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Cost-Effective Density Functional Theory (DFT) to Calculations of Equilibrium Isotopic Fractionation in Large Organic Molecules

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Electronic Supplementary Information

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Description of Additional Corrections to Urey's Model

Liu *et al.* recently evaluated, for small molecules, the Bigeleisen–Mayer equations and various corrections (see refence for full details).[S1] The first two are corrections for vibrational–rotational coupling for the ground (Q_{VrZPE}) and vibrational excited states (Q_{VrEXC}):

$$Q_{VrZPE} = \prod_{\sigma} \left(\frac{\sigma_e}{\sigma_0}\right)^{½} = \left(\frac{A_e}{A_0} \cdot \frac{B_e}{B_0} \cdot \frac{C_e}{C_0}\right)^{½}$$

$$Q_{VrEXC} = 1 = \frac{1}{2} \sum_{i}^{n_{vib}} \frac{\delta_i}{\exp(u_i') - 1}$$

where n_{vib} is the number of vibrational frequencies (degrees of freedom, *i.e.*, 3*N*-5 for linear molecules and 3*N*-6 otherwise), σ_e (and consequently A_e, B_e and C_e) is the equilibrium rotational constant around axis σ (*i.e.,* axes A, B, C), $\sigma_0 = \sigma_e - \sum_i \alpha_{\sigma,i}$ (and consequently A_0, B_0 and C_0) is the rotational constant around axis σ in the vibrational ground state where $\alpha_{\sigma,i}$ is the vibration–rotation coupling constant between axis σ and normal mode i, $u_i' = \frac{hc\nu_i}{k_B T}$ is the equivalent of u_i but with the fundamental frequencies ν_i from an anharmonic frequency calculation and $\delta_i = \sum_\sigma \frac{\alpha_{\sigma,i}}{\sigma_0}$. For a linear molecule, where there is only one rotational constant, one has instead of the above:[S2]

$$Q_{VrZPE} = \frac{\sigma_e}{\sigma_0}$$

The third and fourth correct for deviations due to anharmonicity of the vibrational ground (Q_{AnZPE}) and excited (Q_{AnEXC}) states:

$$Q_{AnZPE} = \exp\left(-\frac{hcG_0}{k_B T}\right) \prod_{i \le j} \exp\left(-\frac{hcx_{ij}}{4k_B T}\right)$$

$$Q_{AnEXC} = 1 - \frac{2hc}{k_B T} \sum_{i} \frac{x_{ii} \cdot \exp(u_i)}{(\exp(u_i) - 1)^2} - \frac{hc}{2k_B T} \sum_{i<j} \frac{x_{ij}\left(\exp(u_i) + \exp(\mathrm{u_j})\right)}{(\exp(u_i) - 1) \cdot \left(\exp(u_j) - 1\right)}$$

where x_{ij} is the anharmonic coupling constant between normal modes i and j, and G_0 is a complicated function of the second, third and fourth force constants. An equivalent expression for Q_{AnZPE} used by Liu *et al.* for reasons of numerical accuracy is:

$$Q_{AnZPE} = \frac{\exp\left(-\frac{ZPE_{tot}}{k_B T}\right)}{\exp\left(-\frac{ZPE_{harm}}{k_B T}\right)}$$

where $ZPE_{harm} = \frac{1}{2}\sum_i hc\omega_i$ and ZPE_{tot} are the harmonic and total (anharmonic) ZPEs, respectively.

The fifth is the quantum mechanical correction for rotation $\left(Q_{QmCorr}\right)$:

$$Q_{QmCorr} = 1 + \frac{1}{12}\cdot\frac{hc}{k_B T}\left(2A_0 + 2B_0 + 2C_0 + \frac{B_0 C_0}{A_0} + \frac{A_0 C_0}{B_0} + \frac{A_0 B_0}{C_0}\right)$$

where all terms are as defined above. For a linear molecule:[S3]

$$Q_{QmCorr} = 1 + \frac{hc}{k_B T}\cdot\frac{\sigma_0}{3} + \cdots$$

The sixth is a correction for centrifugal distortion ($Q_{CenDist}$):

$$Q_{CenDist} = 1 - \frac{hck_B T}{4\hbar^4}\left(3\tau_{aaaa}I_A^2 + 3\tau_{bbbb}I_B^2 + 3\tau_{cccc}I_C^2 + 2\tau_{bbaa}I_B I_A + 2\tau_{ccbb}I_C I_B + 2\tau_{ccaa}I_C I_A\right)$$

where $\tau_{\sigma\sigma\sigma'\sigma'}$ is the quartic centrifugal distortion constant and I_σ is the principle moment of inertia around axis σ.

The seventh is a correction for hindered internal rotation (Q_{HIR}):

$$Q_{HIR} = \prod_{i}^{\substack{hindered \\ torsions}} \frac{(2\pi k_B T)^{1/2}}{s_i \hbar} I_i^{1/2}\cdot\exp\left(-\frac{W_i}{2k_B T}\right)\mathrm{I}_0\left(\frac{W_i}{2k_B T}\right)\left(Q_{Class}^{HO}(\omega_i^{tor})\right)^{-1}$$

where s_i is the symmetry number of torsional mode i (which can be ignored in isotope fractionation calculations) $W_i = 8\pi^2 c^2(\omega_i^{tor})^2 I_i/s_i^2$ is the barrier height for torsion i, I_0 is a zeroth-order modified Bessel function and $Q_{Class}^{HO}(\omega_i^{tor}) = \frac{k_B T}{hc\omega_i^{tor}}$ is the classical harmonic oscillator partition function of torsional mode i ω_i^{tor}. While Q_{HIR} can be calculated independently, it is actually part of the output from the hindered rotor output from GAUSSIAN16 when the appropriate keyword is added; three partition functions are provided – based on derivations by Truhlar(ref), Pitzer and Gwinn(ref) and McClurg(ref) – and based on recommendations by Liu *et al.* the Pitzer–Gwinn approximation is used here.[S1]

Heavy Atom Fractionation – Evaluation of Errors in CNOEIF35

While developing the CNOEIF35 database (Table 10), the reactions were initially considered based on how they were written in the original references. This, however, gave in many cases significant errors. As discussed in the main text, these reactions were reevaluated using slight modifications. As noted, this may include using the acid or conjugate base form of one or more of the reaction species, adding explicit solvent molecules (explicit solvation) and/or using the experimental liquid-gas isotopic fractionation. When calculating the D/H fractionation of ketones with water, the solution β was determined using the calculated gas-phase β and $\alpha_{liq-gas}^{expt}$. For heavy-atom isotopic fractionation, the solvation of H_2O, CO_2 and HCO_3^- are potentially problematic. In these three cases, the β for liquid water and aqueous CO_2 could be determined using the calculated gas-phase β and the experimental gas-solution fractionation $\left(\alpha_{liq-gas}^{expt}\right)$ of water,[S4] CO_2,[S5] or HCO_3^-:[S6]

$$1000\ln\left({}_{H_2O}^{18}\alpha_{liq-gas}^{expt}\right) = \frac{3.5041\times10^8}{T^3} - \frac{1.6664\times10^6}{T^2} + \frac{6.7123\times10^3}{T} - 7.685$$

$$1000\ln\left({}_{CO_2}^{13}\alpha_{aq-gas}^{expt}\right) = 0.0041\cdot T - 1.18$$

$$1000\ln\left({}^{13}\alpha_{HCO_{3(aq)}^{-}-CO_{2(g)}}^{expt}\right) = \frac{9483}{T} - 23.89$$

However, it was found (*vide infra*) that the SMD model actually gives lower errors, albeit occasionally marginally, with respect to the experimental values than when using $\alpha_{liq-gas}^{expt}$. How each reaction is affected by the different changes is outlines in Table S1. Note that not all reactions required this evaluation.

Table S1. Summary of the errors in CNOEIF35 and how there are affected by various changes to the reactions as written in reference, with the final selection highlighted in green.

Reaction		Change to "as written"[a]	MAD (‰)
1	isocitrate → $CO_{2(aq)}$		11
		isocitric acid→	5
		→$CO_{2(g)}$	17
		→$CO_{2(g)}$×$\left({}^{13}_{CO_2}\alpha^{expt}_{aq-gas}\right)$	17
		isocitric acid→$CO_{2(g)}$	11
		isocitric acid→$CO_{2(g)}$×$\left({}^{13}_{CO_2}\alpha^{expt}_{aq-gas}\right)$	12
2	6-phosphogluconate → $CO_{2(aq)}$		1
		6-phosphogluconic acid→	4
		→$CO_{2(g)}$	17
		→$CO_{2(g)}$×$\left({}^{13}_{CO_2}\alpha^{expt}_{aq-gas}\right)$	17
3	malate → $CO_{2(aq)}$		3
		malic acid→	9
		→$CO_{2(g)}$	3
		→$CO_{2(g)}$×$\left({}^{13}_{CO_2}\alpha^{expt}_{aq-gas}\right)$	4
5	malate(CHOH) → pyruvate(C=O)		19
		malate+H_2O→	20
		malic acid→	5
		→pyruvate+H_2O	21
		→pyruvic acid	23
		malic acid→pyruvic acid	10
6	malate(CH_2) → pyruvate(CH_3)		4
		malic acid→	8
		→pyruvic acid	3
		malic acid→pyruvic acid	7

Reaction		Change to "as written"[a]	MAD (‰)
7	carbonate → $HCO_{3(aq)}^-$		2
		→$CO_{2(g)}$× $\left({}^{13}\alpha^{expt}_{HCO^-_{3(aq)}-CO_{2(g)}}\right)$	16
		→$CO_{2(aq)}$	2
		carbamic acid→	5
		carbamic acid→$CO_{2(g)}$× $\left({}^{13}\alpha^{expt}_{HCO^-_{3(aq)}-CO_{2(g)}}\right)$	24
		carbamic acid→$CO_{2(aq)}$	9
8	carbamate → carbamoyl phosphate		2
		carbamic acid→	5
9	N,N-tetramethylenecarbamate → $CO_{2(g)}$	(in dioxane solution)	13
		N,N-tetramethylenecarbamic acid→	7
		→$CO_{2(sol)}$	17
		N,N-tetramethylenecarbamic acid→$CO_{2(sol)}$	5
		(in aqueous solution)	23
20 (21)	NH_4^+ → $NH_{3(g)}$ (ND_4^+ → $ND_{3(g)}$)		11 (10)
		→$NH_{3(aq)}$	11 (10)
		$NH_4^+ \cdot H_2O$→	11 (10)
		$NH_4^+ \cdot H_2O$→$NH_{3(aq)}$	11 (10)
		→$NH_3{\cdot}H_2O$	7 (7)
		$NH_4^+ \cdot H_2O$→$NH_3{\cdot}H_2O$	7 (6)
23	phenylalanine → $NH_{3(aq)}$		26
		→$NH_{3(g)}$	26
		→NH_4^+	4
26	malate → $H_2O_{(l)}$		6
		malic acid→	8
		→$H_2O_{(g)}$×$\left({}^{18}_{H_2O}\alpha^{expt}_{liq-gas}\right)$	16
27	ketoglutarate → $H_2O_{(l)}$		2
		→$H_2O_{(g)}$×$\left({}^{18}_{H_2O}\alpha^{expt}_{liq-gas}\right)$	8

Reaction		Change to "as written"[a]	MAD (‰)
28	*p*-nitrophenyl acetate → *p*-nitrophenolate		3
		→ *p*-nitrophenolate+H_2O	1
29	*p*-nitrophenol → *p*-nitrophenolate		8
		p-nitrophenol+H_2O→	11
		→ *p*-nitrophenolate+H_2O	4
		p-nitrophenol+H_2O→ *p*-nitrophenolate+H_2O	7
30	$HPO_4^{2-} \rightarrow PO_4^{3-}$		12
		$HPO_4^{2-} \cdot H_2O \rightarrow$	10
		$\rightarrow PO_4^{3-} \cdot H_2O$	14
		$HPO_4^{2-} \cdot H_2O \rightarrow PO_4^{3-} \cdot H_2O$	12
31 (32)	$H_2PO_4^- \rightarrow HPO_4^{2-}$ ($D_2PO_4^- \rightarrow DPO_4^{2-}$)		11 (11)
		$H_2PO_4^- \cdot H_2O \rightarrow$	8 (9)
		$\rightarrow HPO_4^{2-} \cdot H_2O$	13 (?)
		$H_2PO_4^- \cdot H_2O \rightarrow HPO_4^{2-} \cdot H_2O$	10 (?)
33	glucose-6-biphosphate → glucose-6-phosphate		7
		glucose-6-biphosphate+H_2O→	3
34	glycerol-3-biphosphate → glycerol-3-phosphate		7
		glycerol-3-biphosphate+H_2O→	1
35	glycerol-3-biphosphate-d → glycerol-3-phosphate		7
		glycerol-3-biphosphate-*d*+H_2O→	2

[a] If not explicitly stated, as written in source.

Table S2. λ_{harm} scale factors for various GGA and meta-GGA exchange–correlation functional–basis set–density fitting basis set combinations.

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
B97-D	SVP	1.0277	1.0379	1.0278	1.0278
	SVPD	1.0278	1.0365	1.0279	1.0279
	TZVP	1.0277	1.0360	1.0278	1.0278
	TZVPD	1.0282	1.0362	1.0283	1.0283
	TZVPP	1.0267	1.0346	1.0268	1.0268
	TZVPPD	1.0269	1.0346	1.0269	1.0269
	QZVP	1.0274	1.0355	1.0275	1.0275
	QZVPD	1.0276	1.0356	1.0277	1.0277
	QZVPP	1.0274	1.0355	1.0275	1.0275
	QZVPPD	1.0276	1.0356	1.0277	1.0277
BLYP	SVP	1.0399	1.0502	1.0400	1.0402
	SVPD	1.0384	1.0469	1.0385	1.0386
	TZVP	1.0371	1.0450	1.0372	1.0371
	TZVPD	1.0374	1.0450	1.0374	1.0374
	TZVPP	1.0354	1.0428	1.0354	1.0354
	TZVPPD	1.0355	1.0426	1.0355	1.0355
	QZVP	1.0364	1.0441	1.0364	1.0364
	QZVPD	1.0366	1.0442	1.0366	1.0366
	QZVPP	1.0364	1.0441	1.0364	1.0364
	QZVPPD	1.0366	1.0442	1.0366	1.0366

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
BP86	SVP	1.0340	1.0247	1.0341	1.0343
	SVPD	1.0341	1.0238	1.0342	1.0343
	TZVP	1.0338	1.0420	1.0339	1.0338
	TZVPD	1.0343	1.0423	1.0344	1.0343
	TZVPP	1.0325	1.0404	1.0326	1.0326
	TZVPPD	1.0327	1.0403	1.0328	1.0328
	QZVP	1.0336	1.0417	1.0337	1.0336
	QZVPD	1.0338	1.0418	1.0339	1.0338
	QZVPP	1.0336	1.0417	1.0337	1.0336
	QZVPPD	1.0338	1.0418	1.0339	1.0338
HCTH	SVP	1.0101	1.0002	1.0102	1.0103
	SVPD	1.0102	0.9998	1.0103	1.0104
	TZVP	1.0124	1.0063	1.0125	1.0124
	TZVPD	1.0129	1.0210	1.0130	1.0129
	TZVPP	1.0115	1.0195	1.0116	1.0115
	TZVPPD	1.0118	1.0196	1.0119	1.0118
	QZVP	1.0122	1.0211	1.0124	1.0122
	QZVPD	1.0125	1.0212	1.0126	1.0125
	QZVPP	1.0122	1.0211	1.0124	1.0122
	QZVPPD	1.0125	1.0212	1.0126	1.0125
M06-L	SVP	0.9957	0.9892	0.9959	0.9959
	SVPD	0.9978	0.9902	0.9979	0.9979
	TZVP	0.9964	1.0065	0.9965	0.9964
	TZVPD	0.9968	1.0066	0.9970	0.9969
	TZVPP	0.9949	1.0045	0.9950	0.9949
	TZVPPD	0.9954	1.0048	0.9955	0.9954
	QZVP	0.9944	1.0045	0.9944	0.9944
	QZVPD	0.9945	1.0046	0.9945	0.9945
	QZVPP	0.9944	1.0045	0.9944	0.9944
	QZVPPD	0.9945	1.0046	0.9945	0.9945

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
M06-L$_{D3}$	SVP	0.9957	1.0063	0.9959	0.9959
	SVPD	0.9978	1.0078	0.9979	0.9979
	TZVP	0.9964	1.0065	0.9965	0.9964
	TZVPD	0.9968	1.0066	0.9970	0.9969
	TZVPP	0.9949	1.0045	0.9950	0.9949
	TZVPPD	0.9954	1.0048	0.9955	0.9954
	QZVP	0.9944	1.0045	0.9944	0.9944
	QZVPD	0.9945	1.0046	0.9945	0.9945
	QZVPP	0.9944	1.0045	0.9944	0.9944
	QZVPPD	0.9945	1.0046	0.9945	0.9945
M11-L	SVP	0.9988	0.9934	0.9990	0.9990
	SVPD	1.0008	0.9952	1.0009	1.0009
	TZVP	0.9973	1.0082	0.9974	0.9973
	TZVPD	0.9979	1.0085	0.9981	0.9979
	TZVPP	0.9983	1.0089	0.9985	0.9983
	TZVPPD	0.9984	1.0088	0.9985	0.9984
	QZVP	0.9977	1.0084	0.9978	0.9977
	QZVPD	0.9982	1.0089	0.9983	0.9982
	QZVPP	0.9977	1.0084	0.9978	0.9977
	QZVPPD	0.9982	1.0089	0.9983	0.9982
MN12-L	SVP	0.9839	0.9820	0.9840	0.9841
	SVPD	0.9858	0.9838	0.9859	0.9860
	TZVP	0.9874	0.9981	0.9875	0.9874
	TZVPD	0.9876	0.9980	0.9878	0.9876
	TZVPP	0.9869	0.9969	0.9870	0.9869
	TZVPPD	0.9869	0.9967	0.9870	0.9869
	QZVP	0.9871	0.9971	0.9873	0.9872
	QZVPD	0.9873	0.9972	0.9874	0.9874
	QZVPP	0.9871	0.9971	0.9873	0.9872
	QZVPPD	0.9873	0.9972	0.9874	0.9874

