

Supporting Information

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1 Second order derivative of dispersion correction terms with respect to a and b

The dispersion correction terms are

$$E_{\text{dis}}^{\text{D2}} = -s_6 \sum_{A,B} \frac{C_6^{AB}}{R_{AB}^6} f_{d,6}^{\text{D2}}(R_{AB}), \quad (1)$$

where the damping function $f_{d,6}^{\text{D2}}(R_{AB})$ is

$$f_{d,6}^{\text{D2}}(R_{AB}) = \frac{1}{1 + \exp(-d(R_{AB}/s_R R_{AB}^0) - 1)}. \quad (2)$$

Before the calculation of the second order derivative of the dispersion correction terms, it is useful to obtain these derivatives:

$$\frac{\partial f_{d,6}^{\text{D2}}(R_{AB})}{\partial R_{AB}} = \frac{d}{s_R R_{AB}^0} (f_{d,6}^{\text{D2}})^2 \exp\left[-\frac{dR_{AB}}{s_R R_{AB}^0} - 1\right] \quad (3)$$

$$\frac{\partial R_{AB}}{\partial a} = \frac{\Delta R_{AB,\{a\}}}{R_{AB}} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \quad (4)$$

$$\frac{\partial \exp\left[-\frac{dR_{AB}}{s_R R_{AB}^0} - 1\right]}{\partial a} = -\frac{d}{s_R R_{AB}^0} \exp\left[-\frac{dR_{AB}}{s_R R_{AB}^0} - 1\right] \frac{\Delta R_{AB,\{a\}}}{R_{AB}} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \quad (5)$$

The first order derivative of the dispersion correction terms are

$$\frac{\partial E_{\text{dis}}^{\text{D2}}}{\partial a} = \sum_{A,B} s_6 C_6^{AB} \left(\frac{d}{s_R R_{AB}^0} (f_{d,6}^{\text{D2}})^2 \exp\left[-\frac{dR_{AB}}{s_R R_{AB}^0} - 1\right] \frac{1}{R_{AB}^7} - 6 \frac{f_{d,6}^{\text{D2}}}{R_{AB}^8} \right) \Delta R_{AB,\{a\}} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a}. \quad (6)$$

Therefore, the second order derivative is

$$\begin{aligned} \frac{\partial^2 E_{\text{dis}}^{\text{D2}}}{\partial a \partial b} = & \sum_{A,B} s_6 C_6^{AB} \left[\left(\frac{d}{s_R R_{AB}^0} (f_{d,6}^{\text{D2}})^2 \exp\left[-\frac{dR_{AB}}{s_R R_{AB}^0} - 1\right] \frac{1}{R_{AB}^7} - 6 \frac{f_{d,6}^{\text{D2}}}{R_{AB}^8} \right) \frac{\partial \Delta R_{AB,\{b\}}}{\partial b} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \right. \\ & \left. + \frac{\partial}{\partial b} \left(\frac{d}{s_R R_{AB}^0} (f_{d,6}^{\text{D2}})^2 \exp\left[-\frac{dR_{AB}}{s_R R_{AB}^0} - 1\right] \frac{1}{R_{AB}^7} - 6 \frac{f_{d,6}^{\text{D2}}}{R_{AB}^8} \right) \Delta R_{AB,\{a\}} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \right], \quad (7) \end{aligned}$$

and, finally, we obtain

$$\begin{aligned}
\frac{\partial^2 E_{\text{dis}}^{\text{D2}}}{\partial a \partial b} = & - \sum_A \sum_B s_6 C_6^{AB} \left[\left(\frac{d}{s_R R_{AB}^0} (f_{d,6}^{\text{D2}})^2 \exp\left[-\frac{d R_{AB}}{s_R R_{AB}^0} - 1\right] \frac{1}{R_{AB}^7} \right. \right. \\
& - 6 \frac{f_{d,6}^{\text{D2}}}{R_{AB}^8} \left. \right) \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \frac{\partial \Delta R_{AB,\{b\}}}{\partial b} \\
& + \frac{2d}{s_R R_{AB}^0} \exp\left[-\frac{d R_{AB}}{s_R R_{AB}^0} - 1\right] \frac{f_{d,6}^{\text{D2}}}{R_{AB}^7} \frac{\partial f_{d,6}^{\text{D2}}}{\partial b} \Delta R_{AB,\{a\}} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \\
& + \frac{d}{s_R R_{AB}^0} \frac{\partial \left(\exp\left[-\frac{d R_{AB}}{s_R R_{AB}^0} - 1\right] \right)}{\partial b} \frac{(f_{d,6}^{\text{D2}})^2}{R_{AB}^7} \Delta R_{AB,\{a\}} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \\
& - 7 \frac{d}{s_R R_{AB}^0} (f_{d,6}^{\text{D2}})^2 \exp\left[-\frac{d R_{AB}}{s_R R_{AB}^0} - 1\right] \frac{1}{R_{AB}^9} \Delta R_{AB,\{a\}} \Delta R_{AB,\{b\}} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \frac{\partial \Delta R_{AB,\{b\}}}{\partial b} \\
& - 6 \frac{\partial f_{d,6}^{\text{D2}}}{\partial b} \frac{\Delta R_{AB,\{a\}}}{R_{AB}^8} \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \\
& + 48 \frac{f_{d,6}^{\text{D2}}}{R_{AB}^{10}} (\Delta R_{AB,\{a\}}) (\Delta R_{AB,\{b\}}) \frac{\partial \Delta R_{AB,\{a\}}}{\partial a} \frac{\partial \Delta R_{AB,\{b\}}}{\partial b} \left. \right]. \tag{8}
\end{aligned}$$

