XAFS and XEOL of tetramesityldigermene – An electronic structure study of a heavy group 14 ethylene analogue

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Abstract. Digermene, the germanium analogue of ethylene, has a multiple bonding motif that differs greatly from that of alkenes and exhibits no pure σ or π type bonds. The electronic structure of digermenes is difficult to study experimentally due to their reactivity, and is computationally challenging because of their shallow potential energy surfaces. Using X-ray absorption near edge structures at both the germanium K and L edges we have been able to directly probe the unoccupied electronic states, or the lowest unoccupied molecular orbital (LUMO), and LUMO+ etc. in the Ge=Ge bond of tetramesityldigermene. We have demonstrated that the LUMO, LUMO+, etc. are composed of hybrid Ge 4s and 4p orbitals. Additionally, our data suggest that the LUMO exhibits relatively more Ge 4s character, whereas the LUMO+ and LUMO+2 exhibit relatively more Ge 4p character. An X-ray excited optical luminescence study of Ge2Mes4 revealed one broad optical emission band at 620 nm, which is significantly red shifted compared to the known energy gap of this molecular germanium compound.

1. Introduction
Multiple bonding in heavier group 14 elements (E = Si, Ge, and Sn) is of great interest due to the structural, and thus electronic structure (bonding) changes about the central element that take place upon descending the group. The multiple bonding motif in ethylene has been well described by both valence bond (VB) and molecular orbital (MO) theory and involves one C-C σ and one C-C π bond, which is consistent with the experimental planar geometry of the molecule. In contrast, most digermenes (R2Ge=GeR2) are pyramidal at germanium and assume a trans-bent geometry. Digermenes have been investigated intensely since the first reports of their isolation [1-4]. The simplest bonding model consists of two polar dative bonds between two germylene fragments [5]. Digermenes are difficult to study due to their reactivity with many different substrates [6-9]. Computational studies of digermenes are also made challenging because shallow potential energy surfaces result in problematic geometry optimizations and difficulties in studying electronic transitions [7, 9, 10].

To directly study the electronic structure of tetramesityldigermene [Ge2Mes4 (henceforth denoted as 1), Mes=2,4,6-trimethylphenyl], a prototypical digermene, we have measured the germanium K and L-edge X-ray absorption near edge structures (XANES). The Ge K and L3,2 edges of 1 were modeled using the ab initio self-consistent real-space-multiple-scattering (RSMS) code of FEFF9. Additionally 1 was observed to visibly luminesce under soft X-ray excitation and we measured X-ray excited optical luminescence (XEOL) from the sample. Herein, we report the preliminary findings of this study.
2. Experimental

Germanium K-edge XANES for \(1\) was collected on the PNC/XSD BM-20 beam-line at the Advanced Photon Source (APS) at Argonne National Laboratory (see M. Ward et al. Chem. Commun. 2010, 46, 7016 and supporting information for more detail). Ge L\(_{3,2}\)-edge XANES for \(1\) was collected on the SGM beam-line at the Canadian Light Source (CLS) in total electron yield (TEY) and total fluorescence yield (FY) detection modes. Briefly, a powdered sample of \(1\) was prepared on carbon tape in a glove bag attached to the vacuum sample load-lock chamber of the SGM beam-line under nitrogen purge and then immediately put under high vacuum. XEOL spectra of \(1\) were collected on the SGM beam-line using an Ocean Optics QE 65000 spectrophotometer in the UV-vis-NIR (200-900 nm) spectral region. The Ge K and L\(_{3,2}\)-edge XANES were modeled for \(1\) using the \textit{ab initio} self-consistent real-space-multiple-scattering (RSMS) code of FEFF9 [11], and included all electrons of molecular clusters based on the molecular structures as experimentally determined by X-ray crystallography, which are then described by a real space relativistic Green’s function formalism [12].

3. Results and Discussion

The change from planar to trans-pyramidal geometry at the metal center, and thus, from D\(_{2h}\) to C\(_{2h}\) molecular symmetry, upon descending the group has been thoroughly studied for heavier homonuclear group 14 alkene analogues [5,13]. Second order Jahn-Teller mixing of \(\sigma^*\) with \(\pi\) and \(\sigma\) with \(\pi^*\) molecular orbitals leads to a simplified MO picture for heavier group 14 alkenes in which both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are non-bonding, \(n, (b_n)\) and \(n^+, (a_g)\) respectively [13]. The experimental and theoretical Ge K and L\(_{3,2}\)-edge XANES are shown in figure 1 (a) and (b), respectively.

