Supplementary Material: Efficient vibrationally correlated calculations using n-mode expansion-based kinetic energy operators

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Results and discussion

Table S1: Deviations of the ground state energy as well as the fundamental and first overtone excitation energies for the triatomic test molecules. Calculated for KEO approximations based on different n-mode expansions of the G matrix and V_{ep}, the Taylor-expansion based KEO variant 2M[G,V]2T as well as the full vibrational polyspherical KEO. Deviations are given relative to the full KEO. Calculated with FVCI. Wave numbers are reported in cm^{-1}.

	state	full	3M[G,V]	2M[G,V]	1M[G,V]	2M[G,V]2T
H_2O	GS	4651.05	0.00	0.00	-0.04	0.42
	ν_{b}	1597.09	-0.00	0.00	-0.15	1.19
	$2\nu_{\mathrm{b}}$	3157.00	-0.00	0.01	-0.44	3.17
	ν_{s}	3669.87	-0.00	0.00	-0.06	0.94
	ν_{as}	3767.77	-0.00	-0.00	-0.01	1.14
	$2\nu_{\mathrm{s}}$	7227.91	-0.00	0.00	-0.09	2.61
	$2\nu_{\mathrm{as}}$	7275.63	-0.00	0.00	-0.06	3.01
	MAD	-	0.00	0.00	0.12	1.78
H_2S	GS	3343.10	-0.00	0.00	-0.01	0.16
	ν_{b}	1183.63	-0.00	0.00	-0.02	0.44
	$2\nu_{\mathrm{b}}$	2356.30	-0.00	0.00	-0.06	1.10
	ν_{s}	2658.75	0.00	0.00	-0.00	0.40
	ν_{as}	2676.08	0.00	-0.00	-0.00	0.46
	$2\nu_{\mathrm{s}}$	5227.48	-0.00	0.00	-0.01	1.23
	$2\nu_{\mathrm{as}}$	5231.61	-0.00	0.00	-0.01	1.28
	MAD	-	0.00	0.00	0.02	0.72
F_2O	GS	1150.88	-0.00	0.00	-0.08	0.01
	ν_{b}	470.75	-0.00	0.00	-0.07	0.03
	ν_{as}	855.27	0.00	-0.00	0.02	0.03
	$2\nu_{\mathrm{b}}, \nu_{\mathrm{s}}$	935.58	-0.00	-0.00	-0.07	-0.05
	$\nu_{\mathrm{s}}, 2\nu_{\mathrm{b}}$	946.56	-0.00	0.00	-0.13	0.15
	$2\nu_{\mathrm{s}}$	1701.44	0.00	-0.00	0.02	0.07
	$2\nu_{\mathrm{as}}$	1784.19	-0.00	0.00	-0.10	0.37
	MAD	-	0.00	0.00	0.07	0.10
HOF	GS	3012.11	0.00	0.00	-0.03	0.39
	ν_{OF}	905.60	0.00	0.00	-0.05	0.00
	ν_{b}	1364.03	0.00	0.00	-0.05	1.08
	$2\nu_{\mathrm{OF}}$	1793.79	0.00	0.00	-0.10	0.01
	$2\nu_{\mathrm{b}}$	2709.26	0.00	0.00	-0.08	2.90
	ν_{OH}	3595.86	0.00	0.00	-0.07	1.80
	$2\nu_{\mathrm{OH}}$	7016.11	-0.00	0.00	-0.06	5.86
	MAD	-	0.00	0.00	0.06	1.72
SO_2	GS	1551.13	-0.00	0.00	-0.01	0.00
	ν_{b}	513.70	-0.00	0.00	-0.02	0.01
	$2\nu_{\mathrm{b}}$	1027.13	-0.00	0.00	-0.03	0.02
	ν_{s}	1170.64	-0.00	0.00	-0.04	0.01
	ν_{as}	1393.15	0.00	-0.00	0.01	0.01
	$2\nu_{\mathrm{s}}$	2334.29	-0.00	0.00	-0.08	0.01
	$2\nu_{\mathrm{as}}$	2551.82	-0.00	0.00	-0.03	0.02
	MAD	-	0.00	0.00	0.03	0.01

