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QM/MM Simulations of Vibrational Spectra in Bacteriorhodopsin and Channelrhodopsin-2

Supporting Information

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Here, we document the performance of different DFT and DFTB methods with respect to the C=O stretch vibration, both in terms of absolute frequencies and effects of hydrogen bonds on the frequencies. We demonstrate, that PBE/def2-TZVP is a suitable reference for the C=O stretch frequency in carboxylic acids. In the following text, the abbreviations ME (mean error), MAE (mean absolute error), MSE (mean squared error) and GGA (generalized gradient approximation) are used.

1 Performance of DFTB and different exchange correlation functionals with respect to the C=O stretch vibration

Table 1. Vibrational harmonic frequencies for the ν_{COOH} band computed with DFTB and DFT methods. All DFT calculations with the def2-TZVP basis set. All numbers given in cm^{-1}

	H_2CO	HCOOH	CH_3COOH	CH_3CH_3COOH	ME	MAE	MSE
exp.	1746.0[1]	1770.0[1]	1779.2[2]	1776.1[2]			
DFTB2/mio[3]	1825.6	1772.7	1775.4	1769.6	+30.5	35.7	64.9
DFTB3/mio[4]	1869.0	1764.4	1775.8	1768.4	+26.5	34.9	61.7
DFTB3/3ob[5]	1842.9	1767.2	1758.5	1751.5	+12.2	36.2	51.0
DFTB3/3ob-f[5]	1759.8	1692.3	1696.8	1689.8	−58.3	65.2	71.7
PBE[6,7]	1767.8	1766.8	1766.1	1758.8	−3.0	13.9	15.5
mPWLYP[8,9]	1744.9	1741.0	1740.6	1733.1	−27.9	27.9	32.3
BLYP[9,10]	1743.0	1739.2	1739.8	1731.2	−29.6	29.6	33.7
BP86[10–12]	1761.9	1759.7	1759.2	1752.2	−9.6	17.5	18.2
TPSS[13]	1770.5	1768.3	1769.8	1761.0	−0.2	12.4	14.9
PBE0[14]	1857.6	1851.6	1848.9	1848.3	+83.8	83.8	85.4
mPW1LYP[8,9]	1835.9	1831.3	1835.8	1825.1	+64.2	64.2	66.1
B3LYP[15]	1822.4	1817.9	1817.9	1810.5	+49.8	49.8	52.4
TPSS0[16]	1859.1	1850.3	1857.2	1850.4	+86.4	86.4	87.8
B2PLYP[17]	1791.3	1804.1	1812.9	1806.0	+35.8	35.8	36.2
mPW2PLYP[18]	1811.1	1823.0	1831.6	1824.6	+54.8	54.8	55.1

The computed harmonic normal modes deviate from the experimental fundamental frequencies in a systematic fashion. Pure DFT exchange correlation functionals of GGA or meta-GGA type underestimate the ν_{COOH} band, with PBE, BP86 and TPSS showing very similar behavior with a MAE of 12 to 18 cm^{-1}, while the similar mPWLYP and BLYP functionals show a larger deviation of 30 cm^{-1}. Hybrid functionals overestimate the experimental frequencies of the four molecules systematically, with an MAE of 50 to 86 cm^{-1}. The double hybrid functional B2PLYP performs only slightly worse than pure DFT with a MAE of 36 cm^{-1}. The other tested hybrid functional, mPW2PLYP, which was originally developed for thermochemistry applications, performs similar to hybrid functionals like B3LYP. DFTB2, DFTB3/mio and DFTB3/3ob perform similar with respect to the MAE, which is only marginally higher than the GGA functionals BLYP and mPWLYP. Compared to the previous DFTB versions, DFTB3/3ob shows the smallest systematic deviation from the experimental frequencies with a mean error of just 12 cm^{-1}. A special parametrization for stretch frequencies "3ob-f"[5] results in a systematic error of -58 cm^{-1} with respect to experiments. It indeed improves the C=O stretch frequency of H_2CO, as reported previously,[5] but is not able to improve the values for the carboxylic acids. DFTB2/mio, DFTB3/mio and DFTB3/3ob significantly deviates from experiment and DFT for H_2CO, so that the performance cannot be extended beyond the tested carboxylic acids. Thus we conclude that the C=O stretch vibration is already well described by the standard 3ob parameter set, thus a special parametrization is not required.

