Polyphenylsilole multilayers - Insight by X-ray electron spectroscopy and density functional theory

Supporting Information

Katharina Diller,*a,b Yong Ma,c,d Yi Luo,c Francesco Allegretti,a Jianshao Liu,e Ben Zhong Tang,e Nian Lin,*f Johannes V. Barth,a and Florian Klappenberger*a

a Physik Department, E20, Technische Universität München, 85748 Garching, Germany; E-mail: katharina.diller@tum.de, florian.klappenberger@tum.de
b current: Institute for Condensed Matter Physics, École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland
c Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, S-106 91 Stockholm, Sweden.
d current: College of Physics and Electronics, Shandong Normal University, Jinan, Shandong 250014, People’s Republic of China
e Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China.
f Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China;
E-mail: phnlin@ust.hk

I. SIMULATION OF SI L-EDGES

FIG. S 1. Experimental (top) and simulated (bottom) NEXAFS Si L-edge spectra of HPS (left) and TPS (right) multilayers.

The Si L-edge NEXAFS spectra were calculated at the DFT level by using the StoBe program.1 Similarly to the C K-edge the full core hole approximation was used to simulate the spectrum. In contrast to the carbon edge, however, simulations for metal L-edges are more difficult, as the spin-orbit interaction from electrons in the p-orbitals has to be taken into account. In general, the interactions between electrons (and hence molecular orbitals) are non-trivial to predict. Unexpected effects can for example include transitions from p-orbitals to p-levels which normally should be forbidden by dipole selection rules, but become possible in some silicon compounds due to the mixing of p and d orbitals.2 One possibility to treat the complicated structure is the utilization of multiple scattering approaches, as demonstrated, for example, by Chaboy, Benfatto, and Davoli for the Si L-edge of SiO23 and by Xiong and co-workers for hexamethyldisilane.4 On a DFT level, typical simulations of metal L-edges employ time-dependent codes which take into account spin-orbit splitting (as for example done for Fe L-edges in ref.5).

In the present work the focus of the NEXAFS simulations lies in assigning the peaks in the experimental NEXAFS spectrum to the different carbon species. The DFT code StoBe together with the double basis set technique6 has been shown to yield excellent results for carbon edges7,8 and is generally well suited for the simulation of NEXAFS spectra. However, the accurate treatment of spin-orbit interactions is not implemented in the present version of the code. For the Si L-edges shown in Fig. S1 we therefore use an approximation based on experimental values; the spin-orbit split...
2p_{1/2} and 2p_{3/2} components were approximately simulated by the calculated spectra of 2p_{x,y,z} with energy splitting of 0.6 eV and intensity ratio 1:2 (experimental values: 0.63 eV for methylsilane, 0.6 eV for silicon oxide).