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
MN15-L	SVP	0.9908	1.0012	0.9909	0.9910
	SVPD	0.9933	1.0028	0.9934	0.9935
	TZVP	0.9976	1.0072	0.9978	0.9976
	TZVPD	0.9984	1.0076	0.9985	0.9984
	TZVPP	0.9967	1.0055	0.9968	0.9967
	TZVPPD	0.9971	1.0058	0.9972	0.9971
	QZVP	0.9982	1.0083	0.9983	0.9982
	QZVPD	0.9983	1.0084	0.9985	0.9983
	QZVPP	0.9982	1.0083	0.9983	0.9982
	QZVPPD	0.9983	1.0084	0.9985	0.9983
mPWPW91	SVP	1.0291	1.0390	1.0292	1.0292
	SVPD	1.0289	1.0375	1.0290	1.0290
	TZVP	1.0288	1.0371	1.0289	1.0289
	TZVPD	1.0293	1.0374	1.0294	1.0294
	TZVPP	1.0277	1.0356	1.0277	1.0277
	TZVPPD	1.0278	1.0356	1.0279	1.0279
	QZVP	1.0286	1.0369	1.0287	1.0287
	QZVPD	1.0289	1.0370	1.0289	1.0289
	QZVPP	1.0286	1.0369	1.0287	1.0287
	QZVPPD	1.0289	1.0370	1.0289	1.0289
N12	SVP	1.0041	0.9960	1.0042	1.0044
	SVPD	1.0033	0.9945	1.0034	1.0035
	TZVP	1.0026	1.0104	1.0027	1.0026
	TZVPD	1.0030	1.0105	1.0031	1.0030
	TZVPP	1.0012	1.0085	1.0012	1.0012
	TZVPPD	1.0013	1.0085	1.0014	1.0013
	QZVP	1.0017	1.0094	1.0017	1.0017
	QZVPD	1.0020	1.0094	1.0020	1.0020
	QZVPP	1.0017	1.0094	1.0017	1.0017
	QZVPPD	1.0020	1.0094	1.0020	1.0020

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
OLYP	SVP	1.0200	1.0303	1.0201	1.0202
	SVPD	1.0197	1.0284	1.0199	1.0199
	TZVP	1.0212	1.0297	1.0213	1.0212
	TZVPD	1.0216	1.0300	1.0218	1.0217
	TZVPP	1.0205	1.0287	1.0206	1.0205
	TZVPPD	1.0207	1.0288	1.0208	1.0207
	QZVP	1.0211	1.0301	1.0213	1.0211
	QZVPD	1.0213	1.0302	1.0215	1.0213
	QZVPP	1.0211	1.0301	1.0213	1.0211
	QZVPPD	1.0213	1.0302	1.0215	1.0213
PBE	SVP	1.0303	1.0213	1.0304	1.0305
	SVPD	1.0303	1.0203	1.0304	1.0304
	TZVP	1.0307	1.0390	1.0308	1.0307
	TZVPD	1.0312	1.0392	1.0313	1.0312
	TZVPP	1.0296	1.0374	1.0296	1.0296
	TZVPPD	1.0298	1.0374	1.0298	1.0298
	QZVP	1.0306	1.0390	1.0307	1.0306
	QZVPD	1.0308	1.0390	1.0309	1.0308
	QZVPP	1.0306	1.0390	1.0307	1.0306
	QZVPPD	1.0308	1.0390	1.0309	1.0308
PBE_{D3BJ}	SVP	1.0303	1.0402	1.0304	1.0304
	SVPD	1.0302	1.0387	1.0303	1.0303
	TZVP	1.0306	1.0389	1.0308	1.0308
	TZVPD	1.0311	1.0392	1.0313	1.0313
	TZVPP	1.0295	1.0374	1.0296	1.0296
	TZVPPD	1.0297	1.0374	1.0298	1.0298
	QZVP	1.0306	1.0389	1.0307	1.0307
	QZVPD	1.0308	1.0390	1.0309	1.0309
	QZVPP	1.0306	1.0389	1.0307	1.0307
	QZVPPD	1.0308	1.0390	1.0309	1.0309

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
revTPSS	SVP	1.0189	1.0083	1.0190	1.0192
	SVPD	1.0193	1.0081	1.0194	1.0195
	TZVP	1.0201	1.0294	1.0202	1.0201
	TZVPD	1.0204	1.0296	1.0206	1.0204
	TZVPP	1.0194	1.0285	1.0194	1.0194
	TZVPPD	1.0194	1.0285	1.0195	1.0195
	QZVP	1.0197	1.0290	1.0198	1.0197
	QZVPD	1.0198	1.0290	1.0199	1.0199
	QZVPP	1.0197	1.0290	1.0198	1.0197
	QZVPPD	1.0198	1.0290	1.0199	1.0199
SOGGA11	SVP	1.0182	1.0281	1.0184	1.0185
	SVPD	1.0114	1.0202	1.0116	1.0116
	TZVP	1.0195	1.0273	1.0196	1.0195
	TZVPD	1.0197	1.0269	1.0198	1.0197
	TZVPP	1.0206	1.0282	1.0206	1.0206
	TZVPPD	1.0208	1.0272	1.0221	1.0208
	QZVP	1.0189	1.0280	1.0192	1.0189
	QZVPD	1.0182	1.0269	1.0189	1.0182
	QZVPP	1.0189	1.0280	1.0192	1.0189
	QZVPPD	1.0182	1.0269	1.0189	1.0182
TPSS	SVP	1.0188	1.0086	1.0190	1.0191
	SVPD	1.0191	1.0083	1.0192	1.0193
	TZVP	1.0193	1.0284	1.0194	1.0193
	TZVPD	1.0198	1.0286	1.0199	1.0198
	TZVPP	1.0188	1.0277	1.0189	1.0188
	TZVPPD	1.0189	1.0276	1.0190	1.0189
	QZVP	1.0192	1.0282	1.0193	1.0192
	QZVPD	1.0194	1.0282	1.0194	1.0194
	QZVPP	1.0192	1.0282	1.0193	1.0192
	QZVPPD	1.0194	1.0282	1.0194	1.0194

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
$TPSS_{D3BJ}$	SVP	1.0188	1.0086	1.0189	1.0190
	SVPD	1.0191	1.0083	1.0192	1.0193
	TZVP	1.0193	1.0282	1.0194	1.0193
	TZVPD	1.0197	1.0286	1.0198	1.0197
	TZVPP	1.0187	1.0276	1.0188	1.0188
	TZVPPD	1.0189	1.0276	1.0190	1.0189
	QZVP	1.0192	1.0281	1.0192	1.0192
	QZVPD	1.0193	1.0282	1.0194	1.0193
	QZVPP	1.0192	1.0281	1.0192	1.0192
	QZVPPD	1.0193	1.0282	1.0194	1.0193
VSXC	SVP	1.0049	1.0146	1.0050	1.0050
	SVPD	1.0060	1.0143	1.0061	1.0061
	TZVP	1.0063	1.0143	1.0064	1.0064
	TZVPD	1.0070	1.0148	1.0072	1.0072
	TZVPP	1.0052	1.0130	1.0053	1.0053
	TZVPPD	1.0055	1.0132	1.0057	1.0057
	QZVP	1.0064	1.0150	1.0065	1.0065
	QZVPD	1.0066	1.0150	1.0067	1.0067
	QZVPP	1.0064	1.0150	1.0065	1.0065
	QZVPPD	1.0066	1.0150	1.0067	1.0067
XLYP	SVP	1.0399	1.0501	1.0400	1.0400
	SVPD	1.0382	1.0467	1.0383	1.0383
	TZVP	1.0370	1.0449	1.0370	1.0370
	TZVPD	1.0373	1.0448	1.0373	1.0373
	TZVPP	1.0353	1.0426	1.0353	1.0353
	TZVPPD	1.0353	1.0425	1.0354	1.0354
	QZVP	1.0363	1.0440	1.0363	1.0363
	QZVPD	1.0365	1.0440	1.0365	1.0365
	QZVPP	1.0363	1.0440	1.0363	1.0363
	QZVPPD	1.0365	1.0440	1.0365	1.0365

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
τHCTH	SVP	1.0151	1.0057	1.0152	1.0153
	SVPD	1.0158	1.0056	1.0159	1.0160
	TZVP	1.0156	1.0237	1.0157	1.0156
	TZVPD	1.0161	1.0241	1.0163	1.0162
	TZVPP	1.0150	1.0230	1.0150	1.0150
	TZVPPD	1.0151	1.0230	1.0152	1.0151
	QZVP	1.0154	1.0241	1.0155	1.0154
	QZVPD	1.0156	1.0241	1.0157	1.0156
	QZVPP	1.0154	1.0241	1.0155	1.0154
	QZVPPD	1.0156	1.0241	1.0157	1.0156

[a] Not using any density fitting.

Table S3. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{harm} for various GGA and meta-GGA exchange–correlation functional–basis set–density fitting basis set combinations.

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
B97-D	SVP	39.98	62.77	39.93	39.93
	SVPD	36.91	60.82	36.91	36.91
	TZVP	28.07	55.05	28.11	28.11
	TZVPD	26.42	55.02	26.53	26.53
	TZVPP	27.21	53.98	27.25	27.25
	TZVPPD	26.20	53.62	26.28	26.28
	QZVP	26.13	54.11	26.20	26.20
	QZVPD	25.89	54.09	25.98	25.98
	QZVPP	26.13	54.11	26.21	26.21
	QZVPPD	25.89	54.09	25.98	25.98
BLYP	SVP	40.66	72.00	40.65	40.99
	SVPD	36.88	67.57	36.88	36.90
	TZVP	30.94	66.37	31.07	30.96
	TZVPD	29.17	65.82	29.38	29.19
	TZVPP	27.92	63.87	28.04	27.94
	TZVPPD	27.32	63.47	27.50	27.34
	QZVP	26.67	63.61	26.87	26.67
	QZVPD	26.70	63.60	26.91	26.71
	QZVPP	26.67	63.61	26.86	26.67
	QZVPPD	26.70	63.60	26.91	26.71

Functional	**Basis Set**	**none[a]**	**def2-SV/TZV**	**W06**	**auto**
BP86	SVP	38.26	143.84	38.23	38.33
	SVPD	35.80	156.11	35.78	35.72
	TZVP	25.51	55.39	25.60	25.53
	TZVPD	24.45	55.38	24.60	24.47
	TZVPP	23.56	53.71	23.65	23.57
	TZVPPD	23.10	53.44	23.23	23.12
	QZVP	22.51	53.53	22.66	22.52
	QZVPD	22.51	53.56	22.66	22.51
	QZVPP	22.51	53.53	22.66	22.51
	QZVPPD	22.51	53.56	22.66	22.51
HCTH	SVP	44.76	126.79	44.72	44.66
	SVPD	42.75	149.91	42.75	42.60
	TZVP	29.31	150.77	29.32	29.32
	TZVPD	27.21	47.39	27.27	27.22
	TZVPP	28.08	46.00	28.13	28.08
	TZVPPD	27.22	46.18	27.29	27.22
	QZVP	26.80	45.95	26.90	26.79
	QZVPD	26.70	46.09	26.80	26.69
	QZVPP	26.80	45.95	26.90	26.80
	QZVPPD	26.70	46.09	26.80	26.69
M06-L	SVP	42.66	123.06	42.63	42.53
	SVPD	41.36	151.50	41.36	41.22
	TZVP	32.22	47.66	32.27	32.23
	TZVPD	32.64	48.50	32.73	32.65
	TZVPP	31.34	45.10	31.31	31.34
	TZVPPD	30.85	44.68	30.85	30.86
	QZVP	29.05	45.07	29.01	29.05
	QZVPD	28.24	44.34	28.18	28.24
	QZVPP	29.05	45.07	29.01	29.04
	QZVPPD	28.24	44.34	28.18	28.24

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
M06-L$_{D3}$	SVP	42.66	53.92	42.63	42.53
	SVPD	41.36	55.02	41.37	41.23
	TZVP	32.22	47.66	32.27	32.23
	TZVPD	32.64	48.49	32.73	32.65
	TZVPP	31.34	45.10	31.31	31.35
	TZVPPD	30.86	44.68	30.86	30.86
	QZVP	29.05	45.07	29.01	29.05
	QZVPD	28.25	44.34	28.19	28.25
	QZVPP	29.05	45.07	29.01	29.05
	QZVPPD	28.25	44.34	28.19	28.25
M11-L	SVP	72.68	141.10	72.59	72.35
	SVPD	71.45	176.09	71.42	71.14
	TZVP	62.35	65.26	62.27	62.35
	TZVPD	60.94	64.74	60.88	60.93
	TZVPP	64.11	66.75	64.06	64.10
	TZVPPD	63.54	66.45	63.50	63.53
	QZVP	59.34	62.84	59.24	59.34
	QZVPD	60.18	63.52	60.09	60.18
	QZVPP	59.34	62.84	59.24	59.34
	QZVPPD	60.18	63.52	60.09	60.18
MN12-L	SVP	46.49	126.54	46.42	46.31
	SVPD	44.33	156.15	44.29	44.06
	TZVP	40.11	57.38	40.10	40.12
	TZVPD	39.24	57.51	39.27	39.24
	TZVPP	41.14	56.55	41.15	41.14
	TZVPPD	40.71	56.20	40.72	40.70
	QZVP	41.67	57.32	41.67	41.67
	QZVPD	41.23	56.91	41.22	41.22
	QZVPP	41.67	57.32	41.67	41.67
	QZVPPD	41.23	56.91	41.22	41.22

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
MN15-L	SVP	47.20	55.84	47.08	46.91
	SVPD	42.70	56.14	42.66	42.45
	TZVP	40.18	51.11	40.14	40.18
	TZVPD	38.41	50.74	38.41	38.40
	TZVPP	40.01	49.57	39.97	40.00
	TZVPPD	38.69	49.33	38.68	38.68
	QZVP	39.33	50.38	39.30	39.33
	QZVPD	39.29	50.40	39.25	39.28
	QZVPP	39.33	50.38	39.30	39.33
	QZVPPD	39.29	50.40	39.25	39.28
mPWPW91	SVP	38.75	63.93	38.73	38.73
	SVPD	36.23	61.57	36.23	36.23
	TZVP	25.21	54.30	25.30	25.30
	TZVPD	23.82	54.23	23.97	23.97
	TZVPP	23.32	52.82	23.41	23.41
	TZVPPD	22.79	52.58	22.92	22.92
	QZVP	22.09	52.49	22.26	22.26
	QZVPD	22.10	52.56	22.27	22.27
	QZVPP	22.09	52.49	22.26	22.26
	QZVPPD	22.10	52.56	22.27	22.27
N12	SVP	39.55	126.13	39.48	39.34
	SVPD	41.91	140.71	41.81	41.58
	TZVP	25.04	48.97	25.02	25.05
	TZVPD	23.06	49.24	23.07	23.07
	TZVPP	24.53	47.50	24.54	24.53
	TZVPPD	24.41	47.97	24.39	24.40
	QZVP	24.32	47.93	24.33	24.32
	QZVPD	24.45	48.21	24.45	24.44
	QZVPP	24.32	47.93	24.33	24.32
	QZVPPD	24.45	48.21	24.45	24.44

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
OLYP	SVP	38.88	61.13	38.85	38.90
	SVPD	36.03	60.04	36.05	35.90
	TZVP	26.52	49.92	26.54	26.54
	TZVPD	21.69	48.49	21.81	21.70
	TZVPP	23.23	47.51	23.29	23.23
	TZVPPD	21.45	47.31	21.57	21.45
	QZVP	21.23	47.26	21.38	21.22
	QZVPD	20.89	47.34	21.05	20.89
	QZVPP	21.23	47.26	21.38	21.22
	QZVPPD	20.89	47.34	21.05	20.89
PBE	SVP	40.53	141.69	40.51	40.56
	SVPD	38.24	154.72	38.23	38.17
	TZVP	26.50	53.49	26.58	26.52
	TZVPD	24.91	53.30	25.05	24.93
	TZVPP	24.41	51.75	24.49	24.42
	TZVPPD	23.88	51.59	23.99	23.89
	QZVP	23.21	51.42	23.36	23.21
	QZVPD	23.25	51.53	23.40	23.25
	QZVPP	23.21	51.42	23.36	23.21
	QZVPPD	23.25	51.53	23.40	23.25
PBE_{D3BJ}	SVP	40.57	63.66	40.55	40.55
	SVPD	38.25	61.46	38.25	38.25
	TZVP	26.53	53.53	26.62	26.62
	TZVPD	24.94	53.33	25.07	25.07
	TZVPP	24.43	51.78	24.51	24.51
	TZVPPD	23.90	51.62	24.01	24.01
	QZVP	23.23	51.45	23.38	23.38
	QZVPD	23.27	51.56	23.42	23.42
	QZVPP	23.23	51.45	23.38	23.38
	QZVPPD	23.27	51.56	23.42	23.42

