Ionization Energies of Fat-Soluble Vitamins in Gas Phase:
Theoretical Study

Fatemeh Abyar, Hossein Farrokhpour *

Table S1. Calculated Hartree-Fock (HF) energies of molecular orbitals of vitamins D2, D3 and K (MK-1) and the dominant natural bonding orbital contributions in them.

Table S2. Calculated Hartree-Fock (HF) energies of molecular orbitals of vitamins E and the dominant natural bonding orbital contributions in them.

Table S3. Calculated Hartree-Fock (HF) energies of molecular orbitals of vitamins A and its derivatives and the dominant natural bonding orbital contributions in them.

Fig. S1: The canonical molecular orbitals of (a) conformer2 of vitamin D2, (b) and (c) are vitamin D3 conformer2 and conformer 3, respectively

Fig. S2: The canonical molecular orbitals of E vitamin included of (a) α-tocopherol b) β-tocopherol c) γ-tocopherol.

Fig. S3: The canonical molecular orbitals of E vitamin included of (a) δ-tocopherol b) tocopherol and c) K (MK-1) vitamin

Fig. S4: The canonical molecular orbitals of A vitamin (a) conformer1 (b) conformer2.

Fig. S5: The canonical molecular orbitals of all-trans retinoic acid (a) conformer1 (b) conformer2 and c) 13-cis retinoic acid.
<table>
<thead>
<tr>
<th>Vitamin D₂</th>
<th>E (eV)</th>
<th>Type$^a$</th>
<th>Main characters</th>
</tr>
</thead>
<tbody>
<tr>
<td>-7.75</td>
<td>$\pi$ (HOMO)</td>
<td>(38.9%)$\pi$(C9- C15); (37.6%)$\pi$(C 17- C19); (9.4%)$\pi$(C23- C29)</td>
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<td>-9.21</td>
<td>$\pi$</td>
<td>(80.8%)$\pi$(C14- C16)</td>
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<td>-9.71</td>
<td>$\pi$</td>
<td>(70.1%)$\pi$(C23- C29); (10.7%)$\pi$(C 9- C15)</td>
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<tr>
<td>-10.98</td>
<td>$\pi$</td>
<td>(19.9%)$\pi$(C17- C19); (9.9%)$\pi$(C 9- C15) ; (11.3%)$\sigma$(C 2- C 4); (7.2%)$\sigma$(C 2-C3)</td>
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<tr>
<td>-11.20</td>
<td>$\sigma$</td>
<td>(10.1%)$\pi$(C17- C19); (9.1%)$\pi$(C 9- C15) ; (15.5%)$\sigma$(C2-C3); (6%)$\sigma$(C 5-C3); (5.6%)$\sigma$(C 7-C11); (5%)$\sigma$(C 8-C14)</td>
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<table>
<thead>
<tr>
<th>Vitamin D₃</th>
<th>E (eV)</th>
<th>Type$^a$</th>
<th>Main characters</th>
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<td>-7.52</td>
<td>$\pi$ (HOMO)</td>
<td>(40.4%) $\pi$ (C9- C15); (37.2%) $\pi$ ( C 18- C20)+ (8.9%) $\pi$ ( C 24- C28)</td>
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<tr>
<td>-9.67</td>
<td>$\pi$</td>
<td>(10.9%) $\pi$ (C9- C15); (69.6%) $\pi$ ( C 24- C28)</td>
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<tr>
<td>-10.71</td>
<td>$\pi$</td>
<td>(10.3%) $\pi$ (C18- C20); (12%) $\sigma$(C2- C4);(7.6%) $\sigma$(C 8-C13);(14.5%) $\sigma$(C 2- C3); (5.5%) $\sigma$(C7- C11)</td>
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<td>-11.05</td>
<td>$\pi$</td>
<td>(7.4%) $\sigma$(C 2- C3);(19.9%) $\pi$(C18- C20); (14.7%) $\pi$(C 9- C15)</td>
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</tr>
<tr>
<td>-11.42</td>
<td>$\sigma$</td>
<td>(11.5%) $\sigma$(C 8- H37); (16.8%) $\sigma$(C 2- C 7); (9.1%) $\sigma$(C2-C4); (5.4%) $\sigma$( C 11- H42); (5.8%) $\sigma$(C 4- C 6); (8.7%) $\sigma$(C 3- C 5); (6.8%) $\sigma$(C 3- C 8)</td>
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<table>
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<tr>
<th>Vitamin K (MK-1)</th>
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<th>Main characters</th>
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<td>$\pi$ (HOMO)</td>
<td>(75.8%) $\pi$ (C10- C14)</td>
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<td>-9.66</td>
<td>$\pi$</td>
<td>(36.9%) $\pi$ (C13- C16);(32.2%)$\pi$(C12- C15);(17.3%)$\pi$* ( C6- C7)</td>
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<tr>
<td>-9.71</td>
<td>$\pi$*</td>
<td>(36.9%) $\pi$(C13- C16);(32.2%)$\pi$(C12- C15);(17.3%)$\pi$ ( C6- C7); (36.9%) $\pi$ (C13- C16) ; (36.9%) $\pi$ (C3- C4)</td>
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<td>-10.28</td>
<td>$\pi$</td>
<td>(8.6%) $\pi$ (O 1- C 8); (8.4%) $\pi$ (O 2- C 9); (7.4%) $\pi$ (C 6- C 7); (45.1%)$\pi$ ( C3- C4)</td>
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</tr>
<tr>
<td>-11.57</td>
<td>$\pi$</td>
<td>(24.7%) LP (O 1); (23.6%) LP (O 2); (6.7%) $\sigma$(C 6- C 7);(7.8%)$\sigma$( C3- C8); (6.6%) $\sigma$(C 7- C 9); (7%)$\sigma$( C4- C9)</td>
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</table>