II. CALCULATED PARTIAL CHARGES

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>Type</th>
<th>Mulliken / e</th>
<th>NBO / e</th>
<th>Atom No.</th>
<th>Type</th>
<th>Mulliken / e</th>
<th>NBO / e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si</td>
<td>1.064458</td>
<td>1.67131</td>
<td>42</td>
<td>H</td>
<td>0.134604</td>
<td>0.21048</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>-0.402763</td>
<td>-0.34128</td>
<td>43</td>
<td>H</td>
<td>0.135180</td>
<td>0.21020</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>0.066390</td>
<td>-0.04666</td>
<td>44</td>
<td>H</td>
<td>0.125251</td>
<td>0.20666</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>0.066412</td>
<td>-0.04758</td>
<td>45</td>
<td>H</td>
<td>0.125558</td>
<td>0.20670</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>-0.402822</td>
<td>-0.34126</td>
<td>46</td>
<td>H</td>
<td>0.123850</td>
<td>0.20549</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>-0.012638</td>
<td>-0.06796</td>
<td>47</td>
<td>H</td>
<td>0.134604</td>
<td>0.21048</td>
</tr>
<tr>
<td>7</td>
<td>C</td>
<td>-0.109305</td>
<td>-0.18358</td>
<td>48</td>
<td>H</td>
<td>0.135177</td>
<td>0.21020</td>
</tr>
<tr>
<td>8</td>
<td>C</td>
<td>-0.108427</td>
<td>-0.18709</td>
<td>49</td>
<td>H</td>
<td>0.125251</td>
<td>0.20666</td>
</tr>
<tr>
<td>9</td>
<td>C</td>
<td>-0.136717</td>
<td>-0.19815</td>
<td>50</td>
<td>H</td>
<td>0.125557</td>
<td>0.20670</td>
</tr>
<tr>
<td>10</td>
<td>C</td>
<td>-0.136441</td>
<td>-0.19710</td>
<td>51</td>
<td>H</td>
<td>0.123850</td>
<td>0.20549</td>
</tr>
<tr>
<td>11</td>
<td>C</td>
<td>-0.116400</td>
<td>-0.20333</td>
<td>52</td>
<td>H</td>
<td>0.138005</td>
<td>0.20927</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>-0.012634</td>
<td>-0.06825</td>
<td>53</td>
<td>H</td>
<td>0.138322</td>
<td>0.20610</td>
</tr>
<tr>
<td>13</td>
<td>C</td>
<td>-0.109306</td>
<td>-0.18357</td>
<td>54</td>
<td>H</td>
<td>0.126893</td>
<td>0.20677</td>
</tr>
<tr>
<td>14</td>
<td>C</td>
<td>-0.108431</td>
<td>-0.18708</td>
<td>55</td>
<td>H</td>
<td>0.126657</td>
<td>0.20629</td>
</tr>
<tr>
<td>15</td>
<td>C</td>
<td>-0.136717</td>
<td>-0.19816</td>
<td>56</td>
<td>H</td>
<td>0.127854</td>
<td>0.20601</td>
</tr>
<tr>
<td>16</td>
<td>C</td>
<td>-0.136441</td>
<td>-0.19710</td>
<td>57</td>
<td>H</td>
<td>0.138002</td>
<td>0.20927</td>
</tr>
<tr>
<td>17</td>
<td>C</td>
<td>-0.116401</td>
<td>-0.20333</td>
<td>58</td>
<td>H</td>
<td>0.138318</td>
<td>0.20610</td>
</tr>
<tr>
<td>18</td>
<td>C</td>
<td>-0.212758</td>
<td>-0.48262</td>
<td>59</td>
<td>H</td>
<td>0.126891</td>
<td>0.20677</td>
</tr>
<tr>
<td>19</td>
<td>C</td>
<td>-0.162178</td>
<td>-0.18047</td>
<td>60</td>
<td>H</td>
<td>0.126655</td>
<td>0.20629</td>
</tr>
<tr>
<td>20</td>
<td>C</td>
<td>-0.164286</td>
<td>-0.18291</td>
<td>61</td>
<td>H</td>
<td>0.127851</td>
<td>0.20601</td>
</tr>
<tr>
<td>21</td>
<td>C</td>
<td>-0.112957</td>
<td>-0.20182</td>
<td>62</td>
<td>H</td>
<td>0.139731</td>
<td>0.20944</td>
</tr>
<tr>
<td>22</td>
<td>C</td>
<td>-0.114939</td>
<td>-0.20397</td>
<td>63</td>
<td>H</td>
<td>0.138965</td>
<td>0.21219</td>
</tr>
<tr>
<td>23</td>
<td>C</td>
<td>-0.130441</td>
<td>-0.19253</td>
<td>64</td>
<td>H</td>
<td>0.122468</td>
<td>0.20482</td>
</tr>
<tr>
<td>24</td>
<td>C</td>
<td>-0.212724</td>
<td>-0.48261</td>
<td>65</td>
<td>H</td>
<td>0.123361</td>
<td>0.20542</td>
</tr>
<tr>
<td>25</td>
<td>C</td>
<td>-0.162179</td>
<td>-0.18047</td>
<td>66</td>
<td>H</td>
<td>0.121335</td>
<td>0.20433</td>
</tr>
<tr>
<td>26</td>
<td>C</td>
<td>-0.164315</td>
<td>-0.18291</td>
<td>67</td>
<td>H</td>
<td>0.139723</td>
<td>0.20944</td>
</tr>
<tr>
<td>27</td>
<td>C</td>
<td>-0.112956</td>
<td>-0.20182</td>
<td>68</td>
<td>H</td>
<td>0.138967</td>
<td>0.21219</td>
</tr>
<tr>
<td>28</td>
<td>C</td>
<td>-0.114936</td>
<td>-0.20397</td>
<td>69</td>
<td>H</td>
<td>0.122468</td>
<td>0.20482</td>
</tr>
<tr>
<td>29</td>
<td>C</td>
<td>-0.130444</td>
<td>-0.19253</td>
<td>70</td>
<td>H</td>
<td>0.123360</td>
<td>0.20542</td>
</tr>
<tr>
<td>30</td>
<td>C</td>
<td>0.055698</td>
<td>-0.09177</td>
<td>71</td>
<td>H</td>
<td>0.121335</td>
<td>0.20433</td>
</tr>
<tr>
<td>31</td>
<td>C</td>
<td>-0.172416</td>
<td>-0.19756</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>C</td>
<td>-0.116622</td>
<td>-0.18162</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>C</td>
<td>-0.137036</td>
<td>-0.20021</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>C</td>
<td>-0.137846</td>
<td>-0.19772</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>C</td>
<td>-0.118140</td>
<td>-0.20665</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>C</td>
<td>0.055669</td>
<td>-0.09178</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>C</td>
<td>-0.172411</td>
<td>-0.19755</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>C</td>
<td>-0.116624</td>
<td>-0.18162</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>C</td>
<td>-0.137032</td>
<td>-0.20021</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>C</td>
<td>-0.137848</td>
<td>-0.19772</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>C</td>
<td>-0.118140</td>
<td>-0.20665</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIG. S 2. HPS (top) and TPS (bottom): atom numbers as used in Tables I and II.
TABLE S II. Calculated partial charges for TPS

