Summary

This thesis deals with the dynamics of charge carriers in optically excited solids and gases. The manner in which the excited electrons relax their energy and their average velocity is of particular importance in terms of technical applications. For example, graphite and, in particular, carbon nanotubes are potential alternatives to traditional semiconductors as base material for smaller and faster electronic devices. Therefore, electrons in these materials should relax their energy as slowly as possible and maintain an electronic current as long as possible when the driving electric field is switched off. The opposite behavior is required for insulating gases in high-voltage devices: Quasifree electrons should decay quickly and exhibit a low mobility in order to prevent short-circuits.

The conductivity of a material is determined by the electrons with the lowest excitation energies, for instance the electrons around the Fermi energy of a metal. Therefore, THz radiation is particularly sensitive to these charge carriers due to its very low photon energy ($2\pi\hbar \cdot 1\,\mathrm{THz} = 4.1\,\mathrm{meV}$). In this thesis, time-resolved THz spectroscopy is the method of choice in which an ultrashort visible laser pulse excites the charge carriers in the sample. After a variable temporal delay, they are probed by a THz pulse.

Two THz spectrometers were built in the course of this work. One of them is driven by a laser oscillator delivering 10-fs laser pulses with a 10-nJ pulse energy. It is used for the measurements of graphite and carbon nanotubes. However, the optical ionization of gas molecules requires much higher intensities and therefore another spectrometer driven by 20-fs laser pulses with a 1-mJ pulse energy. The THz pulses obtained have a duration of about 100 fs and cover the spectral range from 10 to 25 THz. It should be emphasized that the electric *field* of the THz pulse is detected which allows to determine the instantaneous dielectric function of the excited sample. The extraction of the dielectric function in a pump-probe experiment has to take the THz propagation through the excited sample into account. Corresponding relations have been derived in this work.

In the semimetal graphite, the analysis of the transient dielectric function is based on linear-response theory and yields the temporal evolution of 3 important observables of the excited system: The electronic temperature, the plasma frequency, and the Drude scattering rate. Our data exhibit a twofold dynamics: Within the first 500 fs, the electrons thermalize and lose more than 90 % of their initial excess energy. This is an amazing result since the small Fermi surface of graphite implies that only $\sim 1\,\%$ of all phonon modes can directly dissipate the electronic heat. Our simulations based on the 2-temperature

model reveal that strongly coupled optical phonons with quantum energies of up to 0.2 eV dominate the energy transfer until they have heated up. The remaining slow decay of the electronic temperature is due to the cooling of these hot phonons by other, cold vibrational modes with a 5.4-ps time constant. In addition, the Drude collision rate of the electrons is found to increase by more than 30 % during the first ps after excitation. This is at least one order of magnitude larger than found in comparable experiments on doped semiconductors. Numerical estimates show that the hot phonons can explain a significant part of this rise. Therefore, they might limit the performance of graphite and carbon-nanotube circuits at elevated temperatures and high frequencies. On the other hand, these results show a route to populate certain phonon modes selectively which might be exploited in fields like surface femtochemistry.

In our carbon-nanotube sample, the pump pulse excites all types of tubes which can be metallic or exhibit electronic energy gaps of $\sim 20\,\mathrm{meV}$ or $\sim 1\,\mathrm{eV}$. The THz spectra lack a signature of free charge carriers which clearly indicates that strongly bound excitons are the main product of photoexcitation of the tubes with an energy gap of $\sim 1\,\mathrm{eV}$. We find a spectral feature of enhanced transmission which is caused by the blocking of optical transitions in tubes with an energy gap of $\sim 20\,\mathrm{meV}$. Similar to the dynamics in graphite, the decay of this feature is assigned to the cooling of hot optical phonons by other, cold phonons with a time constant of 1 ps. This is significantly faster than in graphite and points to a stronger anharmonic coupling between the phonon modes of the nanotube. Finally, a small and featureless background of increased absorption exhibits a remarkable optical anisotropy. By using simple geometrical arguments, this can be directly traced back to the localization of charge carriers on a length scale of 100 nm. We can consistently assign the localized excitations to optical transitions between higher-lying intraexcitonic levels in the tubes with energy gaps of $\sim 1\,\mathrm{eV}$. These levels are rapidly depopulated with a time constant of 150 fs due to the emission of optical phonons. These findings may be of great importance for the application of carbon nanotubes in photoconductive and nanoelectronic devices.

In the experiments with optically excited gases, the pump pulse is found to ionize about 1 % of all molecules. The THz response of the quasifree electrons is well described by the Drude model and yields the temporal evolution of the electron density n_e and the Drude collision rate Γ. The electrons in ionized Ar decay on a time scale of more than 1 ns which is an order of magnitude slower than in O_2 and due to a lacking dissipation channel for the kinetic and the binding energy of the electron. However, the electron decay can be accelerated enormously by adding the electron scavenger SF_6 to Ar. In pure SF_6, the free-electron decay occurs with a time constant as short as 12 ps which directly demonstrates the ultrafast extinction of free electrons in SF_6. It allows for a reliable estimate of the electronic temperature of 17000 to 23000 K. The Drude scattering rate Γ was found to increase with the electron density. A model based on the Boltzmann equation which only accounts for collisions between electrons and ions and electrons and neutral particles underestimates the measured collision rates significantly. This and the fact that the electron capture by SF_6 does not increase Γ might point to a dominant contribution of electron-electron scattering

to the current relaxation. The measurements demonstrate that THz spectroscopy provides new and important information on the dynamics of quasifree electrons in gases.