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
rev-TPSS	SVP	40.47	143.52	40.51	40.81
	SVPD	32.43	156.66	32.51	32.54
	TZVP	30.44	62.15	30.55	30.46
	TZVPD	29.34	61.68	29.51	29.36
	TZVPP	28.82	60.78	28.91	28.84
	TZVPPD	27.99	60.05	28.13	28.01
	QZVP	28.33	60.96	28.45	28.34
	QZVPD	28.14	60.79	28.27	28.15
	QZVPP	28.33	60.96	28.46	28.34
	QZVPPD	28.14	60.79	28.27	28.15
SOGGA11	SVP	50.77	61.90	50.74	50.52
	SVPD	49.21	66.28	49.18	48.93
	TZVP	29.40	51.54	29.42	29.41
	TZVPD	30.69	49.57	30.74	30.69
	TZVPP	35.84	51.15	35.91	35.83
	TZVPPD	38.10	48.32	41.48	38.00
	QZVP	41.52	54.76	41.71	41.52
	QZVPD	60.36	67.08	59.41	60.35
	QZVPP	41.52	54.76	41.71	41.51
	QZVPPD	60.36	67.08	59.41	60.34
TPSS	SVP	37.64	140.89	37.68	37.98
	SVPD	31.49	154.85	31.56	31.60
	TZVP	26.27	58.76	26.39	26.28
	TZVPD	25.06	58.47	25.23	25.09
	TZVPP	24.68	57.58	24.78	24.70
	TZVPPD	23.99	57.07	24.14	24.01
	QZVP	24.08	57.74	24.24	24.08
	QZVPD	23.97	57.66	24.13	23.97
	QZVPP	24.08	57.74	24.24	24.08
	QZVPPD	23.97	57.66	24.13	23.98

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
$TPSS_{D3BJ}$	SVP	37.66	141.01	37.70	37.99
	SVPD	31.48	154.95	31.55	31.60
	TZVP	23.97	57.68	24.13	23.97
	TZVPD	25.06	58.49	25.24	25.09
	TZVPP	24.68	57.61	24.78	24.70
	TZVPPD	23.99	57.09	24.14	24.01
	QZVP	24.08	57.76	24.24	24.08
	QZVPD	23.97	57.68	24.13	23.97
	QZVPP	24.08	57.76	24.24	24.08
	QZVPPD	23.97	57.68	24.13	23.97
VSXC	SVP	39.19	58.66	39.18	39.18
	SVPD	38.27	59.69	38.29	38.29
	TZVP	26.93	50.88	26.98	26.98
	TZVPD	24.91	50.86	25.01	25.01
	TZVPP	24.98	49.34	25.05	25.05
	TZVPPD	24.41	49.54	24.51	24.51
	QZVP	23.62	49.30	23.74	23.74
	QZVPD	23.53	49.40	23.66	23.66
	QZVPP	23.62	49.30	23.74	23.74
	QZVPPD	23.53	49.40	23.66	23.66
XLYP	SVP	41.01	72.29	41.00	41.00
	SVPD	37.22	67.79	37.22	37.22
	TZVP	30.99	66.29	31.12	31.12
	TZVPD	29.04	65.68	29.25	29.25
	TZVPP	27.84	63.73	27.96	27.96
	TZVPPD	27.20	63.35	27.38	27.38
	QZVP	26.51	63.44	26.71	26.71
	QZVPD	26.56	63.45	26.77	26.77
	QZVPP	26.51	63.44	26.71	26.71
	QZVPPD	26.56	63.45	26.77	26.77

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
τHCTH	SVP	40.11	131.06	40.07	40.08
	SVPD	37.23	153.14	37.23	37.09
	TZVP	26.55	49.04	26.59	26.57
	TZVPD	25.24	49.30	25.33	25.25
	TZVPP	25.64	48.55	25.70	25.65
	TZVPPD	25.02	48.38	25.10	25.02
	QZVP	24.14	49.30	24.24	24.15
	QZVPD	24.02	49.30	24.12	24.02
	QZVPP	24.14	49.30	24.24	24.14
	QZVPPD	24.02	49.30	24.12	24.02

[a] Not using any density fitting.

Table S4. λ_{ZPE} scale factors for various GGA and meta-GGA exchange–correlation functional–basis set–density fitting basis set combinations.

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
B97-D	SVP	1.0148	1.0259	1.0150	1.0150
	SVPD	1.0172	1.0280	1.0174	1.0174
	TZVP	1.0139	1.0237	1.0141	1.0141
	TZVPD	1.0143	1.0239	1.0144	1.0144
	TZVPP	1.0130	1.0224	1.0131	1.0131
	TZVPPD	1.0132	1.0226	1.0133	1.0133
	QZVP	1.0136	1.0233	1.0137	1.0137
	QZVPD	1.0138	1.0234	1.0139	1.0139
	QZVPP	1.0136	1.0233	1.0137	1.0137
	QZVPPD	1.0138	1.0234	1.0139	1.0139
BLYP	SVP	1.0236	1.0346	1.0237	1.0237
	SVPD	1.0253	1.0357	1.0254	1.0255
	TZVP	1.0198	1.0292	1.0199	1.0198
	TZVPD	1.0200	1.0292	1.0200	1.0200
	TZVPP	1.0182	1.0271	1.0183	1.0183
	TZVPPD	1.0184	1.0272	1.0185	1.0185
	QZVP	1.0192	1.0284	1.0193	1.0192
	QZVPD	1.0194	1.0285	1.0195	1.0194
	QZVPP	1.0192	1.0284	1.0193	1.0192
	QZVPPD	1.0194	1.0285	1.0195	1.0194

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
BP86	SVP	1.0208	1.0173	1.0209	1.0209
	SVPD	1.0232	1.0191	1.0233	1.0234
	TZVP	1.0193	1.0289	1.0194	1.0193
	TZVPD	1.0197	1.0292	1.0198	1.0197
	TZVPP	1.0181	1.0274	1.0182	1.0181
	TZVPPD	1.0184	1.0276	1.0185	1.0184
	QZVP	1.0191	1.0287	1.0192	1.0192
	QZVPD	1.0194	1.0289	1.0195	1.0194
	QZVPP	1.0191	1.0287	1.0192	1.0191
	QZVPPD	1.0194	1.0289	1.0195	1.0194
HCTH	SVP	0.9998	0.9951	0.9999	0.9999
	SVPD	1.0021	0.9976	1.0023	1.0023
	TZVP	1.0006	1.0019	1.0007	1.0006
	TZVPD	1.0010	1.0107	1.0012	1.0010
	TZVPP	0.9996	1.0091	0.9997	0.9996
	TZVPPD	1.0000	1.0094	1.0001	1.0000
	QZVP	1.0004	1.0108	1.0006	1.0004
	QZVPD	1.0007	1.0109	1.0008	1.0007
	QZVPP	1.0004	1.0108	1.0006	1.0004
	QZVPPD	1.0007	1.0109	1.0008	1.0007
M06-L	SVP	0.9857	0.9840	0.9859	0.9858
	SVPD	0.9892	0.9883	0.9894	0.9894
	TZVP	0.9823	0.9937	0.9825	0.9823
	TZVPD	0.9828	0.9941	0.9829	0.9828
	TZVPP	0.9818	0.9929	0.9819	0.9818
	TZVPPD	0.9823	0.9934	0.9824	0.9823
	QZVP	0.9813	0.9931	0.9813	0.9813
	QZVPD	0.9814	0.9932	0.9814	0.9814
	QZVPP	0.9813	0.9931	0.9813	0.9813
	QZVPPD	0.9814	0.9932	0.9814	0.9814

Functional	**Basis Set**	**none[a]**	**def2-SV/TZV**	**W06**	**auto**
M06-L_{D3}	SVP	0.9857	0.9976	0.9859	0.9858
	SVPD	0.9893	1.0014	0.9894	0.9894
	TZVP	0.9823	0.9973	0.9825	0.9823
	TZVPD	0.9828	0.9941	0.9829	0.9828
	TZVPP	0.9818	0.9929	0.9819	0.9818
	TZVPPD	0.9823	0.9934	0.9824	0.9823
	QZVP	0.9813	0.9931	0.9813	0.9813
	QZVPD	0.9814	0.9932	0.9814	0.9814
	QZVPP	0.9813	0.9931	0.9813	0.9813
	QZVPPD	0.9814	0.9932	0.9814	0.9814
M11-L	SVP	0.9960	0.9967	0.9962	0.9961
	SVPD	0.9993	1.0026	0.9995	0.9995
	TZVP	0.9913	1.0037	0.9915	0.9913
	TZVPD	0.9918	1.0040	0.9920	0.9918
	TZVPP	0.9925	1.0047	0.9927	0.9925
	TZVPPD	0.9926	1.0048	0.9928	0.9926
	QZVP	0.9914	1.0039	0.9915	0.9914
	QZVPD	0.9922	1.0046	0.9923	0.9922
	QZVPP	0.9914	1.0039	0.9915	0.9914
	QZVPPD	0.9922	1.0046	0.9923	0.9922
MN12-L	SVP	0.9734	0.9755	0.9735	0.9735
	SVPD	0.9768	0.9807	0.9769	0.9769
	TZVP	0.9750	0.9868	0.9751	0.9750
	TZVPD	0.9750	0.9867	0.9751	0.9750
	TZVPP	0.9750	0.9864	0.9751	0.9750
	TZVPPD	0.9751	0.9865	0.9752	0.9751
	QZVP	0.9754	0.9870	0.9755	0.9754
	QZVPD	0.9756	0.9872	0.9758	0.9757
	QZVPP	0.9754	0.9870	0.9755	0.9754
	QZVPPD	0.9756	0.9872	0.9758	0.9757

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
MN15-L	SVP	0.9814	0.9930	0.9815	0.9814
	SVPD	0.9852	0.9968	0.9854	0.9854
	TZVP	0.9856	0.9966	0.9858	0.9856
	TZVPD	0.9863	0.9971	0.9865	0.9863
	TZVPP	0.9849	0.9953	0.9851	0.9849
	TZVPPD	0.9853	0.9956	0.9855	0.9853
	QZVP	0.9869	0.9986	0.9871	0.9869
	QZVPD	0.9871	0.9987	0.9872	0.9871
	QZVPP	0.9869	0.9986	0.9871	0.9869
	QZVPPD	0.9871	0.9987	0.9872	0.9871
mPWPW91	SVP	1.0159	1.0267	1.0160	1.0160
	SVPD	1.0182	1.0286	1.0183	1.0183
	TZVP	1.0147	1.0244	1.0148	1.0148
	TZVPD	1.0151	1.0247	1.0152	1.0152
	TZVPP	1.0136	1.0229	1.0137	1.0137
	TZVPPD	1.0138	1.0231	1.0140	1.0140
	QZVP	1.0145	1.0243	1.0146	1.0146
	QZVPD	1.0148	1.0244	1.0149	1.0149
	QZVPP	1.0145	1.0243	1.0146	1.0146
	QZVPPD	1.0148	1.0244	1.0149	1.0149
N12	SVP	0.9943	0.9901	0.9944	0.9944
	SVPD	0.9961	0.9916	0.9963	0.9963
	TZVP	0.9912	1.0004	0.9913	0.9912
	TZVPD	0.9913	1.0003	0.9914	0.9913
	TZVPP	0.9898	0.9985	0.9898	0.9898
	TZVPPD	0.9900	0.9986	0.9900	0.9900
	QZVP	0.9903	0.9993	0.9903	0.9903
	QZVPD	0.9905	0.9994	0.9906	0.9905
	QZVPP	0.9903	0.9993	0.9903	0.9903
	QZVPPD	0.9905	0.9994	0.9906	0.9905

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
OLYP	SVP	1.0076	1.0188	1.0078	1.0077
	SVPD	1.0099	1.0206	1.0101	1.0101
	TZVP	1.0082	1.0183	1.0084	1.0082
	TZVPD	1.0086	1.0184	1.0087	1.0086
	TZVPP	1.0072	1.0169	1.0074	1.0072
	TZVPPD	1.0076	1.0172	1.0078	1.0076
	QZVP	1.0080	1.0184	1.0081	1.0080
	QZVPD	1.0082	1.0185	1.0084	1.0082
	QZVPP	1.0080	1.0184	1.0081	1.0080
	QZVPPD	1.0082	1.0185	1.0084	1.0082
PBE	SVP	1.0180	1.0148	1.0181	1.0181
	SVPD	1.0204	1.0166	1.0205	1.0205
	TZVP	1.0172	1.0269	1.0173	1.0172
	TZVPD	1.0176	1.0272	1.0177	1.0176
	TZVPP	1.0161	1.0254	1.0162	1.0161
	TZVPPD	1.0164	1.0256	1.0165	1.0164
	QZVP	1.0171	1.0270	1.0173	1.0171
	QZVPD	1.0174	1.0271	1.0175	1.0174
	QZVPP	1.0171	1.0270	1.0173	1.0171
	QZVPPD	1.0174	1.0271	1.0175	1.0174
PBE_{D3BJ}	SVP	1.0179	1.0288	1.0181	1.0181
	SVPD	1.0203	1.0307	1.0205	1.0205
	TZVP	1.0172	1.0269	1.0173	1.0173
	TZVPD	1.0176	1.0271	1.0177	1.0177
	TZVPP	1.0160	1.0253	1.0161	1.0161
	TZVPPD	1.0163	1.0256	1.0164	1.0164
	QZVP	1.0171	1.0269	1.0172	1.0172
	QZVPD	1.0173	1.0270	1.0174	1.0174
	QZVPP	1.0171	1.0269	1.0172	1.0172
	QZVPPD	1.0173	1.0270	1.0174	1.0174

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
revTPSS	SVP	1.0007	0.9955	1.0008	1.0001
	SVPD	1.0030	0.9978	1.0031	1.0031
	TZVP	1.0013	1.0119	1.0015	1.0013
	TZVPD	1.0016	1.0122	1.0017	1.0016
	TZVPP	1.0006	1.0111	1.0007	1.0006
	TZVPPD	1.0008	1.0112	1.0009	1.0008
	QZVP	1.0007	1.0113	1.0008	1.0007
	QZVPD	1.0009	1.0114	1.0010	1.0009
	QZVPP	1.0007	1.0113	1.0008	1.0007
	QZVPPD	1.0009	1.0114	1.0010	1.0009
SOGGA11	SVP	1.0113	1.0221	1.0114	1.0113
	SVPD	1.0054	1.0158	1.0056	1.0055
	TZVP	1.0081	1.0179	1.0082	1.0081
	TZVPD	1.0099	1.0188	1.0101	1.0099
	TZVPP	1.0101	1.0194	1.0102	1.0101
	TZVPPD	1.0089	1.0179	1.0101	1.0089
	QZVP	1.0103	1.0215	1.0107	1.0103
	QZVPD	1.0128	1.0232	1.0137	1.0128
	QZVPP	1.0103	1.0215	1.0107	1.0103
	QZVPPD	1.0128	1.0232	1.0137	1.0128
TPSS	SVP	1.0018	0.9968	1.0019	1.0019
	SVPD	1.0040	0.9991	1.0042	1.0042
	TZVP	1.0019	1.0123	1.0021	1.0020
	TZVPD	1.0023	1.0127	1.0024	1.0023
	TZVPP	1.0013	1.0116	1.0014	1.0130
	TZVPPD	1.0015	1.0118	1.0017	1.0015
	QZVP	1.0015	1.0119	1.0016	1.0015
	QZVPD	1.0017	1.0120	1.0018	1.0017
	QZVPP	1.0015	1.0119	1.0016	1.0015
	QZVPPD	1.0017	1.0120	1.0018	1.0017

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
$TPSS_{D3BJ}$	SVP	1.0017	0.9968	1.0019	1.0018
	SVPD	1.0040	0.9990	1.0041	1.0042
	TZVP	1.0017	1.0120	1.0018	1.0017
	TZVPD	1.0022	1.0126	1.0024	1.0022
	TZVPP	1.0013	1.0115	1.0014	1.0013
	TZVPPD	1.0015	1.0117	1.0016	1.0015
	QZVP	1.0015	1.0119	1.0016	1.0015
	QZVPD	1.0017	1.0120	1.0018	1.0015
	QZVPP	1.0015	1.0119	1.0016	1.0015
	QZVPPD	1.0017	1.0120	1.0018	1.0017
VSXC	SVP	0.9944	1.0055	0.9945	0.9945
	SVPD	0.9976	1.0083	0.9977	0.9977
	TZVP	0.9944	1.0043	0.9945	0.9945
	TZVPD	0.9950	1.0047	0.9951	0.9951
	TZVPP	0.9930	1.0027	0.9932	0.9932
	TZVPPD	0.9935	1.0030	0.9936	0.9936
	QZVP	0.9942	1.0045	0.9943	0.9943
	QZVPD	0.9944	1.0046	0.9945	0.9945
	QZVPP	0.9942	1.0045	0.9943	0.9943
	QZVPPD	0.9944	1.0046	0.9945	0.9945
XLYP	SVP	1.0236	1.0346	1.0238	1.0238
	SVPD	1.0253	1.0357	1.0255	1.0255
	TZVP	1.0199	1.0292	1.0199	1.0199
	TZVPD	1.0200	1.0292	1.0201	1.0201
	TZVPP	1.0182	1.0271	1.0183	1.0183
	TZVPPD	1.0184	1.0272	1.0185	1.0185
	QZVP	1.0192	1.0284	1.0193	1.0193
	QZVPD	1.0194	1.0285	1.0195	1.0195
	QZVPP	1.0192	1.0284	1.0193	1.0193
	QZVPPD	1.0194	1.0285	1.0195	1.0195

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
τHCTH	SVP	1.0032	0.9990	1.0033	1.0033
	SVPD	1.0058	1.0020	1.0059	1.0059
	TZVP	1.0031	1.0127	1.0033	1.0032
	TZVPD	1.0035	1.0130	1.0037	1.0035
	TZVPP	1.0024	1.0119	1.0025	1.0024
	TZVPPD	1.0026	1.0121	1.0027	1.0026
	QZVP	1.0024	1.0130	1.0025	1.0024
	QZVPD	1.0027	1.0130	1.0027	1.0027
	QZVPP	1.0024	1.0130	1.0025	1.0024
	QZVPPD	1.0027	1.0130	1.0027	1.0027

[a] Not using any density fitting.