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>Type</th>
<th>Mulliken / e</th>
<th>NBO / e</th>
<th>Atom No.</th>
<th>Type</th>
<th>Mulliken / e</th>
<th>NBO / e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si</td>
<td>0.959972</td>
<td>1.57727</td>
<td>30</td>
<td>H</td>
<td>0.127911</td>
<td>0.21865</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>-0.482917</td>
<td>-0.57805</td>
<td>31</td>
<td>H</td>
<td>0.127913</td>
<td>0.21962</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>0.072684</td>
<td>-0.03392</td>
<td>32</td>
<td>H</td>
<td>0.140816</td>
<td>0.21361</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>0.072694</td>
<td>-0.03134</td>
<td>33</td>
<td>H</td>
<td>0.134177</td>
<td>0.21069</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>-0.482924</td>
<td>-0.58170</td>
<td>34</td>
<td>H</td>
<td>0.126629</td>
<td>0.20759</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>0.017271</td>
<td>-0.07075</td>
<td>35</td>
<td>H</td>
<td>0.125369</td>
<td>0.20705</td>
</tr>
<tr>
<td>7</td>
<td>C</td>
<td>-0.116814</td>
<td>-0.18175</td>
<td>36</td>
<td>H</td>
<td>0.124648</td>
<td>0.20626</td>
</tr>
<tr>
<td>8</td>
<td>C</td>
<td>-0.135418</td>
<td>-0.18830</td>
<td>37</td>
<td>H</td>
<td>0.140815</td>
<td>0.21362</td>
</tr>
<tr>
<td>9</td>
<td>C</td>
<td>-0.137051</td>
<td>-0.19839</td>
<td>38</td>
<td>H</td>
<td>0.134177</td>
<td>0.21067</td>
</tr>
<tr>
<td>10</td>
<td>C</td>
<td>-0.135999</td>
<td>-0.20150</td>
<td>39</td>
<td>H</td>
<td>0.126629</td>
<td>0.20759</td>
</tr>
<tr>
<td>11</td>
<td>C</td>
<td>-0.116680</td>
<td>-0.20405</td>
<td>40</td>
<td>H</td>
<td>0.125369</td>
<td>0.20705</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>0.017274</td>
<td>-0.07074</td>
<td>41</td>
<td>H</td>
<td>0.124647</td>
<td>0.20626</td>
</tr>
<tr>
<td>13</td>
<td>C</td>
<td>-0.116816</td>
<td>-0.18178</td>
<td>42</td>
<td>H</td>
<td>0.138134</td>
<td>0.20951</td>
</tr>
<tr>
<td>14</td>
<td>C</td>
<td>-0.135419</td>
<td>-0.18830</td>
<td>43</td>
<td>H</td>
<td>0.138793</td>
<td>0.21116</td>
</tr>
<tr>
<td>15</td>
<td>C</td>
<td>-0.137050</td>
<td>-0.19841</td>
<td>44</td>
<td>H</td>
<td>0.125745</td>
<td>0.20662</td>
</tr>
<tr>
<td>16</td>
<td>C</td>
<td>-0.135999</td>
<td>-0.20152</td>
<td>45</td>
<td>H</td>
<td>0.126053</td>
<td>0.20679</td>
</tr>
<tr>
<td>17</td>
<td>C</td>
<td>-0.116680</td>
<td>-0.20407</td>
<td>46</td>
<td>H</td>
<td>0.126080</td>
<td>0.20622</td>
</tr>
<tr>
<td>18</td>
<td>C</td>
<td>-0.197215</td>
<td>-0.45963</td>
<td>47</td>
<td>H</td>
<td>0.138316</td>
<td>0.20952</td>
</tr>
<tr>
<td>19</td>
<td>C</td>
<td>-0.162461</td>
<td>-0.18806</td>
<td>48</td>
<td>H</td>
<td>0.138795</td>
<td>0.21116</td>
</tr>
<tr>
<td>20</td>
<td>C</td>
<td>-0.163429</td>
<td>-0.18107</td>
<td>49</td>
<td>H</td>
<td>0.125745</td>
<td>0.20662</td>
</tr>
<tr>
<td>21</td>
<td>C</td>
<td>-0.113223</td>
<td>-0.20601</td>
<td>50</td>
<td>H</td>
<td>0.126053</td>
<td>0.20679</td>
</tr>
<tr>
<td>22</td>
<td>C</td>
<td>-0.112632</td>
<td>-0.20529</td>
<td>51</td>
<td>H</td>
<td>0.126981</td>
<td>0.20622</td>
</tr>
<tr>
<td>23</td>
<td>C</td>
<td>-0.131362</td>
<td>-0.19598</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>C</td>
<td>-0.197226</td>
<td>-0.45057</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>C</td>
<td>-0.162455</td>
<td>-0.18805</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>C</td>
<td>-0.163421</td>
<td>-0.18098</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>C</td>
<td>-0.113225</td>
<td>-0.20602</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>C</td>
<td>-0.112634</td>
<td>-0.20531</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>C</td>
<td>-0.131360</td>
<td>-0.19597</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. S 3. Visualization of the partial charges listed in Tables I and II.
III. SIMULATED CORE LEVEL SHIFTS

