sample.

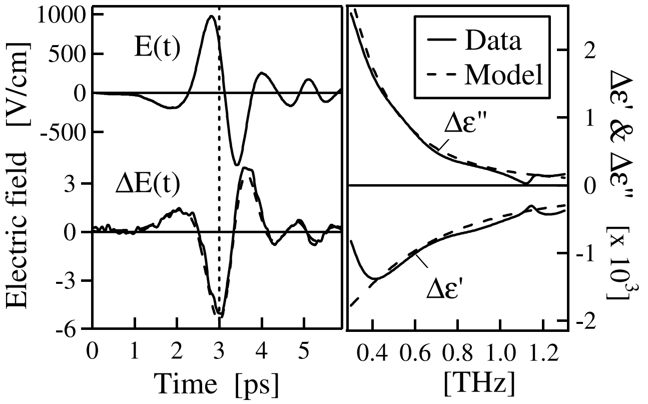

FIG. 2. Left panel: THz waveform $E^{\rm off}(t)$ after transmission through 1 mm of n-hexane (upper trace) and changes in the transmitted THz waveform, $\Delta E(t)$, induced by the UV pump beam (lower trace). The UV pump fluence was 10 mJ/cm^2, with a beam diameter of 0.8 mm and a pump-THz-probe time delay of 67 ps. Right panel: frequency dependence of the change in real ($\Delta\varepsilon'$) and imaginary ($\Delta\varepsilon''$) part of the dielectric constant. The dashed lines are fits to the Drude model.

(IP = 8.6 eV [16]) with UV pulses at a photon energy of 4.5 eV. These pulses, created by frequency tripling 90% of the 810-nm radiation, provided 50 μJ of energy in a spot of 0.2-1-mm diameter at the hexane sample.

Three distinct types of measurements can be performed with this apparatus. In the first scheme, we record the transmitted THz electric field waveform $E(t)$ for any desired sample—be it hexane, photoexcited hexane, or no sample at all—by scanning the delay of the 810-nm sampling pulse versus the THz probe pulse. In the second scheme we obtain the differential THz waveform, $\Delta E(t)$, with and without photoexcitation of the sample. In these measurements, performed at any chosen delay after generation of the electrons, we chop the UV pump beam and monitor the induced modulation in the transmitted THz waveform. In the third scheme, we select a particular point in the THz waveform, $E(t = t_0)$ or $\Delta E(t = t_0)$, and record its variation as a function of the delay after the arrival of the UV pump pulse.

The electric-field waveform $E(t)$ of THz pulses transmitted through the unexcited hexane sample is shown as the upper trace of the left panel of Fig. 2. The waveform has a width of a few picoseconds and exhibits a large transient followed by a few smaller oscillations. The latter arise primarily from absorption by water vapor in air [19]. The THz waveform in the absence of the sample in the beam path exhibits essentially the same shape and amplitude, which indicates small THz absorption of hexane. We do, however, observe a distinct temporal shift; this can be related accurately to the thickness of the sample through the known low-frequency refractive index of $n = 1.42$ [20]. The lower trace in Fig. 2 depicts the pump-induced change in the THz waveform, $\Delta E(t) = E^{\rm on}(t) - E^{\rm off}(t)$. In comparison to $E(t)$, the amplitude of $\Delta E(t)$ is only 0.5% and its waveform displays a distinctly different shape. The relative change in the waveform contains the information on the dielectric properties of the liquid with injected electrons. The induced THz response, $\Delta E(t; \Delta\tau)$, measured at a delay time $\Delta\tau$ after UV excitation varies slowly with $\Delta\tau$ on the time scale of a few picoseconds. We thus consider the solvated electrons probed in our measurements to be in quasi-steady-state and ascribe to them a frequency-dependent dielectric function that depends parametrically on the pump-probe delay time $\Delta\tau$.