2 Performance of DFT with respect to the effect of a hydrogen bond on the C=O stretch vibration

Table 2. The ν_{COOH} frequency computed with DFTB and various DFT exchange correlation functionals for propionic acid (same as Table 1), a model of propionic acid and methanol (model 2 of Fig 1 in the main article) and the propionic acid dimer (model 14). As basis set for the DFT calculation, the def2-TZVP basis was used. All wavenumbers given in cm^{-1}

	CH_3CH_3COOH	model 2	model 14
exp.[2]	1776.1		1721.5
DFTB2/mio	1769.6	1727.0	1687.6
DFTB3/mio	1768.4	1716.5	1667.6
DFTB3/3ob	1751.5	1721.4	1682.0
DFTB3/3ob-f	1689.8	1657.6	1620.2
PBE	1758.8	1727.2	1683.7
mPWLYP	1733.1	1701.7	1665.8
BLYP	1731.2	1699.3	1666.2
BP86	1752.2	1719.3	1676.5
TPSS	1761.0	1729.0	1695.2
PBE0	1848.3	1817.7	1781.4
mPW1LYP	1825.1	1794.4	1760.3
B3LYP	1810.5	1780.1	1747.0
TPSS0	1850.4	1820.6	1785.1
B2PLYP	1806.0	1777.0	1750.5
mPW2PLYP	1824.6	1794.3	1768.4

To estimate the performance of the DFT functionals with respect to the effect of hydrogen bonding on the ν_{COOH} band, we performed calculations on propionic acid, on a model of propionic acid hydrogen-bonded to one methanol molecule (model 2) and the propionic acid dimer (Table 2, Fig. 1). As discussed in the main text, DFTB2 and DFTB3/mio overestimate the shift of ν_{COOH} due to hydrogen-bonding with respect to DFT. This overestimation gets removed with DFTB3/3ob. For shifts of the frequencies, the special 3ob-f parameters perform as well as the standard 3ob.

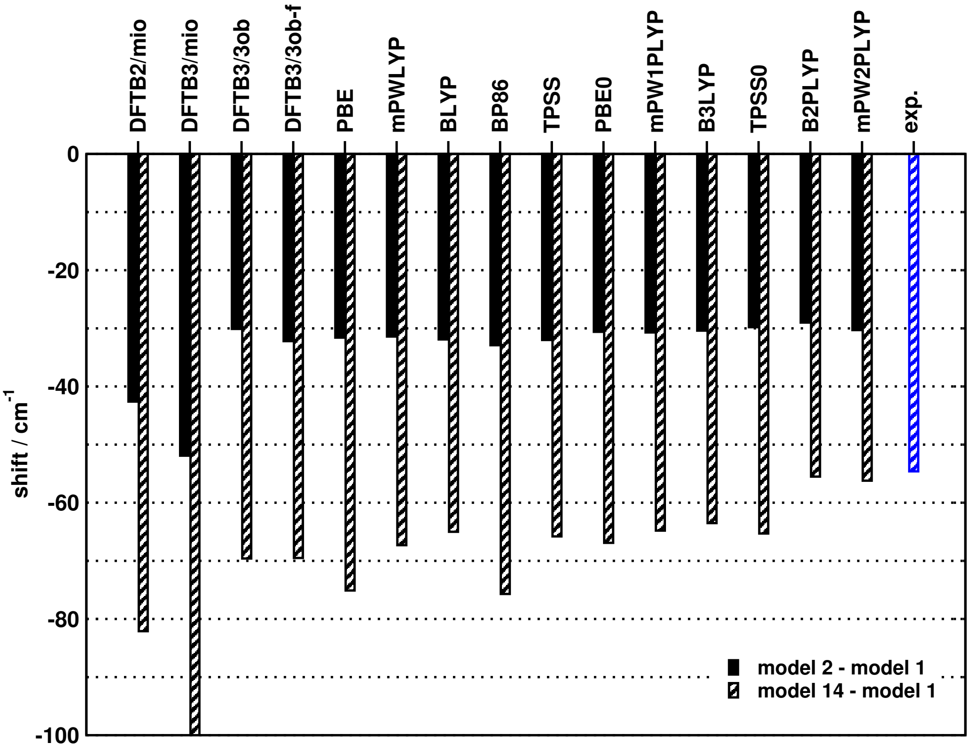

Figure 1. Effect of hydrogen bonds on the C=O stretch frequency, calculated as the shift of model 2 (see Fig. 1 of main article) and propionic acid (black bars), or shift between propinic acid dimer and monomer (black/white) bars. Experimental value refers to shift between dimer and monomer