![Figure 1](image-url)

**Figure 1** – Experimental and calculated XANES of \(1\) at the (a) Ge K-edge and (b) Ge L\(_{3,2}\)-edge

Compound \(1\) has trans-bent (\(\theta\)) and twist (\(\delta\)) angles of 33.4° and 2.9° respectively, (figure 2) and a Ge–Ge bond length of 2.2856(8) Å [14]. The theoretical spectrum of the Ge K-edge is in general agreement with the experimental data for \(1\); however, the intensity of the first resonance (LUMO) is diminished and the second and fourth resonances observed in the experimental data appear as shoulders on the third resonance in the calculated spectra. The experimental and theoretical Ge L\(_{3,2}\)-edge XANES spectra of \(1\) are shown in figure 1b. The calculated spectra are in general agreement with the experimental TEY spectrum in the near-edge region; however, FEFF overestimates the white-line intensities at both edges and the L\(_{3}\)-edge multiple-scattering peak at ca. 1226 eV is blue-shifted ~ 2 eV to 1228 eV. FY results (not shown) are consistent with the TEY spectra suggesting a uniform composition with no surface oxidation. Figure 2(a) depicts a simple orbital diagram of \(1\) showing the HOMO-, HOMO, LUMO, and LUMO+. On the basis of the simplified bonding model depicted in figure 2(a), the bonding between Ge centers in \(1\) is very different from that of alkenes which would render a planar structure. Regardless of the bonding schemes used to describe this situation, Ge 4s and
4p orbitals will participate. Thus the unsaturation at the Ge site can be probed using Ge XANES via dipole transitions at both the K and L\textsubscript{3,2} edges, probing unoccupied electronic states, or the Ge 4p and 4s character respectively in the LUMO and LUMO\textsuperscript{+} orbitals. Figure 2(b) shows the Ge K-edge and L\textsubscript{3,2}-edge XANES displayed in energy relative to the threshold of the Ge K-edge and the Ge L\textsubscript{3}-edge (\(E_0 = 0\) eV).

![Orbital Diagram and XANES Spectra](image)

**Figure 2** – (a) Simplified orbital diagram of Ge\textsubscript{2}Mes\textsubscript{4}. (b) XANES at the Ge K and L\textsubscript{3,2} edges calibrated with respect to the threshold energy (\(E_0\)); the first derivative (dy/dx) is also shown.

The first three resonances (figure 2(b), vertical dashed lines) are in phase and the relative intensity of these resonances suggests that the LUMO (first peak) has more Ge 4s character compared to the LUMO\textsuperscript{+}, which is in contrast to alkenes where the LUMO (\(\pi^*\)) has considerable 2p character in comparison to the LUMO\textsuperscript{+} (\(\sigma^*\)). The next three resonances (figure 2(b), vertical solid lines) are more than 10 eV above the threshold, and are out of phase. We tentatively attribute them to EXAFS with multiple scattering, of which the continuum of the p wave and s/d waves are out of phase. The observation of relatively more Ge 4p character in the LUMO\textsuperscript{+} than the LUMO from analysis of the Ge K-edge XANES of 1 is, at first appearance, at odds with previous reports of bonding in digermenes. From previous bonding models one would expect to see more p character in the LUMO since the LUMO is proposed to be a distortion of the \(\pi^*\) orbital via second order Jahn-Teller (SOJT) mixing of \(\pi^*\) with \(\sigma\) whereas the LUMO\textsuperscript{+} is due to SOJT mixing of \(\sigma^*\) with \(\pi\) and subsequent distortion of a \(\sigma\) orbital. Natural bond orbital (NBO) calculations for 1 at the TPSSTPSS/6-31G level, however, show a LUMO with 90.34\% s and 9.66\% p character, which is in agreement with our observations. The Ge L\textsubscript{3}-edge XANES of 1 is also consistent with the NBO analysis as more Ge 4s character is observed in the LUMO than the LUMO\textsuperscript{+}, however, the white-line (LUMO) is very intense suggesting that there is the possibility of some d-orbital participation. A more thorough theoretical treatment of the Ge K and L edges using a density functional based model, such as WIEN 2K, may be able to provide more detail on the degree of orbital participation and mixing in the LUMO and LUMO\textsuperscript{+} peaks observed in the experimental spectra.

Ge\textsubscript{2}Mes\textsubscript{4} (compound 1) also emits visible light upon X-ray excitation. The XEOL spectra for 1, collected with 1200 eV excitation energy, is shown in figure 3. The XEOL spectrum of 1 exhibits a single peak at \(\sim 2\) eV (620 nm). Its energy is considerably red-shifted compared with the known HOMO-LUMO separation of 1. Thus, the observed emission could be due to one of the following effects: (1) solid state effects which influence the energy levels of the HOMO and LUMO bands, narrowing the band gap, (2) formation of excimers involving neighboring molecules, and (3) decomposition of the molecules into Mes\textsubscript{2}Ge: germylene type moiety. More work needs to be carried out to pinpoint its origin.
4. Conclusion
By directly probing the unoccupied electronic states in Ge₂Mes₄ via germanium K and L-edge XANES we have demonstrated that the LUMO is composed of hybridized Ge 4s and 4p atomic orbitals, of which there is more 4s character. The LUMO+1 and LUMO+2 are also composed of hybridized Ge 4s and 4p atomic orbitals, however, they exhibit more 4p character than the LUMO. Ge₂Mes₄ exhibits an optical luminescence emission band at 620 nm which is significantly red shifted when compared to the HOMO-LUMO separation. This shift in the optical emission band may be a result of solid state effects, excimer formation, or decomposition into germynylene fragments.

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Figure 3 – XEOL of Ge₂Mes₄ measured below the Ge L-edge.