Table S5. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{ZPE} for various GGA and meta-GGA exchange–correlation functional–basis set–density fitting basis set combinations.

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
B97-D	SVP	0.14	0.26	0.14	13.18
	SVPD	0.13	0.24	0.14	12.99
	TZVP	0.10	0.24	0.10	12.23
	TZVPD	0.11	0.25	0.11	13.08
	TZVPP	0.11	0.25	0.11	13.10
	TZVPPD	0.11	0.25	0.11	13.08
	QZVP	0.11	0.25	0.11	13.06
	QZVPD	0.11	0.25	0.11	13.09
	QZVPP	0.11	0.25	0.11	13.09
	QZVPPD	0.11	0.25	0.11	13.09
BLYP	SVP	0.15	0.29	0.15	0.15
	SVPD	0.13	0.27	0.13	0.13
	TZVP	0.12	0.28	0.12	0.12
	TZVPD	0.12	0.29	0.13	0.12
	TZVPP	0.12	0.29	0.12	0.12
	TZVPPD	0.12	0.29	0.12	0.12
	QZVP	0.12	0.29	0.12	0.12
	QZVPD	0.12	0.29	0.12	0.12
	QZVPP	0.12	0.29	0.12	0.12
	QZVPPD	0.12	0.29	0.12	0.12

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
BP86	SVP	0.13	0.63	0.13	0.13
	SVPD	0.11	0.69	0.11	0.11
	TZVP	0.09	0.22	0.09	0.09
	TZVPD	0.09	0.23	0.09	0.09
	TZVPP	0.09	0.23	0.09	0.09
	TZVPPD	0.09	0.23	0.09	0.09
	QZVP	0.09	0.23	0.09	0.09
	QZVPD	0.09	0.23	0.09	0.09
	QZVPP	0.09	0.23	0.09	0.09
	QZVPPD	0.09	0.23	0.09	0.09
HCTH	SVP	0.16	0.56	0.16	0.16
	SVPD	0.14	0.66	0.14	0.14
	TZVP	0.10	0.69	0.10	0.10
	TZVPD	0.11	0.19	0.11	0.11
	TZVPP	0.11	0.18	0.11	0.11
	TZVPPD	0.11	0.19	0.12	0.11
	QZVP	0.11	0.19	0.11	0.11
	QZVPD	0.11	0.19	0.11	0.11
	QZVPP	0.11	0.19	0.11	0.11
	QZVPPD	0.11	0.19	0.11	0.11
M06-L	SVP	0.14	0.53	0.14	0.14
	SVPD	0.14	0.65	0.14	0.14
	TZVP	0.11	0.19	0.11	0.11
	TZVPD	0.12	0.20	0.12	0.12
	TZVPP	0.11	0.20	0.11	0.11
	TZVPPD	0.11	0.19	0.11	0.11
	QZVP	0.10	0.20	0.10	0.10
	QZVPD	0.10	0.19	0.10	0.10
	QZVPP	0.10	0.20	0.10	0.10
	QZVPPD	0.10	0.19	0.10	0.10

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
M06-L_{D3}	SVP	0.17	0.21	0.14	0.14
	SVPD	0.17	0.22	0.14	0.14
	TZVP	0.13	0.21	0.11	0.11
	TZVPD	0.14	0.22	0.12	0.12
	TZVPP	0.13	0.21	0.11	0.11
	TZVPPD	0.13	0.21	0.11	0.11
	QZVP	0.12	0.22	0.10	0.10
	QZVPD	0.12	0.21	0.10	0.10
	QZVPP	0.12	0.22	0.10	0.10
	QZVPPD	0.12	0.21	0.10	0.10
M11-L	SVP	0.27	0.55	0.27	0.27
	SVPD	0.26	0.69	0.26	0.26
	TZVP	0.23	0.21	0.23	0.23
	TZVPD	0.23	0.22	0.23	0.23
	TZVPP	0.24	0.22	0.24	0.24
	TZVPPD	0.24	0.22	0.24	0.24
	QZVP	0.23	0.19	0.23	0.23
	QZVPD	0.23	0.19	0.23	0.23
	QZVPP	0.23	0.19	0.23	0.23
	QZVPPD	0.23	0.19	0.23	0.23
MN12-L	SVP	0.15	0.53	0.15	0.15
	SVPD	0.14	0.65	0.14	0.14
	TZVP	0.13	0.21	0.13	0.13
	TZVPD	0.13	0.22	0.13	0.13
	TZVPP	0.14	0.22	0.14	0.14
	TZVPPD	0.14	0.22	0.14	0.14
	QZVP	0.14	0.22	0.14	0.14
	QZVPD	0.14	0.22	0.14	0.14
	QZVPP	0.14	0.22	0.14	0.14
	QZVPPD	0.14	0.22	0.14	0.14

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
MN15-L	SVP	0.17	0.19	0.17	13.18
	SVPD	0.15	0.18	0.15	12.44
	TZVP	0.14	0.19	0.14	11.75
	TZVPD	0.14	0.21	0.14	12.90
	TZVPP	0.15	0.21	0.15	12.91
	TZVPPD	0.15	0.21	0.15	12.88
	QZVP	0.15	0.21	0.15	12.88
	QZVPD	0.15	0.21	0.15	12.74
	QZVPP	0.15	0.21	0.15	12.74
	QZVPPD	0.15	0.21	0.15	12.74
mPWPW91	SVP	0.13	0.24	0.13	13.18
	SVPD	0.11	0.22	0.11	13.02
	TZVP	0.08	0.22	0.08	11.98
	TZVPD	0.09	0.23	0.09	13.11
	TZVPP	0.09	0.23	0.09	13.13
	TZVPPD	0.09	0.23	0.09	13.12
	QZVP	0.09	0.23	0.09	13.10
	QZVPD	0.09	0.23	0.09	13.11
	QZVPP	0.09	0.23	0.09	13.11
	QZVPPD	0.09	0.23	0.09	13.11
N12	SVP	0.13	0.57	0.13	13.18
	SVPD	0.11	0.64	0.11	12.16
	TZVP	0.07	0.18	0.08	10.26
	TZVPD	0.08	0.20	0.08	11.85
	TZVPP	0.08	0.20	0.08	12.10
	TZVPPD	0.09	0.20	0.09	12.00
	QZVP	0.08	0.20	0.08	12.00
	QZVPD	0.08	0.20	0.08	11.99
	QZVPP	0.08	0.20	0.08	11.98
	QZVPPD	0.08	0.20	0.08	11.99

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
OLYP	SVP	0.13	0.22	0.13	13.18
	SVPD	0.10	0.20	0.11	12.91
	TZVP	0.08	0.18	0.08	11.39
	TZVPD	0.08	0.20	0.08	12.75
	TZVPP	0.08	0.19	0.08	12.81
	TZVPPD	0.09	0.20	0.09	12.90
	QZVP	0.08	0.20	0.08	12.83
	QZVPD	0.08	0.20	0.08	12.83
	QZVPP	0.08	0.20	0.08	12.83
	QZVPPD	0.08	0.20	0.08	12.83
PBE	SVP	0.14	0.62	0.14	13.18
	SVPD	0.11	0.68	0.11	12.88
	TZVP	0.08	0.21	0.09	11.72
	TZVPD	0.09	0.22	0.09	12.97
	TZVPP	0.09	0.22	0.09	13.02
	TZVPPD	0.09	0.22	0.09	13.00
	QZVP	0.09	0.22	0.09	12.97
	QZVPD	0.09	0.22	0.09	12.97
	QZVPP	0.09	0.22	0.09	12.96
	QZVPPD	0.09	0.22	0.09	12.97
PBE_{D3BJ}	SVP	0.14	0.23	0.14	13.18
	SVPD	0.11	0.21	0.11	12.85
	TZVP	0.08	0.21	0.09	11.67
	TZVPD	0.09	0.22	0.09	12.97
	TZVPP	0.09	0.22	0.09	13.02
	TZVPPD	0.09	0.22	0.09	12.99
	QZVP	0.09	0.22	0.09	12.97
	QZVPD	0.09	0.22	0.09	12.97
	QZVPP	0.09	0.22	0.09	12.96
	QZVPPD	0.09	0.22	0.09	12.97

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
revTPSS	SVP	0.13	0.65	0.13	13.18
	SVPD	0.12	0.71	0.12	12.49
	TZVP	0.10	0.26	0.10	13.01
	TZVPD	0.11	0.26	0.11	11.81
	TZVPP	0.10	0.26	0.10	11.87
	TZVPPD	0.10	0.26	0.10	11.79
	QZVP	0.10	0.26	0.10	11.85
	QZVPD	0.10	0.26	0.10	11.62
	QZVPP	0.10	0.26	0.10	11.68
	QZVPPD	0.10	0.26	0.10	11.62
SOGGA11	SVP	0.19	0.22	0.19	13.18
	SVPD	0.15	0.23	0.15	11.77
	TZVP	0.10	0.18	0.10	10.75
	TZVPD	0.10	0.17	0.10	12.28
	TZVPP	0.14	0.22	0.14	11.28
	TZVPPD	0.12	0.21	0.12	12.33
	QZVP	0.16	0.23	0.17	12.68
	QZVPD	0.31	0.24	0.30	11.94
	QZVPP	0.16	0.23	0.17	12.25
	QZVPPD	0.31	0.24	0.30	11.94
TPSS	SVP	0.13	0.64	0.13	13.18
	SVPD	0.12	0.71	0.12	12.84
	TZVP	0.09	0.25	0.09	13.17
	TZVPD	0.10	0.26	0.10	12.42
	TZVPP	0.10	0.25	0.10	12.44
	TZVPPD	0.10	0.25	0.10	12.40
	QZVP	0.10	0.26	0.10	12.45
	QZVPD		0.26	0.10	12.25
	QZVPP		0.26	0.10	12.29
	QZVPPD		0.26	0.10	12.25

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
$TPSS_{D3BJ}$	SVP	0.13	0.64	0.13	13.18
	SVPD	0.12	0.71	0.12	12.84
	TZVP	0.10	0.26	0.10	13.17
	TZVPD	0.10	0.26	0.10	12.28
	TZVPP	0.10	0.25	0.10	12.43
	TZVPPD	0.10	0.25	0.10	12.39
	QZVP	0.10	0.26	0.10	12.45
	QZVPD	0.10	0.26	0.10	12.24
	QZVPP	0.10	0.26	0.10	12.28
	QZVPPD	0.10	0.26	0.10	12.24
VSXC	SVP	0.15	0.22	0.15	13.18
	SVPD	0.12	0.21	0.13	12.46
	TZVP	0.10	0.20	0.10	11.22
	TZVPD	0.10	0.22	0.10	12.55
	TZVPP	0.10	0.21	0.11	12.66
	TZVPPD	0.11	0.22	0.11	12.68
	QZVP	0.10	0.21	0.10	12.66
	QZVPD	0.10	0.21	0.10	12.69
	QZVPP	0.10	0.21	0.10	12.67
	QZVPPD	0.10	0.21	0.10	12.69
XLYP	SVP	0.15	0.29	0.15	13.18
	SVPD	0.13	0.27	0.13	13.13
	TZVP	0.12	0.28	0.12	12.91
	TZVPD	0.12	0.29	0.13	12.86
	TZVPP	0.12	0.28	0.12	12.86
	TZVPPD	0.12	0.29	0.12	12.89
	QZVP	0.11	0.28	0.12	12.93
	QZVPD	0.12	0.29	0.12	12.85
	QZVPP	0.11	0.28	0.12	12.87
	QZVPPD	0.12	0.29	0.12	12.85

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
τHCTH	SVP	0.14	0.58	0.14	13.18
	SVPD	0.12	0.67	0.12	12.83
	TZVP	0.09	0.19	0.10	11.93
	TZVPD	0.10	0.20	0.10	12.75
	TZVPP	0.10	0.20	0.10	12.82
	TZVPPD	0.10	0.20	0.10	12.82
	QZVP	0.09	0.20	0.10	12.79
	QZVPD	0.09	0.20	0.10	12.92
	QZVPP	0.09	0.20	0.10	12.91
	QZVPPD	0.09	0.20	0.10	12.92

[a] Not using any density fitting.

Table S6. λ_{fund} scale factors for various GGA and meta-GGA exchange–correlation functional–basis set–density fitting basis set combinations.

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
B97-D	SVP	0.9896	0.9993	0.9897	0.9897
	SVPD	0.9895	0.9979	0.9896	0.9896
	TZVP	0.9895	0.9975	0.9896	0.9896
	TZVPD	0.9900	0.9977	0.9901	0.9901
	TZVPP	0.9886	0.9962	0.9886	0.9886
	TZVPPD	0.9887	0.9961	0.9888	0.9888
	QZVP	0.9892	0.9971	0.9893	0.9893
	QZVPD	0.9894	0.9971	0.9895	0.9895
	QZVPP	0.9892	0.9971	0.9893	0.9893
	QZVPPD	0.9894	0.9971	0.9895	0.9895
BLYP	SVP	1.0013	1.0112	1.0014	1.0015
	SVPD	0.9997	1.0080	0.9998	0.9999
	TZVP	0.9986	1.0062	0.9986	0.9986
	TZVPD	0.9988	1.0061	0.9989	0.9988
	TZVPP	0.9969	1.0040	0.9969	0.9969
	TZVPPD	0.9970	1.0039	0.9970	0.9970
	QZVP	0.9979	1.0053	0.9979	0.9979
	QZVPD	0.9981	1.0054	0.9981	0.9981
	QZVPP	0.9979	1.0053	0.9979	0.9979
	QZVPPD	0.9981	1.0054	0.9981	0.9981

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
BP86	SVP	0.9956	0.9864	0.9957	0.9958
	SVPD	0.9956	0.9855	0.9957	0.9958
	TZVP	0.9953	1.0033	0.9954	0.9954
	TZVPD	0.9958	1.0035	0.9959	0.9958
	TZVPP	0.9942	1.0017	0.9942	0.9942
	TZVPPD	0.9943	1.0017	0.9944	0.9944
	QZVP	0.9952	1.0030	0.9952	0.9952
	QZVPD	0.9954	1.0031	0.9954	0.9954
	QZVPP	0.9952	1.0030	0.9952	0.9952
	QZVPPD	0.9954	1.0031	0.9954	0.9954
HCTH	SVP	0.9725	0.9628	0.9726	0.9727
	SVPD	0.9726	0.9623	0.9727	0.9728
	TZVP	0.9747	0.9686	0.9748	0.9747
	TZVPD	0.9752	0.9830	0.9754	0.9752
	TZVPP	0.9739	0.9816	0.9740	0.9739
	TZVPPD	0.9741	0.9817	0.9743	0.9742
	QZVP	0.9746	0.9831	0.9747	0.9746
	QZVPD	0.9748	0.9832	0.9749	0.9748
	QZVPP	0.9746	0.9831	0.9747	0.9746
	QZVPPD	0.9748	0.9832	0.9749	0.9748
M06-L	SVP	0.9587	0.9522	0.9588	0.9589
	SVPD	0.9607	0.9532	0.9608	0.9608
	TZVP	0.9594	0.9691	0.9595	0.9594
	TZVPD	0.9598	0.9693	0.9599	0.9598
	TZVPP	0.9579	0.9672	0.9580	0.9579
	TZVPPD	0.9584	0.9675	0.9585	0.9584
	QZVP	0.9574	0.9672	0.9575	0.9574
	QZVPD	0.9575	0.9673	0.9575	0.9575
	QZVPP	0.9574	0.9672	0.9575	0.9574
	QZVPPD	0.9575	0.9673	0.9575	0.9575

Functional	**Basis Set**	**none[a]**	**def2-SV/TZV**	**W06**	**auto**
M06-L_{D3}	SVP	0.9587	0.9689	0.9589	0.9958
	SVPD	0.9607	0.9703	0.9608	0.9608
	TZVP	0.9594	0.9691	0.9595	0.9594
	TZVPD	0.9598	0.9693	0.9600	0.9598
	TZVPP	0.9579	0.9672	0.9580	0.9579
	TZVPPD	0.9584	0.9675	0.9585	0.9584
	QZVP	0.9574	0.9672	0.9575	0.9574
	QZVPD	0.9575	0.9673	0.9575	0.9575
	QZVPP	0.9574	0.9672	0.9575	0.9574
	QZVPPD	0.9575	0.9673	0.9575	0.9575
M11-L	SVP	0.9617	0.9563	0.9619	0.9619
	SVPD	0.9636	0.9580	0.9638	0.9638
	TZVP	0.9603	0.9709	0.9604	0.9603
	TZVPD	0.9609	0.9711	0.9610	0.9609
	TZVPP	0.9613	0.9715	0.9614	0.9613
	TZVPPD	0.9613	0.9714	0.9615	0.9613
	QZVP	0.9606	0.9710	0.9607	0.9606
	QZVPD	0.9611	0.9715	0.9612	0.9611
	QZVPP	0.9606	0.9710	0.9607	0.9606
	QZVPPD	0.9611	0.9715	0.9612	0.9611
MN12-L	SVP	0.9474	0.9454	0.9475	0.9476
	SVPD	0.9492	0.9470	0.9493	0.9494
	TZVP	0.9508	0.9610	0.9509	0.9508
	TZVPD	0.9510	0.9610	0.9511	0.9510
	TZVPP	0.9503	0.9599	0.9504	0.9503
	TZVPPD	0.9503	0.9598	0.9504	0.9503
	QZVP	0.9505	0.9601	0.9506	0.9505
	QZVPD	0.9507	0.9602	0.9508	0.9507
	QZVPP	0.9505	0.9601	0.9506	0.9505
	QZVPPD	0.9507	0.9602	0.9508	0.9507