2 Active Raman modes for vitamin C calculated with FMO-RHF and full RHF

Table S1: Frequencies ω (cm^{-1}) and Raman activities J ($\text{\AA}^4/\text{u}$) for the active Raman modes in vitamin C, computed with FMO-RHF and RHF. This table corresponds to the Raman spectra shown in Figure 2-(a).

FMO-RHF		RHF	
ω	J	ω	J
3796.0	13.124242	3812.0	22.881046
3839.0	18.177326	3921.0	19.352103
3887.0	24.841284	3950.0	19.284676
3924.0	29.497006	3997.0	27.837468
3997.0	31.307158	4012.0	16.499102
4039.0	17.500793	4022.0	19.856159
4072.0	17.513815	4089.0	23.075891
4121.0	12.105306	4168.0	18.546572
4175.0	21.719004	4189.0	19.457739
4227.0	41.916000	4228.0	45.030597

3 Active Raman modes for vitamin E calculated with FMO-RHF and full RHF

Table S2: Frequencies ω (cm^{-1}) and Raman activities J ($\text{\AA}^4/\text{u}$) for the active Raman modes in vitamin E, computed with FMO-RHF and RHF. This table corresponds to the Raman spectra shown in Figure 2-(b).

FMO-RHF		RHF	
ω	J	ω	J
1644.1	17.158430	1644.1	17.092657
3165.2	15.832064	3165.2	16.866146
3174.4	14.007579	3175.5	14.419831
3203.1	113.408707	3203.1	113.148732
3234.9	29.632990	3234.9	28.869345
3251.3	61.426562	3251.3	64.396838
3273.9	17.149296	3272.8	17.082810
3284.1	21.705003	3282.1	19.136445
3336.4	10.644530	3335.4	10.542304
4067.2	8.533676	4066.2	8.442487

4 Active Raman modes for TEMPO calculated with FMO-UHF and full UHF

Table S3: Frequencies ω (cm^{-1}) and Raman activities J ($\text{\AA}^4/\text{u}$) for the active Raman modes in TEMPO, computed with FMO-UHF and UHF. This table corresponds to the Raman spectra shown in Figure 2-(c).

FMO-UHF		UHF	
ω	J	ω	J
1637.1	32.972562	1636.2	32.776545
3211.2	94.194192	3210.3	95.820219
3222.0	76.387953	3222.0	72.915179
3227.4	78.400709	3228.3	75.919765
3279.6	47.550426	3251.7	17.884077
3294.9	35.490204	3280.5	46.878616
3303.9	39.906570	3321.9	14.330078
3334.5	21.637967	3333.6	21.148085
3346.2	17.518328	3344.4	16.834476
3348.0	17.555305	3350.7	17.740914

5 Active Raman and IR modes for polystyrene oligomer

Table S4: Frequencies ω (cm^{-1}), Raman activities J ($\text{\AA}^4/\text{u}$) and IR intensities I ($\text{D}^2/\text{u}(\text{\AA}^2)$) for the active modes in polystyrene oligomer. This table corresponds to the Raman and IR spectra shown in Figure 3-(b).

IR		
mode	ω	IR intensity I
Phenyl,C-C,CH	602	0.455
Phenyl,C-C,CH	780	1.375
Phenyl,C-C,CH	850	0.927
COO sym,CH ₂	1457	1.719
COO asymm	1987	0.890
CH, backbone	3202	0.876
CH, backbone	3218	0.343
CH, backbone	3224	0.380
CH, backbone	3263	1.001
CH, phenyl	3376	1.791
Raman		
mode	ω	Raman activity J
Phenyl,C-C	1091	28.477
backbone,CH	1495	19.542
Phenyl,C-C,CH	1814	23.448
CH,backbone	3203	58.486
CH,backbone	3215	33.394
CH, backbone	3224	43.139
CH, backbone	3254	22.630
CH, phenyl	3357	124.446
CH, phenyl	3365	115.505
CH, phenyl	3384	243.171