In order to extract the complex dielectric function from the experimental data, we take the Fourier transforms of the THz waveforms measured without the sample, with the unexcited sample, and with the photoexcited sample. The ratios of the latter two to the former correspond to the complex transmission factors for the sample in its unperturbed and excited states, respectively. Since the induced change in the dielectric response, $\Delta\varepsilon$, is quite small, we have analyzed the problem perturbationally and find a direct relation between the differential THz waveform, ΔE, and $\Delta\varepsilon$:

$$\Delta\epsilon = 2\epsilon(\omega)\left[i\frac{\omega l}{c/\sqrt{\epsilon(\omega)}} - \frac{\sqrt{\epsilon(\omega)} - \sqrt{\epsilon_{\rm ext}(\omega)}}{\sqrt{\epsilon(\omega)} + \sqrt{\epsilon_{\rm ext}(\omega)}} \right]^{-1} \times \frac{\Delta E(\omega)}{E(\omega)}, \tag{1}$$

where $E(\omega)$ and $\Delta E(\omega)$ denote the Fourier transforms of the corresponding time-domain quantities, $E(t)$ and $\Delta E(t)$, and $\varepsilon(\omega)$ and $\varepsilon_{\rm ext}(\omega)$ are the complex dielectric functions of the unperturbed sample and its surrounding material (e.g., air, sample cell windows), respectively. This expression includes propagation through thickness l of the excited liquid, as well as interfacial transmission losses at the boundary of the sample. The influence of multiple reflections is slight and has been omitted for simplicity. The right panel in Fig. 2 depicts the inferred changes in the real and imaginary parts of the dielectric constant, $\Delta\varepsilon'$ and $\Delta\varepsilon''$, versus frequency.

In principle, the pump-induced changes in the THz waveform could arise from any of the species that are generated by the UV pulse, i.e., ions, excited neutral molecules, and electrons in the bound or quasifree state. *A priori* one would expect the quasifree electrons to dominate: the THz response will be most sensitive to charged particles that can be accelerated most readily by the applied electric field, namely, the quasifree electrons with their low effective mass. Indeed, as will be apparent in the discussion below, all of our experimental findings indicate that quasifree electrons are the source of the observed change in the THz waveform. As a simple representation of this response, we introduce the Drude model to describe the modification of the dielectric function of the liquid $\Delta\varepsilon$:

$$\varepsilon_{\text{tot}} = \varepsilon(\omega) + \Delta\varepsilon(\omega) = \varepsilon(\omega) - \frac{\omega_p^2}{\omega(\omega + i\gamma_0)}. \quad (2)$$

Here γ_0 denotes the electron scattering rate, $\omega_p = [e^2 n_f/(\varepsilon_0 m^*)]^{1/2}$ is the plasma frequency, with m^* the effective electron mass, n_f is the density of quasifree electrons, and ε_0 is the permittivity of free space. The scattering rate γ_0 in this expression characterizes the movement of the electron in the material and is therefore of central importance for the processes of conduction and diffusion.

The dashed lines in Fig. 2 represent a fit of the experimental value of the change in the complex dielectric function, $\Delta\varepsilon(\omega)$, to the Drude model. The agreement between the data and the model is quite good given that the shape of the two curves, $\Delta\varepsilon'(\omega)$ and $\Delta\varepsilon''(\omega)$, is determined entirely by the single parameter of the scattering rate γ_0. For frequencies below 0.4 THz, the THz wavelength is comparable to, or larger than, the limited spot size of the UV pump beam (800 μm). This makes an interpretation of the experimental data below this frequency less clear, since diffraction effects might influence the observations. The indicated fit yields a scattering rate of $\gamma_0 = (330\ \text{fs})^{-1}$ and a plasmon frequency of $(\omega_p/2\pi) = 3.3 \times 10^9$ Hz, which implies a quasifree electron density of $n_f = 7 \times 10^{12}\ \text{cm}^{-3}$ (for $m^* = m_0$). From another set of data taken at higher excitation density, we obtain a similar scattering rate of $(235\ \text{fs})^{-1}$ and a plasmon frequency of $(\omega_p/2\pi) = 2.5 \times 10^{10}$ Hz. A comparison of several experiments leads to an average scattering rate of $\gamma_0 = (270 \pm 60\ \text{fs})^{-1}$, which displays no strong dependence on electron density.

