Towards reliable ab initio sublimation pressures
for organic molecular crystals – Are we there yet?

Supporting Information

CTirad Červinka †,*; Gregory Beran ‡

† Department of Physical Chemistry, University of Chemistry and Technology Prague, Technická 5, CZ-166 28 Prague 6, Czech Republic

‡ Department of Chemistry, University of California, Riverside, California 92521, United States

*Corresponding author: cervinkc@vscht.cz
<table>
<thead>
<tr>
<th>Molecule</th>
<th>$T$ (K)</th>
<th>Data set</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>85</td>
<td>Exp.</td>
<td>4.226</td>
<td>5.623</td>
<td>5.845</td>
<td>90.41</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>DFT@DFT$^b$</td>
<td>3.99</td>
<td>6.89</td>
<td>5.19</td>
<td>70.1</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>HMBI(C,A)@DFT$^c$</td>
<td>4.15</td>
<td>7.18</td>
<td>5.39</td>
<td>69.8</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>HMBI(C,H)@DFT$^d$</td>
<td>4.21</td>
<td>7.30</td>
<td>5.45</td>
<td>69.5</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>HMBI(M,A)@HMBI$^e$</td>
<td>4.05</td>
<td>5.47</td>
<td>5.76</td>
<td>91.1</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>HMBI(C,A)@HMBI$^f$</td>
<td>4.11</td>
<td>5.53</td>
<td>5.96</td>
<td>91.2</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>HMBI(C,H)@HMBI$^g$</td>
<td>4.14</td>
<td>5.56</td>
<td>6.12</td>
<td>91.3</td>
</tr>
<tr>
<td>Methanol</td>
<td>122</td>
<td>Exp.</td>
<td>4.647</td>
<td>4.929</td>
<td>9.040</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>DFT@DFT$^b$</td>
<td>5.03</td>
<td>4.42</td>
<td>9.08</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>HMBI(C,A)@DFT$^c$</td>
<td>4.96</td>
<td>4.41</td>
<td>8.99</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>HMBI(C,H)@DFT$^d$</td>
<td>4.97</td>
<td>4.41</td>
<td>9.00</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>HMBI(M,A)@HMBI$^e$</td>
<td>4.82</td>
<td>4.50</td>
<td>8.90</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>HMBI(C,A)@HMBI$^f$</td>
<td>4.85</td>
<td>4.52</td>
<td>8.98</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>HMBI(C,H)@HMBI$^g$</td>
<td>5.00</td>
<td>4.55</td>
<td>9.14</td>
<td>90.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>298</td>
<td>Exp.</td>
<td>7.287</td>
<td>9.200</td>
<td>6.688</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>DFT@DFT$^b$</td>
<td>7.34</td>
<td>9.33</td>
<td>6.72</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>HMBI(C,A)@DFT$^c$</td>
<td>7.49</td>
<td>9.52</td>
<td>6.88</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>HMBI(C,H)@DFT$^d$</td>
<td>7.72</td>
<td>9.85</td>
<td>7.10</td>
<td>90.0</td>
</tr>
<tr>
<td>Imidazole</td>
<td>298</td>
<td>Exp.</td>
<td>7.326</td>
<td>4.997</td>
<td>9.556</td>
<td>122.68</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>DFT@DFT$^b$</td>
<td>7.35</td>
<td>5.17</td>
<td>9.64</td>
<td>119.1</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>HMBI(C,A)@DFT$^c$</td>
<td>7.53</td>
<td>5.34</td>
<td>9.74</td>
<td>116.7</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>HMBI(C,H)@DFT$^d$</td>
<td>7.66</td>
<td>5.53</td>
<td>9.78</td>
<td>113.3</td>
</tr>
</tbody>
</table>

$^a$ Temperature at which the experiment was performed.

$^b$ Structure optimized with respect to static cohesive energy only, obtained at the PBE-D3(BJ)/PAW level.

$^c$ Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for PBE-D3(BJ)/PAW geometries and phonons, CCSD(T)/CBS+Amoeba HMBI refinement of the cohesive energy.

$^d$ Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for PBE-D3(BJ)/PAW geometries and phonons, CCSD(T)/CBS+pHF HMBI refinement of the cohesive energy.

$^e$ Structure optimized with respect to static cohesive energy only, obtained at the HMBI MP2/avtz+Amoeba level.

$^f$ Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for MP2/avtz+Amoeba HMBI geometries and phonons, with CCSD(T)/CBS+Amoeba HMBI refinement of the cohesive energy.
Structure optimized with respect to quasi-harmonic Helmholtz energy, obtained for MP2/avtz+Amoeba HMBI geometries and phonons, with CCSD(T)/CBS+\textit{pHF} HMBI refinement of the cohesive energy.

**FIGURE S1**
Comparison of percentage deviations of calculated vibrational frequencies for crystalline ethane–lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies measured at 20 K culled from refs.\(^1,2\) Diamonds stand for quasi-harmonic frequencies calculated at the predicted unit-cell volumes at 20 K, circles stand for quasi-harmonic frequencies calculated at the experimental unit-cell volumes at 20 K, and squares stand for harmonic frequencies calculated for the unit-cell optimized with respect to its electronic energy only. Various shades of blue and red are used only to highlight the differences among the individual data sets.

**FIGURE S2**
Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline ethane. Data based on PBE-D3(BJ) geometries/phonons and Amoeba embedding unless stated otherwise. Experimental \(V_m\) and \(C_p\) culled from refs.\(^1,2\) and ref.\(^3,4\), respectively.
FIGURE S3
Comparison of percentage deviations of calculated vibrational frequencies for crystalline methanol – lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies measured at 20 K culled from refs.5–6. Diamonds stand for quasi-harmonic frequencies calculated at the predicted unit-cell volumes at 20 K, circles stand for quasi-harmonic frequencies calculated at the experimental unit-cell volumes at 20 K, and squares stand for harmonic frequencies calculated for the unit-cell optimized with respect to its electronic energy only. See our previous work7 for more details. Various shades of blue and red are used only to highlight the differences among the individual data sets.

FIGURE S4
Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline methanol. Data based on PBE-D3(BJ) geometries/phonons and Amoeba embedding unless stated otherwise. Experimental $V_m$ and $C_p$ culled from refs.8–12 and ref.13, respectively.
FIGURE S5
Comparison of percentage deviations of calculated vibrational frequencies for crystalline benzene – lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies culled from refs. 14-16.

FIGURE S6
Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline benzene. Data based on PBE-D3(BJ) geometries and Amoeba embedding unless stated otherwise. Experimental $V_m$ and $C_p$ culled from refs. 17-22 and ref. 23, respectively.
FIGURE S7
Comparison of percentage deviations of calculated vibrational frequencies for crystalline imidazole – lattice modes (left) and intramolecular modes (right) calculated at various levels of theory. Experimental frequencies culled from refs.24-26

FIGURE S8
Comparison of molar volumes (left) and isobaric heat capacities (right) calculated at various levels of theory for crystalline imidazole. Data based on PBE-D3(BJ) geometries and Amoeba embedding unless stated otherwise. Experimental \( V_m \) and \( C_p \) culled from refs.27-32 and ref. 33, respectively.

References for the SI