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
MN15-L	SVP	0.9540	0.9640	0.9541	0.9542
	SVPD	0.9564	0.9655	0.9565	0.9565
	TZVP	0.9606	0.9698	0.9608	0.9606
	TZVPD	0.9613	0.9702	0.9615	0.9613
	TZVPP	0.9597	0.9682	0.9598	0.9597
	TZVPPD	0.9600	0.9685	0.9602	0.9601
	QZVP	0.9611	0.9709	0.9613	0.9611
	QZVPD	0.9613	0.9710	0.9614	0.9613
	QZVPP	0.9611	0.9709	0.9613	0.9611
	QZVPPD	0.9613	0.9710	0.9614	0.9613
mPWPW91	SVP	0.9908	1.0004	0.9909	0.9909
	SVPD	0.9906	0.9989	0.9907	0.9907
	TZVP	0.9905	0.9985	0.9906	0.9906
	TZVPD	0.9910	0.9988	0.9911	0.9911
	TZVPP	0.9894	0.9971	0.9895	0.9895
	TZVPPD	0.9896	0.9971	0.9897	0.9897
	QZVP	0.9904	0.9984	0.9905	0.9905
	QZVPD	0.9906	0.9984	0.9907	0.9907
	QZVPP	0.9904	0.9984	0.9905	0.9905
	QZVPPD	0.9906	0.9984	0.9907	0.9907
N12	SVP	0.9668	0.9587	0.9669	0.9670
	SVPD	0.9659	0.9572	0.9660	0.9661
	TZVP	0.9653	0.9728	0.9654	0.9653
	TZVPD	0.9657	0.9729	0.9657	0.9657
	TZVPP	0.9639	0.9710	0.9639	0.9690
	TZVPPD	0.9641	0.9709	0.9641	0.9641
	QZVP	0.9644	0.9718	0.9644	0.9644
	QZVPD	0.9647	0.9719	0.9647	0.9647
	QZVPP	0.9644	0.9718	0.9644	0.9644
	QZVPPD	0.9647	0.9719	0.9647	0.9647

Functional	**Basis Set**	**none[a]**	**def2-SV/TZV**	**W06**	**auto**
OLYP	SVP	0.9821	0.9920	0.9822	0.9823
	SVPD	0.9818	0.9901	0.9819	0.9819
	TZVP	0.9832	0.9914	0.9833	0.9832
	TZVPD	0.9836	0.9916	0.9838	0.9836
	TZVPP	0.9825	0.9905	0.9826	0.9825
	TZVPPD	0.9827	0.9905	0.9829	0.9827
	QZVP	0.9831	0.9918	0.9833	0.9831
	QZVPD	0.9833	0.9918	0.9835	0.9833
	QZVPP	0.9831	0.9918	0.9833	0.9831
	QZVPPD	0.9833	0.9918	0.9835	0.9833
PBE	SVP	0.9920	0.9831	0.9921	0.9922
	SVPD	0.9919	0.9821	0.9920	0.9921
	TZVP	0.9924	1.0003	0.9925	0.9924
	TZVPD	0.9929	1.0006	0.9930	0.9929
	TZVPP	0.9913	0.9989	0.9914	0.9913
	TZVPPD	0.9915	0.9989	0.9915	0.9915
	QZVP	0.9923	1.0003	0.9924	0.9923
	QZVPD	0.9925	1.0004	0.9926	0.9925
	QZVPP	0.9923	1.0003	0.9924	0.9923
	QZVPPD	0.9925	1.0004	0.9926	0.9925
PBE_{D3BJ}	SVP	0.9920	1.0016	0.9921	0.9921
	SVPD	0.9919	1.0001	0.9920	0.9920
	TZVP	0.9923	1.0003	0.9924	0.9924
	TZVPD	0.9928	1.0005	0.9929	0.9929
	TZVPP	0.9912	0.9988	0.9913	0.9913
	TZVPPD	0.9914	0.9988	0.9915	0.9915
	QZVP	0.9923	1.0003	0.9923	0.9923
	QZVPD	0.9925	1.0004	0.9926	0.9926
	QZVPP	0.9923	1.0003	0.9923	0.9923
	QZVPPD	0.9925	1.0004	0.9926	0.9926

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
revTPSS	SVP	0.9811	0.9706	0.9812	0.9813
	SVPD	0.9814	0.9704	0.9815	0.9816
	TZVP	0.9822	0.9912	0.9823	0.9822
	TZVPD	0.9825	0.9914	0.9827	0.9825
	TZVPP	0.9815	0.9904	0.9816	0.9815
	TZVPPD	0.9816	0.9903	0.9817	0.9816
	QZVP	0.9818	0.9908	0.9819	0.9818
	QZVPD	0.9820	0.9908	0.9820	0.9820
	QZVPP	0.9818	0.9908	0.9819	0.9818
	QZVPPD	0.9820	0.9908	0.9820	0.9820
SOGGA11	SVP	0.9804	0.9898	0.9805	0.9806
	SVPD	0.9737	0.9822	0.9739	0.9739
	TZVP	0.9816	0.9891	0.9817	0.9816
	TZVPD	0.9817	0.9887	0.9819	0.9818
	TZVPP	0.9826	0.9899	0.9827	0.9826
	TZVPPD	0.9828	0.9890	0.9840	0.9828
	QZVP	0.9810	0.9897	0.9813	0.9810
	QZVPD	0.9803	0.9887	0.9810	0.9803
	QZVPP	0.9810	0.9897	0.9813	0.9810
	QZVPPD	0.9803	0.9887	0.9810	0.9803
TPSS	SVP	0.9810	0.9709	0.9811	0.9812
	SVPD	0.9812	0.9705	0.9813	0.9814
	TZVP	0.9814	0.9902	0.9816	0.9815
	TZVPD	0.9819	0.9904	0.9820	0.9819
	TZVPP	0.9809	0.9895	0.9810	0.9809
	TZVPPD	0.9810	0.9894	0.9811	0.9811
	QZVP	0.9813	0.9900	0.9814	0.9813
	QZVPD	0.9815	0.9900	0.9816	0.9815
	QZVPP	0.9813	0.9900	0.9814	0.9813
	QZVPPD	0.9815	0.9900	0.9816	0.9815

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
$TPSS_{D3BJ}$	SVP	0.9810	0.9709	0.9811	0.9812
	SVPD	0.9812	0.9705	0.9813	0.9814
	TZVP	0.9815	0.9900	0.9815	0.9815
	TZVPD	0.9818	0.9904	0.9819	0.9818
	TZVPP	0.9809	0.9894	0.9810	0.9809
	TZVPPD	0.9810	0.9894	0.9811	0.9810
	QZVP	0.9813	0.9899	0.9814	0.9813
	QZVPD	0.9815	0.9900	0.9815	0.9815
	QZVPP	0.9813	0.9899	0.9814	0.9813
	QZVPPD	0.9815	0.9900	0.9815	0.9815
VSXC	SVP	0.9676	0.9769	0.9677	0.9677
	SVPD	0.9686	0.9766	0.9687	0.9687
	TZVP	0.9688	0.9766	0.9690	0.9690
	TZVPD	0.9696	0.9771	0.9697	0.9697
	TZVPP	0.9678	0.9753	0.9679	0.9679
	TZVPPD	0.9681	0.9755	0.9682	0.9682
	QZVP	0.9690	0.9772	0.9690	0.9690
	QZVPD	0.9691	0.9773	0.9692	0.9692
	QZVPP	0.9690	0.9772	0.9690	0.9690
	QZVPPD	0.9691	0.9773	0.9692	0.9692
XLYP	SVP	1.0013	1.0111	1.0014	1.0014
	SVPD	0.9996	1.0078	0.9997	0.9997
	TZVP	0.9984	1.0060	0.9985	0.9985
	TZVPD	0.9987	1.0060	0.9988	0.9988
	TZVPP	0.9968	1.0039	0.9968	0.9968
	TZVPPD	0.9968	1.0037	0.9969	0.9969
	QZVP	0.9978	1.0052	0.9978	0.9978
	QZVPD	0.9980	1.0052	0.9980	0.9980
	QZVPP	0.9978	1.0052	0.9978	0.9978
	QZVPPD	0.9980	1.0052	0.9980	0.9980

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
τHCTH	SVP	0.9774	0.9681	0.9775	0.9776
	SVPD	0.9780	0.9679	0.9781	0.9782
	TZVP	0.9779	0.9857	0.9780	0.9779
	TZVPD	0.9784	0.9860	0.9785	0.9784
	TZVPP	0.9772	0.9849	0.9773	0.9773
	TZVPPD	0.9774	0.9849	0.9775	0.9774
	QZVP	0.9777	0.9860	0.9777	0.9777
	QZVPD	0.9779	0.9860	0.9779	0.9779
	QZVPP	0.9777	0.9860	0.9777	0.9777
	QZVPPD	0.9779	0.9860	0.9779	0.9779

[a] Not using any density fitting.

Table S7. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{fund} for various GGA and meta-GGA exchange–correlation functional–basis set–density fitting basis set combinations.

Functional	**Basis Set**	**none**[a]	**def2-SV/TZV**	**W06**	**auto**
B97-D	SVP	36.47	59.47	36.36	36.36
	SVPD	38.55	61.21	38.48	38.48
	TZVP	26.44	52.24	26.35	26.35
	TZVPD	25.22	52.43	25.19	25.19
	TZVPP	26.25	51.60	26.19	26.19
	TZVPPD	26.19	51.73	26.17	26.17
	QZVP	25.37	51.33	25.37	25.37
	QZVPD	25.17	51.35	25.17	25.17
	QZVPP	25.37	51.33	25.37	25.37
	QZVPPD	25.17	51.35	25.17	25.17
BLYP	SVP	37.79	68.84	37.73	38.08
	SVPD	40.68	68.76	40.62	40.60
	TZVP	31.16	64.31	31.20	31.17
	TZVPD	30.07	64.03	30.17	30.08
	TZVPP	29.35	62.42	29.39	29.36
	TZVPPD	29.81	62.55	29.90	29.82
	QZVP	28.63	61.97	28.76	28.63
	QZVPD	28.66	61.99	28.80	28.66
	QZVPP	28.63	61.97	28.76	28.63
	QZVPPD	28.66	61.99	28.80	28.66

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
BP86	SVP	36.74	146.07	36.66	36.77
	SVPD	39.37	158.21	39.30	39.22
	TZVP	26.16	53.55	26.12	26.16
	TZVPD	25.56	53.74	25.56	25.56
	TZVPP	25.23	52.42	25.21	25.24
	TZVPPD	25.69	52.61	25.69	25.69
	QZVP	24.53	51.92	24.58	24.53
	QZVPD	24.51	51.96	24.56	24.51
	QZVPP	24.53	51.92	24.58	24.53
	QZVPPD	24.51	51.96	24.56	24.51
HCTH	SVP	43.83	130.40	43.74	43.71
	SVPD	46.08	152.85	46.01	45.87
	TZVP	30.85	152.35	30.75	30.84
	TZVPD	29.64	47.05	29.57	29.64
	TZVPP	30.29	45.72	30.25	30.29
	TZVPPD	30.41	46.42	30.38	30.40
	QZVP	29.69	45.43	29.67	29.69
	QZVPD	29.55	45.55	29.52	29.54
	QZVPP	29.69	45.43	29.67	29.69
	QZVPPD	29.55	45.55	29.52	29.54
M06-L	SVP	40.85	126.02	40.77	40.71
	SVPD	42.05	152.86	42.00	41.85
	TZVP	26.40	41.64	26.30	26.40
	TZVPD	26.75	42.62	26.71	26.74
	TZVPP	27.65	40.80	27.49	27.65
	TZVPPD	27.05	40.40	26.93	27.05
	QZVP	25.73	40.88	25.63	25.72
	QZVPD	25.22	40.33	25.10	25.21
	QZVPP	25.73	40.88	25.63	25.72
	QZVPPD	25.22	40.33	25.10	25.21

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
M06-L_{D3}	SVP	42.66	53.92	40.77	40.71
	SVPD	41.36	55.02	42.00	41.85
	TZVP	32.22	47.66	26.30	26.40
	TZVPD	32.64	48.49	26.71	26.74
	TZVPP	31.34	45.10	27.49	27.66
	TZVPPD	30.86	44.68	26.93	27.05
	QZVP	29.05	45.07	25.63	25.21
	QZVPD	28.25	44.34	25.10	25.73
	QZVPP	29.05	45.07	25.63	25.21
	QZVPPD	28.25	44.34	25.10	40.71
M11-L	SVP	67.55	141.20	67.43	67.22
	SVPD	67.83	174.48	67.76	67.47
	TZVP	55.61	56.46	55.45	55.60
	TZVPD	54.15	56.05	54.03	54.14
	TZVPP	57.10	57.93	56.98	57.09
	TZVPPD	56.77	57.92	56.65	56.75
	QZVP	54.56	56.00	54.43	54.56
	QZVPD	55.44	56.75	55.31	55.43
	QZVPP	54.56	56.00	54.43	54.56
	QZVPPD	55.44	56.75	55.31	55.43
MN12-L	SVP	38.99	127.27	38.86	38.78
	SVPD	39.70	155.58	39.60	39.34
	TZVP	30.20	49.39	30.07	30.20
	TZVPD	29.22	49.73	29.14	29.21
	TZVPP	31.95	49.18	31.84	31.95
	TZVPPD	31.91	49.15	31.81	31.90
	QZVP	33.68	50.33	33.58	33.67
	QZVPD	33.31	50.00	33.20	33.30
	QZVPP	33.68	50.33	33.58	33.67
	QZVPPD	33.31	50.00	33.20	33.30

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
MN15-L	SVP	42.62	52.21	42.45	42.31
	SVPD	41.32	55.50	41.21	41.01
	TZVP	32.49	44.59	32.31	32.48
	TZVPD	30.77	44.53	30.64	30.48
	TZVPP	33.01	43.74	32.86	33.00
	TZVPPD	32.09	43.92	31.98	32.07
	QZVP	33.47	44.98	33.33	33.46
	QZVPD	33.36	44.98	33.22	33.35
	QZVPP	33.47	44.98	33.33	33.46
	QZVPPD	33.36	44.98	33.22	33.35
mPWPW91	SVP	37.46	61.89	37.39	37.39
	SVPD	40.20	63.23	40.14	40.14
	TZVP	26.76	52.95	26.72	26.72
	TZVPD	25.94	53.08	25.95	25.95
	TZVPP	25.76	51.92	25.74	25.74
	TZVPPD	26.30	52.20	26.31	26.31
	QZVP	25.18	51.38	25.23	25.23
	QZVPD	25.20	51.47	25.25	25.25
	QZVPP	25.18	51.38	25.23	25.23
	QZVPPD	25.20	51.47	25.25	25.25
N12	SVP	40.30	129.89	40.18	40.08
	SVPD	46.82	144.31	46.68	46.45
	TZVP	29.68	49.60	29.59	29.68
	TZVPD	28.50	50.01	28.42	28.50
	TZVPP	30.21	48.86	30.16	30.20
	TZVPPD	30.85	49.74	30.78	30.74
	QZVP	30.02	48.57	29.97	30.01
	QZVPD	30.15	48.88	30.10	30.14
	QZVPP	30.02	48.57	29.97	30.01
	QZVPPD	30.15	48.88	30.10	30.14

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
OLYP	SVP	39.05	60.14	38.96	39.04
	SVPD	41.71	63.03	41.65	41.51
	TZVP	30.51	50.44	30.40	30.51
	TZVPD	27.51	49.50	27.46	27.50
	TZVPP	28.12	48.33	28.07	28.11
	TZVPPD	28.00	48.81	27.98	27.99
	QZVP	27.25	47.95	27.23	27.24
	QZVPD	27.06	48.07	27.03	27.06
	QZVPP	27.25	47.95	27.23	27.24
	QZVPPD	27.06	48.07	27.03	27.05
PBE	SVP	39.04	144.06	38.97	39.04
	SVPD	41.80	156.97	41.74	41.65
	TZVP	27.72	52.06	27.67	27.72
	TZVPD	26.75	52.11	26.74	26.75
	TZVPP	26.51	50.79	26.48	26.51
	TZVPPD	27.00	51.15	26.99	27.00
	QZVP	25.96	50.27	25.98	25.95
	QZVPD	25.96	50.38	25.99	25.96
	QZVPP	25.96	50.27	25.98	25.95
	QZVPPD	25.96	50.38	25.99	25.96
PBE_{D3BJ}	SVP	39.06	61.51	38.99	38.99
	SVPD	41.79	63.03	41.73	41.73
	TZVP	27.72	52.09	27.67	27.67
	TZVPD	26.75	52.13	26.74	26.74
	TZVPP	26.50	50.81	26.47	26.47
	TZVPPD	26.99	51.17	26.98	26.98
	QZVP	25.95	50.29	25.97	25.97
	QZVPD	25.96	50.40	25.98	25.98
	QZVPP	25.95	50.29	25.97	25.97
	QZVPPD	25.96	50.40	25.98	25.98

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
revTPSS	SVP	34.31	144.51	34.29	34.65
	SVPD	31.26	157.46	31.25	31.25
	TZVP	25.71	57.62	25.69	25.72
	TZVPD	24.86	57.32	24.90	24.87
	TZVPP	24.27	56.42	24.24	24.28
	TZVPPD	24.23	56.09	24.26	24.24
	QZVP	24.13	56.41	24.18	24.13
	QZVPD	24.00	56.30	24.05	24.00
	QZVPP	24.13	56.41	24.18	24.13
	QZVPPD	24.00	56.30	24.05	24.00
SOGGA11	SVP	52.08	62.96	52.00	51.83
	SVPD	54.06	69.37	53.98	53.73
	TZVP	30.88	51.07	30.77	30.87
	TZVPD	34.87	50.64	34.86	34.86
	TZVPP	37.14	50.67	37.15	37.14
	TZVPPD	40.79	49.23	44.02	40.70
	QZVP	43.91	55.32	43.93	43.90
	QZVPD	62.10	68.14	61.27	62.09
	QZVPP	43.91	55.32	43.93	43.90
	QZVPPD	62.10	68.14	61.27	62.10
TPSS	SVP	33.80	142.65	33.77	34.11
	SVPD	33.00	156.31	32.98	32.99
	TZVP	24.77	55.90	24.75	24.78
	TZVPD	23.94	55.76	23.97	23.95
	TZVPP	23.39	54.85	23.37	23.40
	TZVPPD	23.63	54.75	23.66	23.64
	QZVP	23.21	54.75	23.27	23.22
	QZVPD	23.16	54.71	23.22	23.17
	QZVPP	23.21	54.75	23.26	23.21
	QZVPPD	23.16	54.71	23.22	23.17