The effect of one hydrogen bond (of the propionic acid's hydroxyl group to the methanol oxygen atom) is described consistently with all chosen functionals for the given basis set. The differences are more pronounced in the case of a propionic acid dimer, which may be regarded as an example of very strong hydrogen bonding. Here, DFTB3/3ob, PBE and BP86 overestimate the shift by 15 cm^{-1}. DFTB3/mio severly overestimates this shift, which is the reason for the recommendation against its usage in previous studies. The overestimation with respect to experiment is reduced for BLYP and mPWLYP as well as on the meta-GGA and hybrid functional level and vanishes almost completely on the double hybrid level of theory. We conclude, that DFTB3/3ob is able to describe the effects of hydrogen-bonding on the ν_{COOH} band as reliably as GGA-DFT for all tested systems, while for very strongly hydrogen bonding situation, the description gets improved using hybrid or even double-hybrid functionals.

3 Effect of basis set choice on the C=O stretch frequency

Besides the chosen exchange correlation functional, the basis set naturally influences the performance of the calculation, both in terms of accuracy and computational cost. We tested the Karlsruhe basis sets: def2-SVP[19], def2-TZVP[19], def2-QZVP[20] and Dunning's cc-pVXZ (X=D,T,Q) basis sets[21] both without and augmented with diffuse functions.[22] From this small test, we conclude, that increasing the basis set size beyond triple-ζ quality does not improve the quality of the ν_{COOH} frequencies. Because def2-TZVP is more efficient than cc-pVTZ, we preferred the former for our DFT calculations.

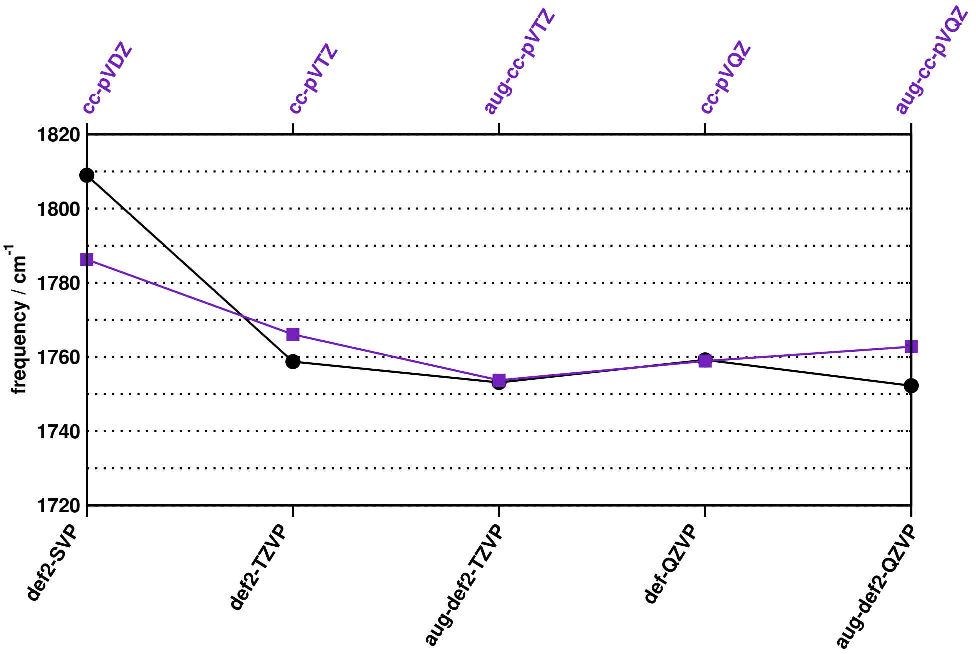

Figure 2. Effect of basis set choice on the ν_{COOH} frequency of propionic acid computed with PBE

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