Table S2: Deviations of the vibrational ground state energy as well as the fundamental and first overtone excitation energies below 4000 cm^{-1} for CH_2O. Calculated for KEO approximations based on different n-mode expansions of the G matrix and V_{ep}, the Taylor expansion-based 2M[G,V]2T KEO variant as well as the full vibrational polyspherical KEO. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

state	full	3M[G,V]	2M[G,V]	1M[G,V]	2M[G,V]2T
GS	5773.68	-0.00	-0.06	1.96	0.63
ν_4	1167.94	-0.00	-0.06	-0.31	1.12
ν_6	1247.15	-0.00	-0.05	1.57	-0.15
ν_3	1499.42	-0.00	0.02	-0.22	1.42
ν_2	1749.62	0.00	0.02	-0.62	0.20
$2\nu_4$	2329.09	-0.01	-0.11	-1.69	3.57
$2\nu_6$	2491.44	0.00	-0.13	3.82	-0.84
ν_1	2782.07	0.01	-0.03	0.05	2.97
ν_5	2843.06	-0.01	-0.05	0.15	0.98
$2\nu_3$	3001.10	-0.01	0.04	-0.15	2.89
$2\nu_2$	3479.55	0.00	0.05	-1.31	0.51
MAX	-	0.01	0.13	3.82	3.57
MAD	-	0.00	0.06	1.08	1.39

Table S3: Deviations of the vibrational ground state energy as well as the fundamental and first overtone excitation energies below 4000 cm^{-1} for H_2O_2. Calculated for KEO approximations based on different n-mode expansions of the G matrix and V_{ep}, the Taylor expansion-based 2M[G,V]2T KEO variant as well as the full vibrational polyspherical KEO. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

state	full	3M[G,V]	2M[G,V]	1M[G,V]	2M[G,V]2T
GS	5346.45	-0.00	-0.01	-0.13	0.26
GS^-	9.98	-0.00	-0.00	-0.00	-0.06
ν_4^+	260.40	-0.00	-0.00	-0.12	0.02
ν_4^-	370.63	-0.00	-0.01	-0.24	-0.33
$2\nu_4^+$	569.80	-0.00	-0.03	-0.43	-0.46
$2\nu_4^-$	774.94	-0.00	-0.04	-0.72	-0.71
ν_3^+	877.39	-0.00	-0.01	-0.09	-0.03
ν_3^-	892.39	-0.00	-0.01	-0.07	0.07
ν_6^+	1270.63	0.00	0.02	-0.39	3.16
ν_6^-	1290.74	0.00	0.03	-0.44	3.56
ν_2^+	1398.10	-0.00	-0.02	0.94	-4.26
ν_2^-	1406.68	-0.00	-0.04	1.06	-4.61
	1738.04	-0.00	-0.01	-0.19	0.01
	1762.29	-0.00	-0.02	-0.22	0.15
$2\nu_6^+$	2522.30	0.00	0.04	-0.27	6.11
$2\nu_6^-$	2580.92	0.00	0.07	-0.63	5.64
$2\nu_2^+$	2776.90	0.00	-0.00	1.25	-8.53
$2\nu_2^-$	2878.86	0.00	-0.09	2.26	-10.09
ν_1^+	3611.46	-0.00	-0.02	-0.22	1.04
ν_5^+	3615.43	0.00	0.00	0.11	2.29
ν_5^-	3625.12	0.00	0.01	0.05	2.28
ν_1^-	3627.52	0.00	-0.09	0.10	-0.62
MAX	-	0.00	0.09	2.26	10.09
MAD	-	0.00	0.03	0.45	2.47