$^a$ Shows the type of molecular orbital in the neutral molecule.
<table>
<thead>
<tr>
<th>E (eV)</th>
<th>Type$^a$</th>
<th>Main characters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>π (HOMO)</td>
<td>(27.5%)π(C19- C24); (29.8%)π(C13- C16); (10.6%)LP (2) O1; (8.6%)LP (2) O2; (16.2%)π*(C21- C26)</td>
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<tr>
<td>-7.87</td>
<td></td>
<td>(11%)π*(C19- C24); (12.3%)π*(C13- C164); (45.9%)π (C21- C26); (15.8%)π(C19- C24); (9.8%)π(C13- C16)</td>
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<td>-9.12</td>
<td>π</td>
<td>(18.1%)σ(C7- C8); (7.4%)σ(C 3- C 5); (12.4%)σ(C4- C6); (6.8%)σ(C 6- C 8); (5%)σ(C 9- C 5); (5.7%)σ(C 10- H40); (11.3%)σ(C 3- C 4)</td>
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<td>-11.25</td>
<td>σ</td>
<td>(18.4%)σ(C14- C15); (16%)σ(C 7- C 10); (10.8%)σ(C11-C14); (5.4%)σ(C22-H58); (10.4%)σ(C10- C11); (6.2%)σ(C15- C22); (5%)σ(C 7- C 18); (5.6%)σ(C17- H50)</td>
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<td>-11.55</td>
<td>σ</td>
<td>(19.9%)σ(C17- C15); (11.2%)σ(C 20- C 23); (10.6%)σ(C23- C25); (5.6%)σ(C 25- C27); (5.1%)σ(C17- C20); (8.5%)σ(C14- H48)</td>
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<td>π (HOMO)</td>
<td>(32.7%)π(C19- C24); (23.7%)π(C12- C14); (10.0%)LP (2) O1; (8.5%)LP (2) O2; (14.4%)π*(C20- C22)</td>
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<td>-8.39</td>
<td>π</td>
<td>(11.2%)π*(C19- C24); (17%)π*(C12- C14); (42.9%)π (C20- C22); (%π(C19- C24); (8.9%)π(C12- C14)</td>
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<td>σ</td>
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<td>σ</td>
<td>(16.1%)σ(C26- C25); (15.4%)σ(C 16- C 18); (10.5%)σ(C21-C25); (11.1%)σ(C16- H52); (6.6%)σ(C26- C30); (13.1%)σ(C18- C21)</td>
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<td>-11.34</td>
<td>σ</td>
<td>(17.6%)σ(C16- C15); (14.9%)σ(C 7- C10); (9.3%)σ(C13- C15); (7.4%)σ(C 7- C17); (5.3%)σ(C16- C23); (12%)σ(C13- C10)</td>
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<td>π (HOMO)</td>
<td>(34.1%)π(C19- C24); (21.4%)π(C13- C16); (10.1%)LP (2) O1; (8.2%)LP (2) O2; (14.2%)π*(C20- C22)</td>
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<td>-8.66</td>
<td>π</td>
<td>(40.6%)π(C21- C26); (11.5%)π (C19- C24); (21.7%)π(C13- C16); (6.6%)π*(C19- C24); (7.8%)π*(C13- C16)</td>
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<td>-11.30</td>
<td>σ</td>
<td>(10.9%)σ(C7- C8); (10.5%)σ(C 3- C 5); (8.5%)σ(C4- C6); (6.6%)σ(C 7- C10); (5.6%)LP (1) O1; (5.5%)σ(C4- C3)</td>
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<td>-11.32</td>
<td>σ</td>