The scattering rate γ_0 can be related to the mobility of the quasifree electrons μ_f by the relation $\mu_f = (e/m^*)\gamma_0$ [10]. Assuming that $m^* = m_0$, we obtain a value of $\mu_f = 470\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$. In earlier radiolysis measurements, researchers found an average electron mobility of $\mu_d = 0.074\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ for electrons in n-hexane [13]. The large discrepancy between μ_f and μ_d arises from the fact that conventional transport measurements deduce the electron mobility using the *total* density of solvated electrons, the experimentally accessible quantity, while our measurements include only the response of the quasifree electrons. Since most of the solvated electrons are in bound states that contribute very little to charge transport, the average mobility of the solvated electrons will be far lower than that of the quasifree electrons. Theoretical estimates for quasifree electron mobilities range from 30 to 400 $\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ in nonpolar liquids [13,21,22], slightly lower than what is observed here. In a quasiballistic model of electron charge transport our experimentally derived scattering time (270 fs) would correspond to the electron lifetime in the quasifree state [23]. By way of comparison, at interfaces a time scale of a few hundred femtoseconds has been observed for a transition from a free to a bound (localized) electron state in solid alkane films [24].

The quasifree electrons observed in the THz measurements constitute only a small fraction of the total electron density. The quasifree electrons are produced by thermal excitation of solvated electrons residing in the bound state and, consequently, their density reflects the temperature of the system. This results in a strong temperature dependence of the average electron mobility, from which an average binding energy of the electron in the bound state of $E_a = 190$ meV was inferred [13]. We applied the THz TDS method to obtain a direct measure of the density of quasifree electrons as a function of temperature. We found a density increase by a factor of 1.6 for an increase in the sample temperature from 287 K to 312 K, corresponding to $E_a = 150$ meV.

The temporal evolution of the solvated electrons can be studied with the THz TDS approach by recording the THz waveform $\Delta E(t)$ as a function of delay time $\Delta\tau$ of the UV pump pulse. We found no change in the shape of $\Delta E(t)$ with variation of either $\Delta\tau$ or pump fluence F. By comparison to the Drude model, we infer that γ_0 is independent of the excitation parameters and that the amplitude of $\Delta E(t)$ is proportional to n_f, the quasifree electron density. Figure 3 displays the resulting time dependence of the n_f for two different pump fluences, $F = 0.3$ and $0.15\ \text{J/cm}^2$. The electron density is found to decrease on a time scale of 400 ps for the high fluence and 1.2 ns for the low fluence, with immeasurably long decay times occurring at still lower fluences. We interpret this decay as a *nongeminate* electron-ion recombination process, the rate of which depends on the hexane-ion concentration and, hence, on the UV pump fluence. Optical and infrared transient absorption experiments of photoexcited alkanes reveal recombination times of a few picoseconds [15,16]. For a probe pulse at 810 nm wavelength, we observed similar results. This faster decay process, which has been attributed to *geminate* recombination of electrons with their parent ions, was not apparent in the THz TDS measurements. The difference in sensitivity of the optical and the THz probe may reflect the somewhat reduced time resolution of the THz measurement. It may also indicate that electrons undergoing geminate recombination—and,

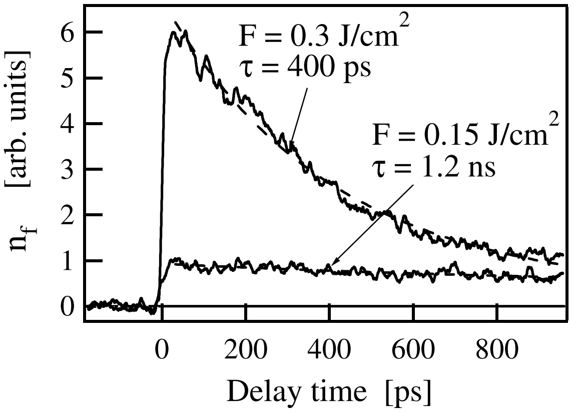

FIG. 3. Dependence of $\Delta E(t)$ (measured at its maximum) on the UV pump-THz-probe delay. As discussed in the text, $\Delta E \propto n_f$, the quasifree electron density. The fluence-dependent decay is interpreted as a nongeminate recombination of the photogenerated electrons with n-hexane ions.

consequently, moving in the strong Coulomb field of their parent ions—exhibit reduced response to the THz field.

In summary, terahertz time-domain spectroscopy has been applied to examine the charge transport properties and dynamics of electrons in liquid hexane. To our knowledge, this is the first report of the frequency dependence of the conductivity of electrons in any liquid. Over a wide range of THz frequencies, both the real and imaginary parts of the complex response function could be well described by the Drude model. This analysis directly yields the scattering time and density of the quasifree electrons. The time evolution of the quasifree electron density reveals the presence of a nongeminate electron-ion recombination process. The method demonstrated here appears to have considerable potential to investigate charge transport in other liquids, as well as in wide-gap semiconductors and insulators.