Table S4: Deviations of the vibrational ground state energy as well as fundamental and first overtone excitation energies below 4000 cm^{-1} for *trans*-HCOOH. Calculated for KEO approximations based on different static-grid n-mode expansions of the G matrix and V_{ep}, the Taylor expansion-based 2M[G,V]2T KEO variant as well as the full vibrational polyspherical KEO. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

state	full	3M[G,V]	2M[G,V]	1M[G,V]	2M[G,V]2T
GS	7328.25	-0.01	-0.05	1.21	0.95
ν_7	624.72	-0.01	-0.01	0.26	0.14
ν_9	636.90	-0.03	-0.03	-0.15	0.26
ν_8	1031.34	-0.00	-0.03	-0.23	0.78
ν_6	1106.33	-0.06	-0.04	-0.44	0.33
$2\nu_9$	1216.49	-0.35	-0.37	-0.51	1.31
$2\nu_7$	1268.69	-0.03	-0.01	0.58	0.21
ν_5	1300.84	0.30	0.29	0.49	-0.38
ν_4	1375.47	0.05	0.04	-0.41	0.81
ν_3	1775.47	-0.01	-0.03	-0.17	-0.08
$2\nu_8$	2057.62	-0.01	-0.07	-0.36	1.91
$2\nu_6$	2207.71	-0.03	0.00	-0.95	0.67
$2\nu_5$	2493.15	-0.04	-0.03	-0.79	1.12
$2\nu_4$	2758.31	0.19	0.17	1.19	1.35
ν_2	2940.96	0.08	0.07	0.02	1.68
$2\nu_3$	3545.57	-0.03	-0.05	-0.33	-0.18
ν_1	3568.13	0.00	0.02	-0.27	2.79
MAX	-	0.35	0.37	1.21	2.79
MAD	-	0.07	0.08	0.49	0.88

Table S5: Deviations of the vibrational ground state energy as well as fundamental and first overtone excitation energies below 4000 cm^{-1} for *trans*-HCOOH. Calculated for the 1M[G,V] KEO approximation with different coefficient screening thresholds (given in the column labels) as well as the full vibrational polyspherical KEO. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

state	full	0.0	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	1.0
GS	7328.25	1.21	1.21	1.21	1.21	1.20	-0.58	21.01
ν_7	624.72	0.26	0.26	0.26	0.26	0.37	-4.95	2.36
ν_9	636.90	-0.15	-0.15	-0.15	-0.15	-0.16	-1.63	-0.49
ν_8	1031.34	-0.23	-0.23	-0.23	-0.23	-0.21	-0.63	12.26
ν_6	1106.33	-0.44	-0.44	-0.44	-0.44	-0.43	0.27	4.19
$2\nu_9$	1216.49	-0.51	-0.51	-0.51	-0.51	-0.57	-2.72	13.54
$2\nu_7$	1268.69	0.58	0.58	0.58	0.58	0.79	-10.16	4.31
ν_5	1300.84	0.49	0.49	0.49	0.49	0.47	-2.03	-4.74
ν_4	1375.47	-0.41	-0.41	-0.41	-0.41	-0.47	-3.60	14.39
ν_3	1775.47	-0.17	-0.17	-0.17	-0.17	-0.18	1.15	9.87
$2\nu_8$	2057.62	-0.36	-0.36	-0.36	-0.36	-0.30	-1.23	35.86
$2\nu_6$	2207.71	-0.95	-0.95	-0.95	-0.95	-0.93	0.95	8.81
$2\nu_5$	2493.15	-0.79	-0.79	-0.79	-0.80	-0.84	-2.81	18.50
$2\nu_4$	2758.31	1.19	1.19	1.19	1.19	1.14	-7.27	28.01
ν_2	2940.96	0.02	0.02	0.02	0.02	0.01	1.07	14.75
$2\nu_3$	3545.57	-0.33	-0.33	-0.33	-0.33	-0.33	3.38	4.83
ν_1	3568.13	-0.27	-0.27	-0.27	-0.27	-0.26	-1.56	15.48