Functional	Basis Set	none[a]	def2-SV/TZV	W06	auto
$TPSS_{D3BJ}$	SVP	33.78	142.75	33.75	34.09
	SVPD	32.97	156.39	32.94	32.96
	TZVP	23.12	54.72	23.18	23.12
	TZVPD	23.90	55.77	23.93	23.92
	TZVPP	23.36	54.85	23.33	23.36
	TZVPPD	23.59	54.76	23.62	23.60
	QZVP	23.17	54.75	23.22	23.17
	QZVPD	23.12	54.72	23.18	23.12
	QZVPP	23.17	54.75	23.22	23.17
	QZVPPD	23.12	54.72	23.18	23.12
VSXC	SVP	40.50	58.74	40.43	40.43
	SVPD	43.65	62.89	43.60	43.60
	TZVP	31.02	51.59	30.93	30.93
	TZVPD	29.78	51.77	29.73	29.73
	TZVPP	30.07	50.49	30.04	30.04
	TZVPPD	30.38	51.10	30.35	30.35
	QZVP	29.29	50.14	29.30	29.30
	QZVPD	29.23	50.26	29.23	29.23
	QZVPP	29.29	50.14	29.30	29.30
	QZVPPD	29.23	50.26	29.23	29.23
XLYP	SVP	37.94	69.00	37.88	37.88
	SVPD	40.94	68.95	40.88	40.88
	TZVP	31.17	64.22	31.21	31.21
	TZVPD	29.93	63.89	30.04	30.04
	TZVPP	29.22	62.25	29.26	29.26
	TZVPPD	29.69	62.41	29.78	29.78
	QZVP	28.49	61.81	28.62	28.62
	QZVPD	28.54	61.84	28.68	28.68
	QZVPP	28.49	61.81	28.62	28.62
	QZVPPD	28.54	61.84	28.68	28.68

Functional	**Basis Set**	**none[a]**	**def2-SV/TZV**	**W06**	**auto**
τHCTH	SVP	38.09	134.03	38.00	38.04
	SVPD	39.49	155.16	39.42	39.28
	TZVP	27.22	47.44	27.13	27.23
	TZVPD	26.31	47.85	26.27	26.31
	TZVPP	26.74	47.14	26.69	26.47
	TZVPPD	27.00	47.45	26.97	26.99
	QZVP	25.24	47.85	25.26	25.24
	QZVPD	25.17	47.85	25.19	25.17
	QZVPP	25.24	47.85	25.26	25.23
	QZVPPD	25.17	47.85	25.19	25.17

[a] Not using any density fitting.

Table S8. λ_{harm} scale factors for various hybrid-GGA and hybrid-meta-GGA exchange–correlation functional–basis set combinations.

Functional	**APFD**	**B1B95**	**B3LYP**	**B3P86**	**B97-1**
SVP	0.9947	0.9901	1.0045	0.9962	1.0023
SVPD	0.9964	0.9913	1.0045	0.9974	1.0031
TZVP	0.9974	0.9925	1.0044	0.9979	1.0034
TZVPD	0.9979	0.9929	1.0047	0.9984	1.0038
TZVPP	0.9965	0.9913	1.0029	0.9968	1.0023
TZVPPD	0.9967	0.9915	1.0031	0.9971	1.0025
QZVP	0.9973	0.9922	1.0038	0.9977	1.0029
QZVPD	0.9975	0.9923	1.0039	0.9978	1.0031
QZVPP	0.9973	0.9922	1.0038	0.9977	1.0029
QZVPPD	0.9975	0.9923	1.0039	0.9978	1.0031
Functional	**B97-2**	**B98**	**BMK**	**HISS**	**HSE06**
SVP	0.9909	1.0014	0.9868	0.9664	0.9925
SVPD	0.9922	1.0022	0.9881	0.9686	0.9939
TZVP	0.9934	1.0023	0.9878	0.9694	0.9950
TZVPD	0.9939	1.0027	0.9883	0.9700	0.9955
TZVPP	0.9926	1.0012	0.9862	0.9684	0.9940
TZVPPD	0.9927	1.0014	0.9866	0.9687	0.9942
QZVP	0.9932	1.0017	0.9872	0.9695	0.9948
QZVPD	0.9934	1.0019	0.9873	0.9696	0.9949
QZVPP	0.9932	1.0017	0.9872	0.9695	0.9948
QZVPPD	0.9934	1.0019	0.9873	0.9696	0.9949

Functional	LC-BLYP	LC-TPSS	LC-ωPBE	M06	M06-2X
SVP	0.9759	0.9660	0.9784	0.9991	0.9857
SVPD	0.9775	0.9688	0.9806	1.0007	0.9874
TZVP	0.9777	0.9700	0.9817	0.9979	0.9872
TZVPD	0.9784	0.9707	0.9823	0.9984	0.9877
TZVPP	0.9764	0.9693	0.9809	0.9958	0.9865
TZVPPD	0.9767	0.9696	0.9811	0.9961	0.9868
QZVP	0.9778	0.9704	0.9820	0.9957	0.9870
QZVPD	0.9779	0.9705	0.9822	0.9959	0.9871
QZVPP	0.9778	0.9704	0.9820	0.9957	0.9870
QZVPPD	0.9779	0.9705	0.9822	0.9959	0.9871
Functional	**M08-HX**	**M11**	**MN12-SX**	**MN15**	**mPW1PW91**
SVP	0.9900	0.9950	0.9863	0.9863	0.9904
SVPD	0.9916	0.9968	0.9876	0.9876	0.9918
TZVP	0.9913	0.9963	0.9880	0.9883	0.9928
TZVPD	0.9918	0.9970	0.9881	0.9892	0.9933
TZVPP	0.9898	0.9936	0.9877	0.9871	0.9919
TZVPPD	0.9899	0.9939	0.9877	0.9876	0.9920
QZVP	0.9905	0.9970	0.9879	0.9886	0.9926
QZVPD	0.9907	0.9972	0.9881	0.9888	0.9927
QZVPP	0.9905	0.9970	0.9879	0.9886	0.9926
QZVPPD	0.9907	0.9972	0.9881	0.9888	0.9927

Functional	N12-SX	O3LYP	PBE0	PW6B95	SOGGA11-X
SVP	0.9855	1.0032	0.9915	0.9896	0.9785
SVPD	0.9862	1.0035	0.9930	0.9903	0.9807
TZVP	0.9867	1.0052	0.9944	0.9911	0.9823
TZVPD	0.9871	1.0056	0.9949	0.9914	0.9827
TZVPP	0.9853	1.0044	0.9935	0.9898	0.9808
TZVPPD	0.9855	1.0046	0.9937	0.9899	0.9810
QZVP	0.9859	1.0050	0.9943	0.9906	0.9821
QZVPD	0.9861	1.0052	0.9944	0.9908	0.9822
QZVPP	0.9859	1.0050	0.9943	0.9906	0.9821
QZVPPD	0.9861	1.0052	0.9944	0.9908	0.9822

Functional	TPSSh	X3LYP	τHCTHhyb	ωB97X-D
SVP	1.0042	1.0025	1.0069	0.9891
SVPD	1.0052	1.0025	1.0078	0.9910
TZVP	1.0058	1.0026	1.0073	0.9914
TZVPD	1.0062	1.0029	1.0077	0.9920
TZVPP	1.0052	1.0011	1.0064	0.9901
TZVPPD	1.0054	1.0012	1.0066	0.9903
QZVP	1.0057	1.0019	1.0070	0.9910
QZVPD	1.0058	1.0021	1.0071	0.9911
QZVPP	1.0057	1.0019	1.0070	0.9910
QZVPPD	1.0058	1.0021	1.0071	0.9911

Table S9. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{harm} for various hybrid-GGA and hybrid-meta-GGA exchange–correlation functional–basis set combinations.

Functional	**APFD**	**B1B95**	**B3LYP**	**B3P86**	**B97-1**
SVP	42.77	43.99	38.83	39.93	35.75
SVPD	41.54	42.49	35.98	38.79	34.25
TZVP	31.90	31.32	26.75	28.39	23.96
TZVPD	31.92	31.51	26.63	28.43	23.33
TZVPP	32.27	31.29	25.95	28.30	24.10
TZVPPD	32.00	31.09	25.56	28.00	23.57
QZVP	31.89	30.92	25.34	27.81	23.75
QZVPD	31.90	30.94	25.37	27.84	23.65
QZVPP	31.89	30.92	25.34	27.81	23.75
QZVPPD	31.90	30.94	25.37	27.84	23.65
Functional	**B97-2**	**B98**	**BMK**	**HISS**	**HSE06**
SVP	39.73	36.63	53.81	49.82	43.68
SVPD	37.99	35.12	54.41	49.37	42.01
TZVP	27.80	25.65	41.89	41.40	31.90
TZVPD	27.65	25.07	41.34	41.52	31.99
TZVPP	28.11	25.94	44.90	41.96	32.17
TZVPPD	27.79	25.38	44.02	41.66	31.91
QZVP	27.54	25.60	44.37	41.38	31.65
QZVPD	27.51	25.49	44.20	41.41	31.67
QZVPP	27.54	25.60	44.37	41.38	31.65
QZVPPD	27.51	25.49	44.20	41.41	31.67

Functional	LC-BLYP	LC-TPSS	LC-ωPBE	M06	M06-2X
SVP	64.03	63.44	54.99	51.34	49.64
SVPD	62.37	62.36	53.66	51.35	47.82
TZVP	55.14	55.85	45.77	41.63	37.26
TZVPD	55.01	55.79	45.78	41.47	37.64
TZVPP	54.58	55.64	45.70	42.29	37.54
TZVPPD	54.01	55.36	45.42	41.82	37.23
QZVP	53.73	55.09	45.15	40.01	36.93
QZVPD	53.86	55.16	45.26	39.54	36.95
QZVPP	53.73	55.09	45.15	40.01	36.93
QZVPPD	53.86	55.16	45.26	39.54	36.95
Functional	**M08-HX**	**M11**	**MN12-SX**	**MN15**	**mPW1PW91**
SVP	55.61	53.06	45.36	49.63	41.67
SVPD	54.20	53.45	44.46	51.04	40.02
TZVP	44.76	47.87	34.19	35.49	30.62
TZVPD	45.07	48.04	33.93	35.31	30.70
TZVPP	44.05	46.79	35.78	35.97	30.91
TZVPPD	44.03	46.46	35.52	35.38	30.65
QZVP	44.07	46.32	34.67	35.15	30.42
QZVPD	44.50	46.20	34.39	35.21	30.45
QZVPP	44.07	46.32	34.67	35.15	30.42
QZVPPD	44.50	46.20	34.39	35.21	30.45

Functional	N12-SX	O3LYP	PBE0	PW6B95	SOGGA11-X
SVP	42.03	39.14	43.82	42.04	42.53
SVPD	43.41	36.60	42.22	40.04	40.26
TZVP	31.27	25.45	32.21	28.73	33.41
TZVPD	31.35	23.67	32.28	28.98	33.67
TZVPP	31.87	24.56	32.54	28.43	33.62
TZVPPD	31.92	23.81	32.29	28.29	33.45
QZVP	32.47	23.57	32.10	28.04	33.80
QZVPD	32.58	23.45	32.12	28.09	33.62
QZVPP	32.47	23.57	32.10	28.04	33.80
QZVPPD	32.58	23.45	32.12	28.09	33.62
Functional	**TPSSh**	**X3LYP**	**τHCTHhyb**	**ωB97X-D**	
SVP	35.11	39.80	35.94	43.10	
SVPD	29.89	36.85	34.27	41.64	
TZVP	23.87	27.49	23.56	33.33	
TZVPD	23.34	27.43	22.90	33.21	
TZVPP	23.14	26.79	23.45	33.91	
TZVPPD	22.58	26.42	22.93	33.49	
QZVP	22.49	26.21	22.81	33.59	
QZVPD	22.42	26.25	22.69	33.52	
QZVPP	22.49	26.21	22.81	33.59	
QZVPPD	22.42	26.25	22.69	33.52	

Table S10. λ_{ZPE} scale factors for various hybrid-GGA and hybrid-meta-GGA exchange–correlation functional–basis set combinations.

Functional	**APFD**	**B1B95**	**B3LYP**	**B3P86**	**B97-1**
SVP	0.9844	0.9801	0.9912	0.9855	0.9903
SVPD	0.9882	0.9831	0.9935	0.9883	0.9929
TZVP	0.9860	0.9806	0.9896	0.9855	0.9900
TZVPD	0.9866	0.9810	0.9899	0.9860	0.9903
TZVPP	0.9852	0.9796	0.9883	0.9845	0.9890
TZVPPD	0.9855	0.9799	0.9885	0.9848	0.9892
QZVP	0.9861	0.9805	0.9891	0.9853	0.9896
QZVPD	0.9862	0.9806	0.9893	0.9855	0.9897
QZVPP	0.9861	0.9805	0.9891	0.9853	0.9896
QZVPPD	0.9862	0.9806	0.9893	0.9855	0.9897
Functional	**B97-2**	**B98**	**BMK**	**HISS**	**HSE06**
SVP	0.9802	0.9892	0.9757	0.9573	0.9824
SVPD	0.9832	0.9919	0.9786	0.9607	0.9854
TZVP	0.9814	0.9888	0.9744	0.9585	0.9833
TZVPD	0.9818	0.9892	0.9751	0.9591	0.9837
TZVPP	0.9805	0.9878	0.9732	0.9576	0.9823
TZVPPD	0.9808	0.9880	0.9737	0.9580	0.9826
QZVP	0.9812	0.9883	0.9745	0.9587	0.9831
QZVPD	0.9813	0.9885	0.9746	0.9588	0.9833
QZVPP	0.9812	0.9883	0.9745	0.9587	0.9831
QZVPPD	0.9813	0.9885	0.9746	0.9588	0.9833

Functional	LC-BLYP	LC-TPSS	LC-ωPBE	M06	M06-2X
SVP	0.9667	0.9580	0.9696	0.9915	0.9762
SVPD	0.9701	0.9619	0.9733	0.9951	0.9795
TZVP	0.9662	0.9598	0.9710	0.9876	0.9755
TZVPD	0.9670	0.9606	0.9718	0.9880	0.9760
TZVPP	0.9652	0.9593	0.9703	0.9860	0.9748
TZVPPD	0.9656	0.9597	0.9707	0.9863	0.9751
QZVP	0.9666	0.9603	0.9715	0.9856	0.9753
QZVPD	0.9667	0.9605	0.9717	0.9857	0.9754
QZVPP	0.9666	0.9603	0.9715	0.9856	0.9753
QZVPPD	0.9667	0.9605	0.9717	0.9857	0.9754
Functional	**M08-HX**	**M11**	**MN12-SX**	**MN15**	**mPW1PW91**
SVP	0.9817	0.9853	0.9774	0.9790	0.9799
SVPD	0.9853	0.9889	0.9804	0.9826	0.9830
TZVP	0.9817	0.9856	0.9772	0.9789	0.9809
TZVPD	0.9823	0.9864	0.9771	0.9799	0.9813
TZVPP	0.9803	0.9833	0.9774	0.9779	0.9800
TZVPPD	0.9805	0.9837	0.9775	0.9786	0.9803
QZVP	0.9805	0.9868	0.9775	0.9796	0.9807
QZVPD	0.9808	0.9871	0.9778	0.9798	0.9809
QZVPP	0.9805	0.9868	0.9775	0.9796	0.9807
QZVPPD	0.9808	0.9871	0.9778	0.9798	0.9809

Functional	N12-SX	O3LYP	PBE0	PW6B95	SOGGA11-X
SVP	0.9761	0.9918	0.9817	0.9788	0.9684
SVPD	0.9787	0.9944	0.9848	0.9814	0.9719
TZVP	0.9755	0.9929	0.9830	0.9785	0.9701
TZVPD	0.9759	0.9932	0.9835	0.9788	0.9705
TZVPP	0.9743	0.9919	0.9822	0.9773	0.9688
TZVPPD	0.9745	0.9923	0.9824	0.9776	0.9690
QZVP	0.9750	0.9926	0.9829	0.9781	0.9702
QZVPD	0.9752	0.9928	0.9831	0.9783	0.9703
QZVPP	0.9750	0.9926	0.9829	0.9781	0.9702
QZVPPD	0.9752	0.9928	0.9831	0.9783	0.9703
Functional	**TPSSh**	**X3LYP**	**τHCTHhyb**	**ωB97X-D**	
SVP	0.9888	0.9895	0.9949	0.9788	
SVPD	0.9914	0.9918	0.9976	0.9821	
TZVP	0.9897	0.9880	0.9941	0.9791	
TZVPD	0.9901	0.9883	0.9946	0.9796	
TZVPP	0.9891	0.9867	0.9933	0.9779	
TZVPPD	0.9894	0.9869	0.9936	0.9782	
QZVP	0.9894	0.9875	0.9937	0.9788	
QZVPD	0.9895	0.9877	0.9939	0.9789	
QZVPP	0.9894	0.9875	0.9937	0.9788	
QZVPPD	0.9895	0.9877	0.9939	0.9789	

Table S11. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{harm} for various hybrid-GGA and hybrid-meta-GGA exchange–correlation functional–basis set combinations.