We acknowledge generous support from the National Science Foundation (CHE-96-12294) and the Air Force Office of Scientific Research (F-49620-98-1-0132), the Royal Netherlands Academy of Arts and Sciences and Robert Robinson (M. B.), and the Humboldt Foundation (E. K.).

---

*Present address: Department of Physics, Rowan University, Glassboro, New Jersey 08028.

[1] M. van Exter and D. Grischkowsky, Appl. Phys. Lett. **56**, 1694 (1990); P. G. Huggard *et al.,* J. Appl. Phys. **87**, 2382 (2000).
[2] B. I. Greene *et al.,* Opt. Lett. **16**, 48 (1991); S. S. Prabhu *et al.,* Appl. Phys. Lett. **70**, 2419 (1997); J. Zielbauer and M. Wegener, Appl. Phys. Lett. **68**, 1223 (1996); M. Schall and P. U. Jepsen, Opt. Lett. **25**, 13 (2000).
[3] R. H. M. Groeneveld and D. Grischkowsky, J. Opt. Soc. Am. B **11**, 2502 (1994).
[4] S. Spielman *et al.,* Phys. Rev. Lett. **73**, 1537 (1994); O. Morikawa *et al.,* Appl. Phys. Lett. **75**, 3387 (1999).
[5] R. D. Averitt *et al.,* J. Opt. Soc. Am. B **17**, 327 (2000).
[6] G. Haran *et al.,* Chem. Phys. Lett. **274**, 365 (1997).
[7] R. McElroy and K. Wynne, Phys. Rev. Lett. **79**, 3078 (1997).
[8] J. J. Thompson, Nature (London) **55**, 606 (1897).
[9] L. Onsager, Phys. Rev. **54**, 554 (1938).
[10] R. A. Holroyd and W. F. Schmidt, Annu. Rev. Phys. Chem. **40**, 439 (1989); B. S. Yakovlev and L. V. Lukin, in *Photodissociation and Photoionization*, edited by K. P. Lawley (Wiley, New York, 1985); W. F. Schmidt, in *Liquid State Electronics of Insulating Liquids* (CRC Press, Boca Raton, FL, 1997).
[11] J. M. Warman, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis,* edited by J. H. Baxendale and F. Busi (Reidel, Dordrecht, 1982).
[12] R. C. Munoz *et al.,* J. Phys. Chem. **91**, 4639 (1987).
[13] N. Gee, P. C. Senanayake, and G. R. Freeman, J. Chem. Phys. **89**, 3710 (1988).
[14] T. W. Scott and C. L. Braun, Can. J. Chem. **63**, 228 (1985); F. F. Brazgun *et al.,* Chem. Phys. **211**, 469 (1996); A. Volkmer, K. Wynne, and D. J. S. Birch, Chem. Phys. Lett. **299**, 395 (1999).
[15] R. M. Bowman, H. Lu, and K. B. Eisenthal, J. Chem. Phys. **89**, 606 (1988); M. Sander *et al.,* J. Phys. Chem. **97**, 8378 (1993).
[16] L. D. A. Siebbeles *et al.,* J. Chem. Phys. **107**, 9339 (1997).
[17] K. Itoh, R. C. Munoz, and R. A. Holroyd, J. Chem. Phys. **90**, 1128 (1989).
[18] A. Nahata, A. S. Weling, and T. F. Heinz, Appl. Phys. Lett. **69**, 2321 (1996).
[19] M. van Exter, C. Fattinger, and D. Grischkowsky, Opt. Lett. **14**, 1128 (1989).
[20] J. E. Pedersen and S. R. Keiding, IEEE J. Quantum Electron. **28**, 2518 (1992).
[21] R. Schiller, S. Vass, and J. Mandics, Int. J. Radiat. Phys. Chem. **5**, 491 (1973).
[22] Y. A. Berlin, L. Nyikos, and R. Schiller, J. Chem. Phys. **69**, 2401 (1978).
[23] A. Mozumder, Res. Chem. Intermed. **25**, 243 (1999).
[24] N.-H. Ge *et al.,* Science **279**, 202 (1998).