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UV photoexcitation of a dissolved metalloid Ge_9 cluster compound and its extensive ultrafast response.

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Femtosecond pump-probe absorption spectroscopy in tetrahydrofuran solution has been used to investigate the dynamics of a metalloid cluster compound $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ 1. Upon UV photoexcitation, the transients in the near-infrared spectral region showed signatures reminiscent to excess electrons in THF (bound or quasi-free) whereas in the visible part excited state dynamics of the cluster complex dominates.

Recent progress in nanotechnology brings the size range between molecules and the solid state more and more into the focus of various research efforts. In particular, elucidation of the structural and electronic properties, and photodynamics for materials of this size range can have great scientific impact with applications in solar energy harvesting[1], optoelectronic technologies,[2] sensors[3] and biological and medical imaging.[4] Group 14 elements are thereby of particular interest as the size of nanoelectronic components routinely made from them is approaching the sub 10 nanometer range. For example, it was recently shown that field effect transistors can be built using silicon nanowires.[5] Somewhere in the nanometer range, a transition from solid state to molecular compounds occurs for all chemical systems, often associated with large changes to the underlying chemical and physical properties. Sometimes truly novel properties emerge relative to the bulk regime: e.g. visible photoluminescence (PL) can be seen in germanium nanoparticles although elemental germanium shows no PL in the bulk regime.[6] However, nanoparticles in general are obtained as a mixture with a certain size distribution and are thus poorly structurally characterized.[7] Structural information can come from ligand-stabilized “metalloid” cluster compounds, which are ideal model compounds for nanoparticles and whose structures can be accurately determined by X-ray crystallography. Hence, the comprehensive synthesis and structural characterization of a homologous series of such cluster compounds can ultimately lead to a better understanding of the relationship between structure and property of nanoparticles. For the bottom-up synthesis of metalloid cluster compounds, kinetic stabilization e.g. by bulky ligands is necessary in order to arrest metastable intermediates from growing further on their way to the bulk phase. In this respect the metalloid Ge_9 cluster $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **1** is unusual as the germanium core is shielded rather incompletely by the three bulky $Si(SiMe_3)_3$-ligands (Figure 1), leading to a comparatively high secondary reactivity. Growth is arrested but the crystals containing **1** ignite spontaneously when exposed to air. More recently, one of the authors illustrated[8] that **1**, due to its open ligand shell, is a good starting material for subsequent reactions leading to transition metal linked “dimeric” nineteen atomic cluster cores constituting $\{MGe_{18}[Si(SiMe_3)_3]_6\}^X$ compounds (X = -1: M = Cu, Ag, Au; X = 0: M = Zn, Cd, Hg).[9]

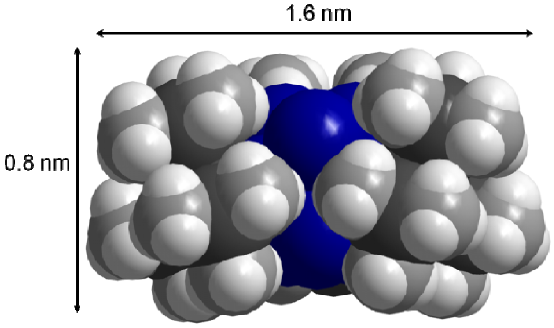

Figure 1. Space filling Model of $Ge_9R_3^-$ **1**; R = $Si(SiMe_3)_3$.

Due to the unusual properties of the metalloid cluster compound $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **1**,[10] further research concerning its physical properties is of great interest and as a result e.g. gas phase measurements of its fragmentation properties as well as redox chemistry of **1** have recently been carried out.[11] Here we present results concerning the optical and electronic properties of **1**. For this we employed a combination of femtosecond transient absorption spectroscopy in the liquid (solution) phase and density functional theory (DFT) calculations.

An absorption spectrum of $[Li(THF)_4][Ge_9\{Si(SiMe_3)_3\}_3])$ in THF solution is shown in Figure 2. It is characterized by a broad, almost featureless UV-absorption. We have performed linear response density functional theory[12] calculations at the PBE[13] level (see methods section in supporting information, SI) of $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **1** to obtain a first order description of these spectra. Though the computational gas-phase spectrum agrees reasonably well with the experimentally obtained UV-Vis spectrum, it is important to also analyze possible effects of the solvent on the absorption spectrum. Therefore, an optimization of **1** in THF using the COSMO[14] implicit solvation model was performed with the

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asymptotically correct exchange LB94 functional[15] in ADF[16] (for more information see methods section in SI). A comparison of the ADF predictions with and without solvent illustrates that solvation does not greatly affect the absorption spectrum near threshold (Figure S1). It should be pointed out, that this result is similar to the metalloid gold cluster $Au_{25}(SH)_{18}^{-}$, in which the optical transitions originated from the atomic orbital contributions in the gold core[17]. Similarly, we find that the lowest-lying, optically-allowed excited states correspond primarily to single excitations from/into these orbitals (Figure S2 and Table S1).

