Equilibrium and non-equilibrium spectroscopy on Mo$_{6}$S$_{9-x}$I$_{x}$ nanowires

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Abstract. We studied the electron relaxation of MoSI nanowire thin films via femtosecond pump-probe spectroscopy. The obtained spectra show a combination of absorption bleaching and a structured excited state absorption. A relaxation behaviour involving three characteristic time scales is found and discussed in the framework of previously published band-structure calculations.

1. Introduction
Quasimetallic molecular wires of Mo$_{6}$S$_{9}$I$_{x}$ stoichiometry (MoSI NWs) [1] (see figure 1a) can easily be dispersed in a large number of polar solvents without any covalent functionalisation or surfactants [2]. Debundling into individual NWs is achievable[3], although small bundles (~3nm diameter) are more typical. When co-dissolved with gold nanoparticles they form networks with the nanoparticles acting as junctions between 2-4 MoSI NWs [4], which offers excellent scope for assembly of two- and three-dimensional functional structures.

Non-equilibrium electron dynamics plays a crucial role for the optical and electronic functionalities of any material. We study it with the femtosecond pump-probe technique [5], where a femtosecond laser pulse (the pump) induces a non-equilibrium electron distribution the relaxation behaviour is monitored by scanning the delay of a second pulse (the probe), which measures the change in reflection or transmission. Upon resonant excitation we observe a relaxation behaviour that involves three characteristic timescales.

2. Methods
The synthesis and purification of the Mo$_{6}$S$_{9}$I$_{6}$ NWs used in this study is described elsewhere [6]. Thin oriented films as shown in figure 1b were prepared on a quartz substrate by rubbing.

Pulses of sub-100 fs duration from a regenerative amplifier provided 3.1 eV pump via second harmonic generation and white light continuum probe from 1.2-2.5 eV via self-phase modulation in a Sapphire plate. Both beams are focussed on a 100 µm spot on the sample, with pump energy 100 nJ per pulse.

3. Equilibrium optical properties
Thin oriented films of MoSI NWs show a strongly anisotropic absorption [7]. For light polarised perpendicular to the long NW axis the spectrum is almost structureless, while for parallel polarisation two resonance peaks A$_{1}$ and A$_{2}$ (plus higher energy peaks) are clearly visible at 1.8 and 2.7 eV (see...
figure 1b). Figure 1c shows the difference between the absorption for parallel polarizations and a straight line that approximates the featureless absorption for perpendicular polarization and a fit with four Gaussian peaks. A FWHM of 280 meV and 580 meV is obtained for $A_1$ and $A_2$, respectively. The reasons for the broad resonances can be a multitude of overlapping subbands, mechanical deformation of the nanowires or an intrinsic distribution of transition energies.

For increasing sample temperatures one observes a slight broadening and lowering of the absorption peaks. If the area and centre position of the peaks remain unchanged, the difference between spectra at different temperatures should have a second derivative lineshape. In figure 1c we show the difference between the absorption at 333 and 296 K, together with second derivatives of the Gaussian fit curves corresponding to a FWHM increase of 10 meV for $A_1$ and 6 meV for $A_2$. This illustrates that indeed further broadening of the resonances is the main effect of sample heating.

4. Non-equilibrium optical properties

Figure 2a shows the spectra for different polarisations of pump and probe beams. We will refer to the increased transmission around 1.8 eV as photo-bleaching (PB) and to the reduced transmission elsewhere as photoinduced absorption (PA).
ΔT/T has a lineshape similar to the temperature-induced absorption change, but it is shifted up in energy by almost 100 meV. If trivial sample heating were the only origin of the ΔT/T signal, then its magnitude would correspond to roughly 30 K, which cannot explain the shift of the peak. Therefore there must be a much more substantial redistribution of electrons between those bands that are involved in the A_1 and A_2 absorption peaks. Consequently, the PB peak results from depletion of the A_1 absorption and the PA peaks originate from absorption on photopopulated states.

**Figure 2.** a) Pump-probe spectrum ΔT/T for 10 ps pump-probe delay. Squares: pump polarised along the NW axis, up triangles: perpendicular. Closed signs: probe polarised along the NW axis, open: perpendicular. Dotted line: thermal change in absorbance (sign inverted to compare better with ΔT/T graph) b): ΔT/T for both pump and probe polarized along the NW axis for 300 fs (diamonds), 1 ps (down triangles), 3 ps (open diamonds), and 10 ps (circles). c) Differential transmission traces at probe energies 1.4 eV (dash-dot), 1.9 eV (solid), and 2.1 eV (dash). Inset shows 2.1 eV trace on a longer time scale

From the polarisation dependence of the ΔT/T signal one sees that both excitation and probing is more efficient by a factor 2-3 for light polarised along the NW axis, which confirms the high anisotropy of the sample. Only for the PA below 1.7 eV the signal magnitude is almost independent of the probe polarisation, which hints towards randomly oriented transition dipoles.

The shape of the ΔT/T spectrum changes with pump-probe delay, especially the signal below 1.5 eV completely disappears (figure 2b). Figure 2c shows the temporal evolution of ΔT/T at three selected probe wavelengths. At 1.4 eV the PA decays to 0 with a time constant of approximately 300 fs. A contribution with the same timescale can also be seen for PB and for the PA at 2.1 eV. The latter, however, is dominated by a slower decay with a time constant around 3 ps. This component is absent in the bleaching, therefore it does not represent a recovery of ground state absorption, but rather a redistribution between different excited states’ populations. The population reached after this redistribution does not decay appreciably on a 100 ps time scale (see inset).
5. Discussion and Outlook

We have found a structured pump-probe spectrum and intricate electronic relaxation behaviour with three characteristic timescales, whose physical origin needs further investigation. Recently optical limiting has been demonstrated for MoSi NWs at 2.33 eV and, to a lesser extent, also at 1.17 eV [8]. This is consistent with our pump-probe probe spectra, assuming that the 2.33 eV photons weakly excite A$_2$ (or some other transition via a two-photon process) and instantaneously the PA band above 2 eV is formed. At 1.17 eV excitation of A$_1$ is not efficient and probably a two-photon process is needed to excite the weaker, short-lived PA signal at 1.2 eV. Our findings also imply that there should be a saturable absorber effect around 1.8 eV (and probably also at 2.7 eV). Both non-linear optical effects should have very short switch-on times below 100 fs, and in the spectral region above 1.5 eV maintain their switched-on state for several ns, while below that energy they essentially switch off within less than 1 ps. This provides scope for both very fast switching times as well as some short-term memory.

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