TABLE S III. Simulated core level shifts for the carbon atoms in HPS, given with respect to the C-Si atom in the silole core. For the atom numbering see Fig. S2. Broadening of these values results in the spectrum displayed in Fig. 2b.

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>relative core level shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.00 eV</td>
</tr>
<tr>
<td>3</td>
<td>0.91 eV</td>
</tr>
<tr>
<td>12</td>
<td>1.15 eV</td>
</tr>
<tr>
<td>13</td>
<td>0.87 eV</td>
</tr>
<tr>
<td>14</td>
<td>0.85 eV</td>
</tr>
<tr>
<td>15</td>
<td>1.05 eV</td>
</tr>
<tr>
<td>16</td>
<td>1.06 eV</td>
</tr>
<tr>
<td>17</td>
<td>0.96 eV</td>
</tr>
<tr>
<td>24</td>
<td>0.71 eV</td>
</tr>
<tr>
<td>25</td>
<td>1.03 eV</td>
</tr>
<tr>
<td>26</td>
<td>1.06 eV</td>
</tr>
<tr>
<td>27</td>
<td>1.18 eV</td>
</tr>
<tr>
<td>28</td>
<td>1.17 eV</td>
</tr>
<tr>
<td>29</td>
<td>1.16 eV</td>
</tr>
<tr>
<td>36</td>
<td>1.08 eV</td>
</tr>
<tr>
<td>37</td>
<td>0.56 eV</td>
</tr>
<tr>
<td>38</td>
<td>0.56 eV</td>
</tr>
<tr>
<td>39</td>
<td>0.88 eV</td>
</tr>
<tr>
<td>40</td>
<td>0.86 eV</td>
</tr>
<tr>
<td>41</td>
<td>0.68 eV</td>
</tr>
</tbody>
</table>

TABLE S IV. Simulated core level shifts for the carbon atoms in TPS, given with respect to the C-Si atom in the silole core. For the atom numbering see Fig. S2. Broadening of these values results in the spectrum displayed in Fig. 4b.

<table>
<thead>
<tr>
<th>Atom No.</th>
<th>relative core level shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.00 eV</td>
</tr>
<tr>
<td>3</td>
<td>1.45 eV</td>
</tr>
<tr>
<td>12</td>
<td>1.43 eV</td>
</tr>
<tr>
<td>13</td>
<td>1.07 eV</td>
</tr>
<tr>
<td>14</td>
<td>1.12 eV</td>
</tr>
<tr>
<td>15</td>
<td>1.26 eV</td>
</tr>
<tr>
<td>16</td>
<td>1.28 eV</td>
</tr>
<tr>
<td>17</td>
<td>1.17 eV</td>
</tr>
<tr>
<td>24</td>
<td>0.84 eV</td>
</tr>
<tr>
<td>25</td>
<td>1.18 eV</td>
</tr>
<tr>
<td>26</td>
<td>1.17 eV</td>
</tr>
<tr>
<td>27</td>
<td>1.32 eV</td>
</tr>
<tr>
<td>28</td>
<td>1.32 eV</td>
</tr>
<tr>
<td>29</td>
<td>1.30 eV</td>
</tr>
</tbody>
</table>

REFERENCES