Functional	**APFD**	**B1B95**	**B3LYP**	**B3P86**	**B97-1**
SVP	0.26	0.31	0.18	0.24	0.18
SVPD	0.21	0.27	0.15	0.20	0.14
TZVP	0.22	0.28	0.17	0.22	0.15
TZVPD	0.22	0.28	0.17	0.22	0.15
TZVPP	0.24	0.30	0.18	0.23	0.17
TZVPPD	0.23	0.30	0.18	0.23	0.17
QZVP	0.23	0.29	0.17	0.22	0.16
QZVPD	0.22	0.28	0.17	0.22	0.16
QZVPP	0.23	0.29	0.17	0.22	0.16
QZVPPD	0.22	0.28	0.17	0.22	0.16
Functional	**B97-2**	**B98**	**BMK**	**HISS**	**HSE06**
SVP	0.30	0.19	0.38	0.62	0.29
SVPD	0.26	0.15	0.35	0.57	0.24
TZVP	0.27	0.17	0.37	0.59	0.25
TZVPD	0.27	0.17	0.37	0.58	0.25
TZVPP	0.28	0.18	0.40	0.61	0.27
TZVPPD	0.28	0.18	0.39	0.60	0.27
QZVP	0.28	0.18	0.38	0.59	0.26
QZVPD	0.27	0.17	0.38	0.59	0.26
QZVPP	0.28	0.18	0.38	0.59	0.26
QZVPPD	0.27	0.17	0.38	0.59	0.26

Functional	LC-BLYP	LC-TPSS	LC-ωPBE	M06	M06-2X
SVP	0.24	0.62	0.46	0.22	0.37
SVPD	0.22	0.57	0.40	0.19	0.32
TZVP	0.20	0.59	0.43	0.23	0.36
TZVPD	0.20	0.58	0.42	0.23	0.35
TZVPP	0.20	0.60	0.44	0.25	0.37
TZVPPD	0.20	0.59	0.43	0.24	0.36
QZVP	0.19	0.58	0.42	0.25	0.36
QZVPD	0.19	0.58	0.42	0.24	0.36
QZVPP	0.19	0.58	0.42	0.25	0.36
QZVPPD	0.19	0.58	0.42	0.24	0.36
Functional	**M08-HX**	**M11**	**MN12-SX**	**MN15**	**mPW1PW91**
SVP	0.31	0.27	0.33	0.34	0.31
SVPD	0.27	0.23	0.29	0.29	0.26
TZVP	0.30	0.26	0.32	0.31	0.28
TZVPD	0.29	0.26	0.33	0.30	0.28
TZVPP	0.31	0.29	0.33	0.33	0.29
TZVPPD	0.31	0.28	0.33	0.32	0.29
QZVP	0.32	0.25	0.32	0.30	0.28
QZVPD	0.31	0.24	0.32	0.30	0.28
QZVPP	0.32	0.25	0.32	0.30	0.28
QZVPPD	0.31	0.24	0.32	0.30	0.28

Functional	N12-SX	O3LYP	PBE0	PW6B95	SOGGA11-X
SVP	0.36	0.18	0.29	0.32	0.46
SVPD	0.32	0.13	0.25	0.28	0.41
TZVP	0.35	0.13	0.26	0.31	0.42
TZVPD	0.35	0.13	0.25	0.31	0.42
TZVPP	0.37	0.14	0.27	0.32	0.44
TZVPPD	0.36	0.14	0.27	0.32	0.44
QZVP	0.36	0.13	0.26	0.31	0.43
QZVPD	0.36	0.13	0.26	0.31	0.42
QZVPP	0.36	0.13	0.26	0.31	0.43
QZVPPD	0.36	0.13	0.26	0.31	0.42

Functional	TPSSh	X3LYP	τHCTHhyb	ωB97X-D
SVP	0.19	0.20	0.14	0.32
SVPD	0.15	0.17	0.11	0.28
TZVP	0.16	0.19	0.11	0.31
TZVPD	0.16	0.19	0.11	0.30
TZVPP	0.17	0.20	0.12	0.32
TZVPPD	0.16	0.20	0.12	0.32
QZVP	0.16	0.19	0.11	0.31
QZVPD	0.16	0.19	0.11	0.31
QZVPP	0.16	0.19	0.11	0.31
QZVPPD	0.16	0.19	0.11	0.31

Table S12. λ_{fund} scale factors for various hybrid-GGA and hybrid-meta-GGA exchange–correlation functional–basis set combinations.

Functional	**APFD**	**B1B95**	**B3LYP**	**B3P86**	**B97-1**
SVP	0.9578	0.9534	0.9672	0.9592	0.9651
SVPD	0.9594	0.9545	0.9671	0.9604	0.9658
TZVP	0.9604	0.9556	0.9671	0.9609	0.9661
TZVPD	0.9609	0.9561	0.9674	0.9614	0.9665
TZVPP	0.9595	0.9545	0.9657	0.9598	0.9651
TZVPPD	0.9597	0.9547	0.9658	0.9600	0.9652
QZVP	0.9603	0.9554	0.9665	0.9606	0.9657
QZVPD	0.9604	0.9555	0.9666	0.9608	0.9658
QZVPP	0.9603	0.9554	0.9665	0.9606	0.9657
QZVPPD	0.9604	0.9555	0.9666	0.9608	0.9658
Functional	**B97-2**	**B98**	**BMK**	**HISS**	**HSE06**
SVP	0.9541	0.9643	0.9501	0.9305	0.9556
SVPD	0.9553	0.9649	0.9514	0.9326	0.9570
TZVP	0.9565	0.9651	0.9512	0.9334	0.9580
TZVPD	0.9570	0.9655	0.9517	0.9340	0.9585
TZVPP	0.9557	0.9640	0.9496	0.9325	0.9571
TZVPPD	0.9559	0.9642	0.9500	0.9327	0.9572
QZVP	0.9563	0.9645	0.9505	0.9335	0.9578
QZVPD	0.9565	0.9647	0.9507	0.9337	0.9580
QZVPP	0.9563	0.9645	0.9505	0.9335	0.9578
QZVPPD	0.9565	0.9647	0.9507	0.9337	0.9580

Functional	LC-BLYP	LC-TPSS	LC-ωPBE	M06	M06-2X
SVP	0.9398	0.9302	0.9421	0.9620	0.9491
SVPD	0.9413	0.9329	0.9442	0.9635	0.9508
TZVP	0.9415	0.9340	0.9453	0.9609	0.9506
TZVPD	0.9421	0.9347	0.9459	0.9613	0.9510
TZVPP	0.9402	0.9334	0.9445	0.9589	0.9499
TZVPPD	0.9405	0.9337	0.9447	0.9591	0.9502
QZVP	0.9416	0.9344	0.9456	0.9588	0.9504
QZVPD	0.9417	0.9345	0.9457	0.9589	0.9505
QZVPP	0.9416	0.9344	0.9456	0.9588	0.9504
QZVPPD	0.9417	0.9345	0.9457	0.9589	0.9505
Functional	**M08-HX**	**M11**	**MN12-SX**	**MN15**	**mPW1PW91**
SVP	0.9533	0.9581	0.9497	0.9497	0.9537
SVPD	0.9548	0.9598	0.9509	0.9509	0.9550
TZVP	0.9545	0.9593	0.9514	0.9516	0.9559
TZVPD	0.9550	0.9601	0.9514	0.9524	0.9564
TZVPP	0.9531	0.9568	0.9511	0.9504	0.9550
TZVPPD	0.9532	0.9571	0.9510	0.9509	0.9552
QZVP	0.9537	0.9600	0.9512	0.9519	0.9557
QZVPD	0.9539	0.9602	0.9514	0.9520	0.9559
QZVPP	0.9537	0.9600	0.9512	0.9519	0.9557
QZVPPD	0.9539	0.9602	0.9514	0.9520	0.9559

Functional	N12-SX	O3LYP	PBE0	PW6B95	SOGGA11-X
SVP	0.9489	0.9659	0.9547	0.9529	0.9422
SVPD	0.9495	0.9662	0.9561	0.9535	0.9442
TZVP	0.9500	0.9678	0.9575	0.9543	0.9458
TZVPD	0.9505	0.9682	0.9580	0.9546	0.9462
TZVPP	0.9487	0.9671	0.9566	0.9530	0.9444
TZVPPD	0.9489	0.9673	0.9568	0.9532	0.9445
QZVP	0.9492	0.9676	0.9573	0.9538	0.9456
QZVPD	0.9494	0.9678	0.9575	0.9540	0.9457
QZVPP	0.9492	0.9676	0.9573	0.9538	0.9456
QZVPPD	0.9494	0.9678	0.9575	0.9540	0.9457

Functional	TPSSh	X3LYP	τHCTHhyb	ωB97X-D
SVP	0.9670	0.9653	0.9695	0.9524
SVPD	0.9678	0.9653	0.9703	0.9542
TZVP	0.9684	0.9653	0.9698	0.9546
TZVPD	0.9689	0.9656	0.9703	0.9552
TZVPP	0.9679	0.9639	0.9690	0.9533
TZVPPD	0.9680	0.9640	0.9692	0.9536
QZVP	0.9683	0.9647	0.9696	0.9542
QZVPD	0.9685	0.9648	0.9697	0.9543
QZVPP	0.9683	0.9647	0.9696	0.9542
QZVPPD	0.9685	0.9648	0.9697	0.9543

Table S13. Root-mean-square deviations (RMSD, cm-1) of λ_{fund} for various hybrid-GGA and hybrid-meta-GGA exchange–correlation functional–basis set combinations.

Functional	**APFD**	**B1B95**	**B3LYP**	**B3P86**	**B97-1**
SVP	37.67	38.20	32.20	35.19	32.00
SVPD	40.10	40.36	34.90	37.83	35.38
TZVP	25.94	24.40	19.52	22.50	20.30
TZVPD	26.26	24.94	19.96	22.79	20.10
TZVPP	27.10	25.35	20.00	23.40	21.46
TZVPPD	27.44	25.76	20.57	23.70	21.78
QZVP	26.88	25.12	19.51	22.87	21.21
QZVPD	26.86	25.14	19.52	22.86	21.07
QZVPP	26.88	25.12	19.51	22.87	21.21
QZVPPD	26.86	25.14	19.52	22.86	21.07
Functional	**B97-2**	**B98**	**BMK**	**HISS**	**HSE06**
SVP	35.85	31.92	47.86	42.49	38.11
SVPD	37.96	35.17	51.48	44.63	40.05
TZVP	23.71	20.55	33.38	32.65	25.28
TZVPD	23.89	20.34	32.95	32.96	25.69
TZVPP	24.81	21.84	37.81	33.98	26.40
TZVPPD	25.18	22.07	37.10	34.05	26.75
QZVP	24.34	21.58	37.12	33.41	25.97
QZVPD	24.30	21.43	36.96	33.41	25.97
QZVPP	24.34	21.58	37.12	33.41	25.97
QZVPPD	24.30	21.43	36.96	33.41	25.97

Functional	LC-BLYP	LC-TPSS	LC-ωPBE	M06	M06-2X
SVP	51.95	53.06	46.55	46.47	40.82
SVPD	53.15	53.98	47.97	49.31	42.24
TZVP	41.88	44.35	36.49	34.39	27.89
TZVPD	42.06	44.43	36.81	34.42	28.59
TZVPP	41.94	44.52	36.93	36.68	28.46
TZVPPD	41.77	44.50	37.14	36.56	28.60
QZVP	41.22	44.01	36.56	34.43	28.27
QZVPD	41.34	44.08	36.69	34.06	28.29
QZVPP	41.22	44.01	36.56	34.43	28.27
QZVPPD	41.34	44.08	36.69	34.06	28.29
Functional	**M08-HX**	**M11**	**MN12-SX**	**MN15**	**mPW1PW91**
SVP	46.48	43.88	38.73	45.76	36.15
SVPD	48.10	47.27	41.41	50.46	38.22
TZVP	36.13	38.75	26.93	32.01	24.09
TZVPD	36.66	39.03	26.88	32.21	24.46
TZVPP	36.12	39.14	29.10	33.11	25.18
TZVPPD	36.59	39.16	29.40	33.14	25.58
QZVP	36.04	38.00	29.17	32.93	24.83
QZVPD	36.57	38.10	29.08	32.93	24.87
QZVPP	36.04	38.00	29.17	32.93	24.83
QZVPPD	36.57	38.10	29.08	32.93	24.87

Functional	N12-SX	O3LYP	PBE0	PW6B95	SOGGA11-X
SVP	38.19	36.75	38.38	36.07	36.24
SVPD	43.19	39.13	40.30	38.43	37.59
TZVP	27.19	25.04	25.80	21.95	25.67
TZVPD	27.53	24.08	26.18	22.69	26.07
TZVPP	28.78	24.65	26.88	22.77	27.25
TZVPPD	29.35	25.08	27.25	23.43	27.50
QZVP	29.65	24.28	26.61	22.59	27.25
QZVPD	29.70	24.19	26.61	22.65	27.13
QZVPP	29.65	24.28	26.61	22.59	27.25
QZVPPD	29.70	24.19	26.61	22.65	27.13
Functional	**TPSSh**	**X3LYP**	**τHCTHhyb**	**ωB97X-D**	
SVP	29.35	32.64	32.42	36.32	
SVPD	29.12	35.19	35.37	38.35	
TZVP	18.52	19.51	20.82	25.38	
TZVPD	18.29	20.05	20.49	25.50	
TZVPP	18.02	20.09	21.38	27.20	
TZVPPD	18.39	20.69	21.72	27.31	
QZVP	17.68	19.67	20.67	26.64	
QZVPD	17.65	19.69	20.56	26.60	
QZVPP	17.68	19.67	20.67	26.64	
QZVPPD	17.65	19.69	20.56	26.60	

Table S14. λ_{harm} scale factors for various double hybrid exchange–correlation functional–basis set combinations.

Functional	**B2GP-PLYP**	**B2K-PLYP**	**B2PLYP**	**B2PLYP-D3BJ**
SVP	0.9854	0.9801	0.9952	0.9952
SVPD	0.9901	0.9853	0.9989	0.9989
TZVP	0.9911	0.9866	0.9995	0.9995
TZVPD	0.9926	0.9882	1.0009	1.0008
TZVPP	0.9892	0.9846	0.9977	0.9977
TZVPPD	0.9901	0.9855	0.9985	0.9985
QZVP	0.9897	0.9850	0.9983	0.9983
QZVPD	0.9900	0.9854	0.9987	0.9986
QZVPP	0.9897	0.9850	0.9983	0.9983
QZVPPD	0.9900	0.9854	0.9987	0.9986
Functional	**B2T-PLYP**	**DSD-BLYP-D3BJ**	**DSD-PBEP86**	**mPW2PLYP**
SVP	0.9881	1.0757	0.9907	0.9892
SVPD	0.9923	1.0834	0.9962	0.9927
TZVP	0.9932	1.0868	0.9979	0.9935
TZVPD	0.9946	1.0895	0.9997	0.9947
TZVPP	0.9913	1.0850	0.9957	0.9917
TZVPPD	0.9921	1.0865	0.9967	0.9924
QZVP	0.9919	1.0858	0.9961	0.9923
QZVPD	0.9922	1.0865	0.9965	0.9926
QZVPP	0.9919	1.0858	0.9961	0.9923
QZVPPD	0.9922	1.0865	0.9965	0.9926

Functional	mPW2PLYP-D2	PBE0-DH	PBE-QIDH	MP2
SVP	0.9899	0.9748	0.9711	0.9835
SVPD	0.9935	0.9783	0.9764	0.9928
TZVP	0.9942	0.9801	0.9785	0.9946
TZVPD	0.9954	0.9811	0.9799	0.9976
TZVPP	0.9924	0.9791	0.9770	0.9913
TZVPPD	0.9931	0.9796	0.9778	0.9931
QZVP	0.9930	0.9797	0.9775	0.9915
QZVPD	0.9933	0.9799	0.9777	0.9920
QZVPP	0.9930	0.9797	0.9775	0.9915
QZVPPD	0.9933	0.9799	0.9777	0.9920

Table S15. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{harm} for various double hybrid exchange–correlation functional–basis set combinations.

Functional	**B2GP-PLYP**	**B2K-PLYP**	**B2PLYP**	**B2PLYP-D3BJ**
SVP	21.71	21.49	23.06	23.08
SVPD	23.78	23.21	25.44	25.42
TZVP	12.27	12.24	14.03	14.02
TZVPD	12.53	12.56	13.99	13.97
TZVPP	10.45	10.76	11.71	11.68
TZVPPD	11.14	11.28	12.51	12.47
QZVP	10.44	11.01	11.28	11.24
QZVPD	10.69	11.21	11.55	11.52
QZVPP	10.44	11.01	11.28	11.24
QZVPPD	10.69	11.21	11.55	11.52
Functional	**B2T-PLYP**	**DSD-BLYP-D3BJ**	**DSD-PBEP86**	**mPW2PLYP**
SVP	22.14	33.65	22.38	23.51
SVPD	24.05	30.97	23.33	24.65
TZVP	12.37	29.08	12.00	12.86
TZVPD	12.63	25.48	11.35	13.20
TZVPP	10.46	25.42	9.97	11.06
TZVPPD	11.11	24.40	10.20	11.55
QZVP	10.36	22.58	9.62	11.04
QZVPD	10.60	22.65	9.75	11.27
QZVPP	10.36	22.58	9.62	11.04
QZVPPD	10.60	22.65	9.75	11.27

Functional	mPW2PLYP-D2	PBE0-DH	PBE-QIDH	MP2
SVP	23.81	37.01	28.46	35.87
SVPD	24.90	36.26	28.14	39.28
TZVP	13.54	27.56	19.06	31.78
TZVPD	13.70	27.74	19.15	31.02
TZVPP	12.00	28.25	19.60	30.78
TZVPPD	12.23	27.92	19.17	32.05
QZVP	11.98	28.18	20.03	29.73
QZVPD	12.14	28.15	19.98	30.03
QZVPP	11.98	28.18	20.03	29.73
QZVPPD	12.14	28.15	19.98	30.03

Table S16. λ_{ZPE} scale factors for various double hybrid exchange–correlation functional–basis set combinations.