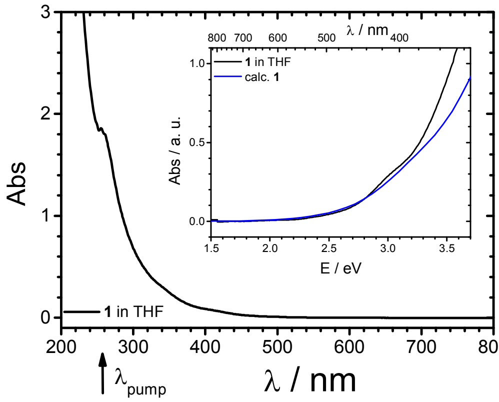

Figure 2. UV-Vis spectra of **1** in THF at a concentration of 2.65 µmol/L. The excitation wavelength of the femtosecond experiments is indicated by an arrow. Inset: Comparison between measured and calculated (blue) spectra (applied spectral width 0.3 eV). Please note that no adjustments of the calculated spectra were made except arbitrary intensity scaling (color online).

Figure 3 shows selected transients acquired upon 258 nm (4.8 eV) pumping and probing at selected visible (Vis) and near-infrared (NIR) wavelengths between 500 and 1580 nm (for more transients and experimental details see Figure S4 and methods section in SI). Typical concentrations of the cluster compound **1** in THF solution were on the order of 1 µmol/L. For better comparison, transients are normalized with respect to their ΔOD values (i.e., the pump-induced change of the absorbance) at a time delay of 10 ps where the time-dependent change of ΔOD is negligible. Around time zero the transient is dominated by a [1+1] absorption of the solvent (see figure S3 in SI as an example).[18] From these considerations, one can conclude that direct ionization of the solvent can be excluded under our experimental conditions.

As can be seen in Figure 3, pump-induced absorption dominates at all probe wavelengths. The corresponding transients all show clearly non-exponential decay. Furthermore, global fitting analysis with fixed time constants for all probe wavelengths failed, indicating that different processes are responsible for the pump-induced absorption at different probe wavelengths. In fact, two time constants are required in order to obtain adequate fits (Table S2). The first time constant is roughly 0.5 ps in the Vis and ~ 1.5 ps in the NIR region. The second time constant fluctuates around the maximal, experimentally accessible delay time of 100 ps. The analysis of the relative amplitudes reveals a maximum value for the second amplitude B (prefactor of the second time constant), which peaks around 1000 nm while decaying to both spectral parts (s. Table S2).

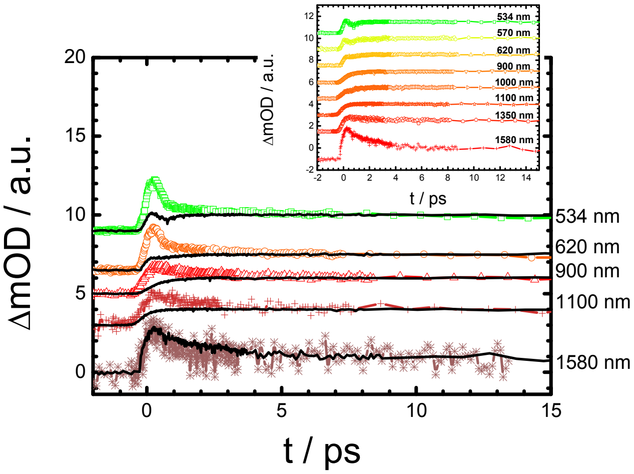

Figure 3. Comparison of selected transients of **1** (symbols) and NaI (lines) in THF after 258 UV photoexcitation (ordinate shifted for better clarity) at selected probe wavelengths (inset: transients of NaI (symbols) in THF at various probe wavelengths, color online).

Given the obtained vertical detachment energy of 3.37 eV from photoelectron spectroscopy in the gas phase[19], fs excitation of **1** at 258 nm (4.8 eV) provides sufficient energy for electron detachment from the solvated cluster anion, where the excess electron is localized on the germanium cluster core according to previous calculations.[20] Considering a liquid environment, transient spectra after UV photoexcitation should thus show either full electron detachment into the solvent, electron transfer to the ligand/THF perimeter and/or dynamics of the neutral germanium cluster. Subsequent dynamics would then be governed by: (i) decay of the neutral radical cluster species formed, (ii) relaxation of the detached “excess” electron interacting with its local environment and also (iii) (geminate) recombination. Overall, the spectral accuracy of 50 to 100 nm achieved over the extended spectral range covered here (from 500 to 1580 nm) only allows for a rough estimation of the underlying processes. The transient spectra (Figure 4) show prominent absorption in the Vis part and lower absorption in the NIR spectral region. Our calculations (Table S1 and Figure S2) indicate numerous transitions to higher excited states in the Vis range of the cluster – either of a state retaining the excess electron in the germanium cluster core or of a cluster radical formed upon electron transfer. We further speculate that additional channels such as ligand elimination are also energetically accessible[11] or they are related to trapped states like $(Li^+/e^-)_{THF}$ contact pairs that peak around 1180 nm.[21] According to our knowledge, no time-resolved studies exist for the latter system, but extensive investigations have been performed for charge transfer of NaI to THF[22-29] that show a similar signature of so-called tight-contact pairs of the form (Na^+, e^-