Table S6: Deviations of the vibrational ground state energy as well as fundamental and first overtone excitation energies below 4000 cm^{-1} for *trans*-HCOOH. Calculated for the 2M[G,V] KEO approximation with different coefficient screening thresholds (given in the column labels) as well as the full vibrational polyspherical KEO. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

state	full	0.0	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	1.0
GS	7328.25	-0.05	-0.05	-0.05	-0.05	-0.06	-2.03	21.01
ν_7	624.72	-0.01	-0.01	-0.01	-0.01	0.11	-5.33	2.36
ν_9	636.90	-0.03	-0.03	-0.03	-0.03	-0.04	-1.47	-0.49
ν_8	1031.34	-0.03	-0.03	-0.03	-0.03	0.00	-0.43	12.26
ν_6	1106.33	-0.04	-0.04	-0.04	-0.04	-0.02	0.44	4.19
$2\nu_9$	1216.49	-0.37	-0.37	-0.37	-0.37	-0.45	-2.33	13.54
$2\nu_7$	1268.69	-0.01	-0.01	-0.01	-0.01	0.22	-11.03	4.31
ν_5	1300.84	0.29	0.29	0.29	0.29	0.28	-2.32	-4.74
ν_4	1375.47	0.04	0.04	0.04	0.04	-0.03	-3.40	14.39
ν_3	1775.47	-0.03	-0.03	-0.03	-0.03	-0.03	1.14	9.87
$2\nu_8$	2057.62	-0.07	-0.07	-0.07	-0.07	0.01	-0.85	35.86
$2\nu_6$	2207.71	0.00	0.00	0.00	0.00	0.04	1.49	8.81
$2\nu_5$	2493.15	-0.03	-0.03	-0.03	-0.03	-0.07	-2.42	18.50
$2\nu_4$	2758.31	0.17	0.17	0.17	0.17	0.04	-8.04	28.01
ν_2	2940.96	0.07	0.07	0.07	0.07	0.08	1.19	14.75
$2\nu_3$	3545.57	-0.05	-0.05	-0.05	-0.05	-0.06	3.00	4.83
ν_1	3568.13	0.02	0.02	0.02	0.02	0.05	-1.54	15.48

Table S7: Deviations of the vibrational ground state energy as well as fundamental and first overtone excitation energies below 4000 cm^{-1} for *trans*-HCOOH. Calculated for the 3M[G,V] KEO approximation with different coefficient screening thresholds (given in the column labels) as well as the full vibrational polyspherical KEO. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

state	full	0.0	10^{-9}	10^{-8}	10^{-7}	10^{-6}	10^{-5}	1.0
GS	7328.25	-0.01	-0.01	-0.01	-0.01	-0.04	-2.03	21.01
ν_7	624.72	-0.01	-0.01	-0.01	-0.01	0.10	-5.34	2.36
ν_9	636.90	-0.03	-0.03	-0.03	-0.03	-0.04	-1.47	-0.49
ν_8	1031.34	-0.00	-0.00	-0.00	-0.00	0.03	-0.42	12.26
ν_6	1106.33	-0.06	-0.06	-0.06	-0.06	-0.03	0.43	4.19
$2\nu_9$	1216.49	-0.35	-0.35	-0.35	-0.35	-0.44	-2.30	13.54
$2\nu_7$	1268.69	-0.03	-0.03	-0.03	-0.02	0.20	-11.05	4.31
ν_5	1300.84	0.30	0.30	0.30	0.30	0.29	-2.32	-4.74
ν_4	1375.47	0.05	0.05	0.05	0.05	-0.03	-3.40	14.39
ν_3	1775.47	-0.01	-0.01	-0.01	-0.01	-0.02	1.14	9.87
$2\nu_8$	2057.62	-0.01	-0.01	-0.01	-0.01	0.07	-0.82	35.86
$2\nu_6$	2207.71	-0.03	-0.03	-0.03	-0.03	0.00	1.45	8.81
$2\nu_5$	2493.15	-0.04	-0.04	-0.04	-0.04	-0.08	-2.45	18.50
$2\nu_4$	2758.31	0.19	0.19	0.19	0.19	0.06	-8.01	28.01
ν_2	2940.96	0.08	0.08	0.08	0.08	0.08	1.18	14.75
$2\nu_3$	3545.57	-0.03	-0.03	-0.03	-0.03	-0.04	3.01	4.83
ν_1	3568.13	0.00	0.00	0.00	0.00	0.02	-1.55	15.48