<td>(15.9%)σ(C23- C25); (15.4%)σ(C 15- C 17); (13.2%)σ(C17-C20); (11.1%)σ(C15- H51); (10.6%)σ(C20- C23); (6.7%)σ(C25- C29)</td>
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<td>σ</td>
<td>(13.4%)σ(C14- C15); (10.0%)σ(C 7- C10); (9.8%)σ(C10- C11); (6.8%)σ(C 7- C18); (6.2%)σ(C11- C14)</td>
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<td>π (HOMO)</td>
<td>(12.6%)π(C20- C24); (24.8%)π(C22- C26); (34.8%)π*(C15- C16); (10.6%)LP (2) O1; (8.5%)LP (2) O2</td>
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<td>π</td>
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<td>σ</td>
<td>(15.8%)σ(C23- C25); (14.9%)σ(C 14- C 17); (13.2%)σ(C17- C19); (11.1%)σ(C 14- H51); (10.4%)σ(C 19- C23); (10.4%)σ(C 25- C29)</td>
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<td>-11.31</td>
<td>σ</td>
<td>(11.9%)σ(C7- C9); (8.9%)σ(C 14- C 13); (8.5%)σ(C11- C13); (8%)σ(C 7- C8); (8%)σ(C 9- C11)</td>
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<tr>
<td></td>
<td>$\sigma$</td>
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<td>------------------------------------------------------------------</td>
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<tr>
<td>δ-tocopherol</td>
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<td>(8.7%)$\sigma$(C5- C3); (7.8%)$\sigma$(C7- C8); (7.2%)$\sigma$(C14- C13); (7%)$\sigma$(C4- C6); (6.8%)$\sigma$(C3- C4); (5.6%)$\sigma$(C9- C11); (5.1%)$\sigma$(C6- C8)</td>
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<td></td>
<td>-7.82</td>
<td>(32.6%)$\pi$(C15- C16); (27.6%)$\pi$(C23- C26); (11.4%)LP (2) O1; (8.4%)LP (2) O2; (13.0%)$\pi^*$ (C22- C25)</td>
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<td>-8.86</td>
<td>(50.2%)$\pi$(C22- C25); (11.3%)$\pi$(C23- C26); (12.0%)$\pi^<em>$ (C23- C26); (9.3%)$\pi$ (C15- C16); (9.4%)$\pi^</em>$ (C15- C16)</td>
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<tr>
<td>δ-tocopherol</td>
<td>-11.30</td>
<td>(16.6%)$\sigma$(C21- C24); (16.4%)$\sigma$(C12- C17); (13.3%) $\sigma$ (C17- C19); (11.2%)$\sigma$(C19- C21); (11.2%)$\sigma$(C12- H45); (7%) $\sigma$ (C24- H28)</td>
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<td>-11.32</td>
<td>(16.1%)$\sigma$(C9- C5); (15.3%)$\sigma$(C12- C13); (11%) $\sigma$ (C10- C13); (9.3%)$\sigma$(C9- C10); (6.5%)$\sigma$(C12- C20)</td>
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<tr>
<td></td>
<td>-11.39</td>
<td>(12.5%)$\sigma$(C5- C8); (10.2%)$\sigma$(C3- C7); (9.7%) $\sigma$ (C4- C6); (9%)$\sigma$(C3- C4); (6.7%)$\sigma$(C6- C8); (6%)$\sigma$(C5- H32)</td>
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</table>