Functional	**B2GP-PLYP**	**B2K-PLYP**	**B2PLYP**	**B2PLYP-D3BJ**
SVP	0.9716	0.9666	0.9808	0.9808
SVPD	0.9773	0.9727	0.9859	0.9858
TZVP	0.9753	0.9710	0.9832	0.9832
TZVPD	0.9767	0.9725	0.9844	0.9844
TZVPP	0.9738	0.9694	0.9818	0.9818
TZVPPD	0.9746	0.9703	0.9825	0.9825
QZVP	0.9743	0.9700	0.9824	0.9824
QZVPD	0.9747	0.9703	0.9827	0.9827
QZVPP	0.9743	0.9700	0.9824	0.9824
QZVPPD	0.9747	0.9703	0.9827	0.9827
Functional	**B2T-PLYP**	**DSD-BLYP-D3BJ**	**DSD-PBEP86**	**mPW2PLYP**
SVP	0.9742	1.0575	0.9774	0.9754
SVPD	0.9795	1.0668	0.9838	0.9803
TZVP	0.9773	1.0669	0.9825	0.9778
TZVPD	0.9785	1.0693	0.9842	0.9789
TZVPP	0.9758	1.0654	0.9808	0.9763
TZVPPD	0.9766	1.0667	0.9817	0.9770
QZVP	0.9764	1.0664	0.9814	0.9770
QZVPD	0.9767	1.0671	0.9817	0.9773
QZVPP	0.9764	1.0664	0.9814	0.9770
QZVPPD	0.9767	1.0671	0.9817	0.9773

Functional	**mPW2PLYP-D2**	**PBE0-DH**	**PBE-QIDH**	**MP2**
SVP	0.9763	0.9648	0.9601	0.9697
SVPD	0.9813	0.9693	0.9661	0.9791
TZVP	0.9787	0.9683	0.9655	0.9784
TZVPD	0.9798	0.9692	0.9669	0.9812
TZVPP	0.9773	0.9674	0.9644	0.9760
TZVPPD	0.9780	0.9679	0.9651	0.9775
QZVP	0.9779	0.9680	0.9649	0.9764
QZVPD	0.9782	0.9683	0.9652	0.9769
QZVPP	0.9779	0.9680	0.9649	0.9764
QZVPPD	0.9782	0.9683	0.9652	0.9769

Table 17. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{ZPE} for various double hybrid exchange–correlation functional–basis set combinations.

Functional	**B2GP-PLYP**	**B2K-PLYP**	**B2PLYP**	**B2PLYP-D3BJ**
SVP	0.39	0.46	0.27	0.27
SVPD	0.32	0.38	0.21	0.21
TZVP	0.34	0.40	0.23	0.23
TZVPD	0.32	0.38	0.22	0.22
TZVPP	0.36	0.42	0.25	0.25
TZVPPD	0.35	0.41	0.24	0.25
QZVP	0.35	0.41	0.24	0.24
QZVPD	0.35	0.41	0.24	0.24
QZVPP	0.35	0.41	0.24	0.24
QZVPPD	0.35	0.41	0.24	0.24
Functional	**B2T-PLYP**	**DSD-BLYP-D3BJ**	**DSD-PBEP86**	**mPW2PLYP**
SVP	0.36	0.72	0.31	0.34
SVPD	0.29	0.84	0.23	0.28
TZVP	0.31	0.83	0.24	0.30
TZVPD	0.30	0.86	0.22	0.29
TZVPP	0.33	0.81	0.26	0.32
TZVPPD	0.32	0.83	0.25	0.32
QZVP	0.32	0.83	0.25	0.32
QZVPD	0.32	0.83	0.25	0.31
QZVPP	0.32	0.83	0.25	0.32
QZVPPD	0.32	0.83	0.25	0.31

Functional	mPW2PLYP-D2	PBE0-DH	PBE-QIDH	MP2
SVP	0.33	0.50	0.56	0.44
SVPD	0.27	0.43	0.47	0.32
TZVP	0.29	0.44	0.48	0.32
TZVPD	0.28	0.43	0.46	0.28
TZVPP	0.31	0.46	0.49	0.35
TZVPPD	0.30	0.45	0.48	0.33
QZVP	0.30	0.45	0.48	0.34
QZVPD	0.30	0.45	0.48	0.33
QZVPP	0.30	0.45	0.48	0.34
QZVPPD	0.30	0.45	0.48	0.33

Table S18. λ_{fund} scale factors for various double hybrid exchange–correlation functional–basis set combinations.

Functional	**B2GP-PLYP**	**B2K-PLYP**	**B2PLYP**	**B2PLYP-D3BJ**
SVP	0.9487	0.9436	0.9582	0.9581
SVPD	0.9532	0.9486	0.9617	0.9617
TZVP	0.9542	0.9499	0.9623	0.9623
TZVPD	0.9557	0.9515	0.9636	0.9636
TZVPP	0.9523	0.9479	0.9605	0.9605
TZVPPD	0.9532	0.9488	0.9613	0.9613
QZVP	0.9529	0.9484	0.9612	0.9611
QZVPD	0.9532	0.9487	0.9615	0.9615
QZVPP	0.9529	0.9484	0.9612	0.9611
QZVPPD	0.9532	0.9487	0.9615	0.9615
Functional	**B2T-PLYP**	**DSD-BLYP-D3BJ**	**DSD-PBEP86**	**mPW2PLYP**
SVP	0.9513	1.0357	0.9538	0.9524
SVPD	0.9553	1.0430	0.9591	0.9558
TZVP	0.9562	1.0464	0.9608	0.9565
TZVPD	0.9576	1.0489	0.9625	0.9577
TZVPP	0.9544	1.0446	0.9586	0.9548
TZVPPD	0.9552	1.0461	0.9596	0.9555
QZVP	0.9550	1.0454	0.9590	0.9554
QZVPD	0.9553	1.0460	0.9594	0.9557
QZVPP	0.9550	1.0454	0.9590	0.9554
QZVPPD	0.9553	1.0460	0.9594	0.9557

Functional	**mPW2PLYP-D2**	**PBE0-DH**	**PBE-QIDH**	**MP2**
SVP	0.9531	0.9385	0.9350	0.9468
SVPD	0.9565	0.9419	0.9400	0.9557
TZVP	0.9572	0.9437	0.9421	0.9575
TZVPD	0.9584	0.9446	0.9435	0.9604
TZVPP	0.9555	0.9427	0.9406	0.9543
TZVPPD	0.9562	0.9432	0.9414	0.9560
QZVP	0.9561	0.9433	0.9411	0.9545
QZVPD	0.9564	0.9435	0.9414	0.9550
QZVPP	0.9561	0.9433	0.9411	0.9545
QZVPPD	0.9564	0.9435	0.9414	0.9550

Table S19. Root-mean-square deviations (RMSD, cm^{-1}) of λ_{fund} for various double hybrid exchange–correlation functional–basis set combinations.

Functional	**B2GP-PLYP**	**B2K-PLYP**	**B2PLYP**	**B2PLYP-D3BJ**
SVP	31.23	31.07	32.14	32.12
SVPD	36.44	35.84	37.88	37.85
TZVP	24.31	23.81	25.94	25.90
TZVPD	24.47	24.00	26.01	25.96
TZVPP	25.43	25.24	26.48	26.43
TZVPPD	26.33	26.06	27.44	27.40
QZVP	25.39	25.28	26.30	26.25
QZVPD	25.39	25.26	26.32	26.27
QZVPP	25.39	25.28	26.30	26.25
QZVPPD	25.39	25.26	26.32	26.27
Functional	**B2T-PLYP**	**DSD-BLYP-D3BJ**	**DSD-PBEP86**	**mPW2PLYP**
SVP	30.71	37.20	32.88	29.38
SVPD	36.07	41.01	36.90	34.85
TZVP	23.66	35.53	25.02	21.60
TZVPD	23.87	33.23	24.75	21.95
TZVPP	24.67	33.77	26.27	22.56
TZVPPD	25.58	34.05	26.97	23.55
QZVP	24.62	32.73	26.12	22.61
QZVPD	24.61	32.75	26.07	22.62
QZVPP	24.62	32.73	26.12	22.61
QZVPPD	24.61	32.75	26.07	22.62

Functional	mPW2PLYP-D2	PBE0-DH	PBE-QIDH	MP2
SVP	28.98	35.27	33.25	50.17
SVPD	34.48	37.48	35.71	54.51
TZVP	21.14	24.54	23.63	45.35
TZVPD	21.40	24.84	23.68	44.79
TZVPP	22.21	26.28	25.61	46.46
TZVPPD	23.10	26.45	25.82	47.68
QZVP	22.26	26.32	25.96	45.77
QZVPD	22.25	26.23	25.85	45.88
QZVPP	22.26	26.32	25.96	45.77
QZVPPD	22.25	26.23	25.85	45.88

Table S1. Isotopic fractionation α at 50°C with respect to liquid water calculated with selected exchange-correlation functionals, the def2-TZVP basis set and SMD solvation model for a series of ketones, compared to Wang *et al.*'s experimental (expt) and calculated (calc) values, calculated using Liu *et al.*'s formula Eq. 1) for β using ZPE_{harm} scaled by λ_{ZPE}.

ketone	Wang (expt[a])	Wang (calc[a,b])	M06-L	M06-L$_{D3}$	SOGGA11	OLYP	τHCTH	τHCTH$_{D3BJ}$	HCTH	HCTH$_{D3BJ}$	M11-L	O3LYP	τHCTHhyb	B3LYP
2,2,6-trimethylcyclohexanone	0.969	0.965	0.959	0.959	0.911	0.950	0.933	0.952	0.950	0.960	0.832	0.944	0.951	0.970
2,4-dimethyl-3-pentanone	1.004	1.012	0.995	0.999	0.970	1.000	0.992	0.997	1.006	1.013	0.866	0.997	0.984	1.027
2-heptanone	0.855	0.854	0.866	0.870	0.808	0.861	0.849	0.844	0.855	0.857	0.748	0.850	0.847	0.875
2-methyl-3-hexanone	0.935	0.923	0.921	0.918	0.882	0.919	0.904	0.908	0.915	0.917	0.800	0.910	0.898	0.933
2-methylcyclohexanone	0.895	0.924	0.927	0.921	0.870	0.918	0.902	0.909	0.911	0.917	0.802	0.905	0.899	0.931
3,5-dimethyl-4-heptanone	0.982	0.988	0.969	0.970	0.994	1.005	0.995	0.990	0.985	0.982	0.849	1.006	0.985	1.000
3-methylcyclohexanone	0.846	0.904	0.910	0.904	0.865	0.903	0.886	0.894	0.894	0.901	0.787	0.888	0.883	0.914
4-heptanone	0.871	0.877	0.883	0.894	0.798	0.895	0.845	0.879	0.888	0.854	0.771	0.848	0.849	0.880
4-methylcyclohexanone	0.858	0.904	0.913	0.905	0.859	0.902	0.885	0.892	0.893	0.898	0.788	0.887	0.883	0.914
5-nonanone	0.888	0.871	0.897	0.871	0.906	0.897	0.879	0.849	0.890	0.892	0.775	0.884	0.869	0.902
cyclohexanone	0.842	0.907	0.914	0.906	0.856	0.903	0.886	0.893	0.894	0.899	0.791	0.888	0.884	0.915
MAD		0.023	0.027	0.027	0.032	0.026	0.023	0.024	0.020	0.021	0.103	0.022	0.021	0.029
RMSD		0.032	0.036	0.033	0.039	0.032	0.027	0.029	0.026	0.029	0.108	0.026	0.025	0.038
$\sqrt{\frac{\pi}{2}}\left(\frac{MUE}{RMSD}\right)$		0.902	0.955	1.014	1.041	1.018	1.081	1.046	0.933	0.921	1.201	1.062	1.076	0.960
regression[c] slope (m)		1.017	1.019	1.016	0.977	1.020	1.000	1.005	1.013	1.014	0.885	1.005	0.998	1.031
R^2		0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
$\lvert 1-m \rvert$		0.017	0.019	0.016	0.023	0.020	0.000	0.005	0.013	0.014	0.115	0.005	0.002	0.031

[a] Data taken from ref.[S7-8] [b] Calculated at the B3LYP/6-311G(d,p) level of theory using a Poisson–Boltzmann continuum solvation model. [c] Linear regression with the *y*-intercept b = 0 of $\alpha_{calculated}$ versus $\alpha_{experimental}$.

Table S2. Isotopic fractionation α at 70°C with respect to liquid water calculated with selected exchange-correlation functionals, the def2-TZVP basis set and SMD solvation model for a series of ketones, compared to Wang *et al.*'s experimental (expt) and calculated (calc) values, calculated using Liu *et al.*'s formula Eq. 1) for β using ZPE_{harm} scaled by λ_{ZPE}.

ketone	Wang (expt[a])	Wang (calc[a,b])	M06-L	M06-L$_{D3}$	SOGGA11	OLYP	τHCTH	τHCTH$_{D3BJ}$	HCTH	HCTH$_{D3BJ}$	M11-L	O3LYP	τHCTHhyb	B3LYP
2,2,6-trimethylcyclohexanone	0.966	0.956	0.950	0.951	0.911	0.931	0.926	0.944	0.943	0.940	0.832	0.937	0.943	0.960
2,4-dimethyl-3-pentanone	0.975	0.999	0.983	0.988	0.970	0.976	0.981	0.985	0.994	0.988	0.863	0.986	0.973	1.013
2-heptanone	0.860	0.857	0.869	0.872	0.808	0.853	0.853	0.848	0.858	0.849	0.758	0.853	0.850	0.877
2-methyl-3-hexanone	0.910	0.918	0.917	0.914	0.882	0.903	0.901	0.905	0.911	0.902	0.804	0.906	0.895	0.928
2-methylcyclohexanone	0.897	0.919	0.922	0.917	0.870	0.902	0.899	0.906	0.908	0.902	0.806	0.902	0.896	0.926
3,5-dimethyl-4-heptanone	0.968	0.977	0.959	0.960	0.994	0.980	0.983	0.979	0.974	0.959	0.848	0.993	0.974	0.988
3-methylcyclohexanone	0.861	0.902	0.908	0.902	0.865	0.889	0.885	0.893	0.893	0.888	0.793	0.887	0.882	0.911
4-heptanone	0.888	0.877	0.883	0.893	0.798	0.883	0.847	0.879	0.887	0.845	0.778	0.850	0.851	0.880
4-methylcyclohexanone	0.863	0.902	0.910	0.903	0.859	0.889	0.885	0.891	0.892	0.886	0.793	0.886	0.883	0.911
5-nonanone	0.872	0.872	0.896	0.872	0.906	0.885	0.879	0.851	0.890	0.880	0.781	0.883	0.870	0.901
cyclohexanone	0.848	0.905	0.911	0.904	0.856	0.889	0.886	0.892	0.893	0.886	0.796	0.887	0.883	0.912
MAD		0.020	0.024	0.020	0.030	0.016	0.019	0.018	0.017	0.019	0.096	0.020	0.015	0.030
RMSD		0.027	0.030	0.026	0.040	0.021	0.024	0.022	0.022	0.023	0.099	0.023	0.020	0.035
$\sqrt{\frac{\pi}{2}}\left(\frac{MUE}{RMSD}\right)$		0.955	0.977	0.940	0.958	0.974	1.012	1.064	0.974	1.046	1.218	1.064	0.982	1.075
regression[c] slope (m)		1.017	1.019	1.016	0.981	1.007	1.001	1.006	1.013	1.001	0.893	1.006	0.999	1.030
R^2		0.999	0.999	0.999	0.998	1.000	0.999	0.999	1.000	0.999	0.999	0.999	1.000	0.999
$\lvert 1-m \rvert$		0.017	0.019	0.016	0.019	0.007	0.001	0.006	0.013	0.001	0.107	0.006	0.001	0.030

[a] Data taken from ref.[S7-8] [b] Calculated at the B3LYP/6-311G(d,p) level of theory using a Poisson–Boltzmann continuum solvation model. [c] Linear regression with the *y*-intercept b = 0 of $\alpha_{calculated}$ versus $\alpha_{experimental}$.

References

S1. Q. Liu, J. A. Tossell and Y. Liu, *Geochim. Cosmochim. Acta*, 2010, **74**, 6965-6983.

S2. J. Bron, C. F. Chang and M. Wolfsberg, *Z. Naturforsch., A: Phys. Sci.*, 1973, **28**, 129-136.

S3. P. Richet, Y. Bottinga and M. Javoy, *Ann. Rev. Earth Planet. Sci.*, 1977, **5**, 65-110.

S4. J. Horita and D. J. Wesolowski, *Geochim. Cosmochim. Acta*, 1994, **58**, 3425-3437.

S5. J. C. Vogel, P. M. Grootes and W. G. Mook, *Zeitschrift für Physik A Hadrons and Nuclei*, 1970, **230**, 225-238.

S6. W. G. Mook, J. C. Bommerson and W. H. Staverman, *Earth Planet. Sci. Lett.*, 1974, **22**, 169-176.

S7. (a) Y. Wang, A. L. Sessions, R. J. Nielsen and W. A. Goddard, III, *Geochim. Cosmochim. Acta*, 2009, **73**, 7060-7075; (b) Y. Wang, A. L. Sessions, R. J. Nielsen and W. A. Goddard, III, *Geochim. Cosmochim. Acta*, 2013, **107**, 82-95.