)$_{THF}$ peaking around 870 nm[30] (full squares in Figure 4). This analogy prompted us to directly compare dynamics of **1** and of NaI in THF (see Figure 3) resulting in similar transients especially towards the NIR. Discrepancies can be attributed to germanium cluster core dynamics. More importantly, the analogy indicates charge transfer from the Ge$_9^-$ core to the ligand/THF perimeter to produce transient Ge$_9^0$ that may eventually form contact pairs with the adjacent electron and surrounding THF entities. To conclude the assignment and in line with previous results[31], transient absorption further in the NIR may be explained as quasi-free solvated electrons.[32]

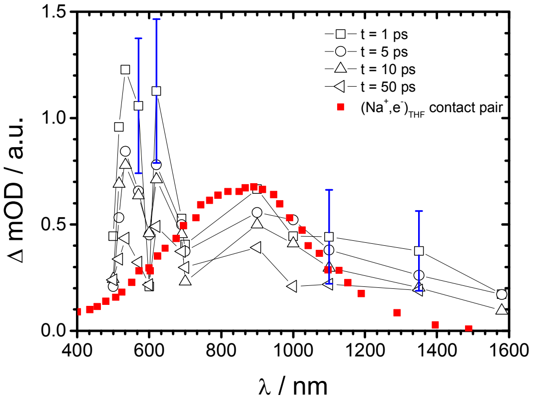

Figure 4. Transient absorption spectra and exemplary error bars (blue; color online) of {Ge$_9$[Si(SiMe$_3$)$_3$]$_3$}$^-$ **1** in THF after 258 UV photoexcitation reconstructed from transients of Figure S4 at delay times as indicated. Superimposed is the steady-state spectrum of tight-bound contact pairs of the form (Na$^+$, e$^-$)$_{THF}$ (red squares; color online) re-digitized from ref. **30** and arbitrarily scaled to match the absorbance of **1** at 900 nm.

Candidates of the longer lasting component (≥ 40 ps) can be regarded as a measure of trapped state(s), e.g. (pre-) solvated electrons or slowly recombining ligand-separated "contact pairs" comprising a transient Ge$_9^0$ and a close lying electron ion contact pair. Intersystem crossing and triplet state formation[33] is unlikely because our calculations do not show suitable energy matches for triplet states under the experimental conditions. Also, luminescence has never been observed in this system – neither in transient nor steady-state measurements.

We explored photodetachment (or related electron transfer) by ultrafast time-resolved spectroscopy, which showed pump-induced broad-band absorption of **1** over the Vis and NIR regime. We assign the observed ample absorption from 500 to 1580 nm to different intermediate species: (i) excited clusters having undergone core-photodetachment plus additional absorption from other excited states of the cluster not involving electron transfer (primarily Vis part) and/or ii) excess electron formation (trapped or quasi-free) upon UV excitation (primarily NIR part). From these findings we suggest that **1** dissolved in THF at room temperature can undergo UV photoexcitation mediated transfer of an electron from the cluster core to either the ligand and/or possibly the solvent environment. Subsequent steps in such a generic detachment scenario will depend on the nature of the ligand and the size of the cluster core. Clearly, further experiments are necessary to establish the influence of solvents and ligands surrounding the cluster core – including their dynamics.[34] To our knowledge, this is the first detailed study into the photodynamics of metalloid group 14 clusters. We hope that these results will stimulate further efforts towards novel photochemical technologies in general and novel detachment systems in particular, incorporating metalloid clusters.

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[32] The room temperature spectrum of “free” solvated electrons in THF is typically very broad and featureless peaking further in the NIR regime around 2120 nm (i.e. beyond our detection window).

[33] The anion is a closed shell system with 40 electrons; thereby having zero spin and a singlet multiplicity (Multiplicity = S + 1; see ref. 20 for more details on the electronic structure).

[34] Currently, **1** is only stable in THF preventing solvent-dependent investigations. On the other hand, ligand variation might now be possible via the rational synthesis described in ref. 10.