- Shows the type of molecular orbital in the neutral molecule.
<table>
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<th>Orbital</th>
<th>Assignment</th>
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<td>π(HOMO)</td>
<td>(27.8%)π(C13- C15); (22.2%)π(C16- C17); (20.4%)π(C10- C12); (11.1%)π(C18- C20); (9.2%)π(C5- C7)</td>
</tr>
<tr>
<td>Conformer I</td>
<td>-8.67</td>
<td>π</td>
<td>(45.4%)π(C5- C7); (14.9%) π(C18- C20); (11.6%)π(C16- C17); (7.5%)π(C10- C12)</td>
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<tr>
<td>Conformer I</td>
<td>-9.87</td>
<td>π</td>
<td>(17.7%)π(C5- C7); (30.3%)π(C18- C20); (14.6%)π(C13- C15); (15.1%)π(C10- C12)</td>
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<tr>
<td>Conformer I</td>
<td>-11.11</td>
<td>π</td>
<td>(9.8%)π(C13- C15); (14.6%)π(C18- C20); (10.3%)π(C16- C17); (29.4%)π(C10- C12)</td>
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<tr>
<td>Conformer I</td>
<td>-11.49</td>
<td>σ</td>
<td>(18%)σ(C2- C3); (10.1%)σ(C6- C7); (7.8%)σ(C10- C5); (12.4%)σ(C4- H24); (5.7%)σ(C2- C5)</td>
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<td>π(HOMO)</td>
<td>(27.6%)π(C13- C15); (22.0%)π(C16- C17); (20.5%)π(C10- C12); (11.0%)π(C18- C20); (9.5%)π(C5- C7)</td>
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<td>Conformer II</td>
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<td>π</td>
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<td>π</td>
<td>(9.5%)π(C13- C15); (14.3%)π(C18- C20); (10.4%)π(C16- C17); (29.6%)π(C10- C12)</td>
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<tr>
<td>Conformer II</td>
<td>-11.49</td>
<td>σ</td>
<td>(18.2%)σ(C2- C3); (10.1%)σ(C6- C7); (7.8%)σ(C10- C5); (12.5%)σ(C4- H24); (5.8%)σ(C2- C5)</td>
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<tr>
<td>all-trans-retinoic acid</td>
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<td>-8.97</td>
<td>π</td>
<td>(45.4%)π(C6- C8); (14.9%) π(C17- C18); (11.6%)π(C19- C21)</td>
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<td>Conformer I</td>
<td>-11.32</td>
<td>π</td>
<td>(17.7%)π(C19- C21); (30.3%)π(C11- C13); (14.6%)π(C6- C8); (15.1%)π(C14- C16)</td>
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<td>π</td>
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<td>Conformer II</td>
<td>-11.57</td>
<td>π</td>
<td>(32%)π(C13- C11); (16.4%)π(C19- C21); (11.6%)π(C14- C16); (8.9%)π(C17- C18)</td>
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<td>Conformer II</td>
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<td>σ</td>
<td>(17.7%)σ(C4- C3); (11%)σ(C8- C7); (7.1%)σ(C3- C6); (12.3%)σ(C5- H26); (8.4%)σ(C6- C11); (5.7%)σ(C8- C12)</td>
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<td>13-cis-retinoic acid</td>
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<td>Conformer</td>
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<td>(28%)π(C14- C16); (22%)π(C11- C13); (20.1%)π(C17- C18); (11%)π(C6- C8); (7.5%)π(C19- C21)</td>
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<td>Conformer</td>
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<td>π</td>
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<tr>
<td>Conformer</td>
<td>-11.20</td>
<td>π</td>
<td>(32.1%)π(C19- C21); (17%)π(C11- C13); (14.5%)π(C6- C8); (11.5%)π(C14- C16)</td>
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<tr>
<td>-11.57</td>
<td>$\pi$</td>
<td>$(24.7%)\pi(C11- C13); (16.7%)\pi(C19- C21); (9.2%)\pi(C14- C16); (8.6%)\pi(C17- C18); (5.1%)\pi(C3- C6)$</td>
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<tr>
<td>-11.82</td>
<td>$\sigma$</td>
<td>$(18.2%)\sigma(C4- C3); (9.4%)\sigma(C8- C7); (7%)\sigma(C6- C11); (12.2%)\sigma(C5- H26); (6%)\sigma(C11- C13); (5.5%)\sigma(C9- H30)$</td>
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