Table S8: Deviations of the vibrational ground state energy as well as fundamental and first overtone excitation energies below 4000 cm^{-1} for *trans*-HCOOH, the 1M[G,V] and 2M[G,V] KEO variants and different maximum total polynomial orders of the functions in the fitting basis (FBMO) for the KEO n-mode expansions. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

				FBMO (1M[G,V] KEO)		
state	full	12	10	8	6	4
GS	7328.25	1.21	1.90	-2.08	10.12	-14.41
ν_7	624.72	0.26	0.36	-0.17	1.46	-2.15
ν_9	636.90	-0.15	1.20	-6.70	16.58	-31.32
ν_8	1031.34	-0.23	-0.19	-0.39	0.28	-1.06
ν_6	1106.33	-0.44	-0.07	-2.21	3.75	-9.42
$2\nu_9$	1216.49	-0.51	2.54	-11.81	23.91	-43.79
$2\nu_7$	1268.69	0.58	0.80	-0.28	3.03	-4.34
ν_5	1300.84	0.49	0.04	-1.07	9.99	-27.30
ν_4	1375.47	-0.41	-0.50	-0.79	1.96	-5.46
ν_3	1775.47	-0.17	-0.13	-0.36	0.46	-1.50
$2\nu_8$	2057.62	-0.36	-0.29	-0.66	0.60	-1.72
$2\nu_6$	2207.71	-0.95	-0.59	-3.39	5.88	-19.47
$2\nu_5$	2493.15	-0.79	-0.39	-2.90	6.74	-13.18
$2\nu_4$	2758.31	1.19	1.00	-0.45	5.75	-16.59
ν_2	2940.96	0.02	0.12	-1.29	-2.32	-1.39
$2\nu_3$	3545.57	-0.33	-0.21	-0.72	2.18	-3.39
ν_1	3568.13	-0.27	-0.02	-0.97	0.55	-2.40
MAX	-	1.21	2.54	11.81	23.91	43.79
MAD	-	0.49	0.61	2.13	5.62	11.70
				FBMO (2M[G,V] KEO)		
state	full	12	10	8	6	4
GS	7328.25	-0.05	0.65	-3.50	9.20	-16.49
ν_7	624.72	-0.01	0.10	-0.46	1.28	-2.75
ν_9	636.90	-0.03	1.33	-6.89	17.18	-32.72
ν_8	1031.34	-0.03	0.01	-0.20	0.56	-1.12
ν_6	1106.33	-0.04	0.36	-2.05	4.53	-10.85
$2\nu_9$	1216.49	-0.37	2.94	-12.65	25.85	-47.69
$2\nu_7$	1268.69	-0.01	0.21	-0.94	2.69	-5.41
ν_5	1300.84	0.29	-0.43	-0.90	8.83	-26.10
ν_4	1375.47	0.04	-0.10	-0.26	2.15	-5.07
ν_3	1775.47	-0.03	0.02	-0.23	0.68	-1.58
$2\nu_8$	2057.62	-0.07	0.01	-0.40	1.05	-2.01
$2\nu_6$	2207.71	0.00	0.40	-2.74	7.46	-9.32
$2\nu_5$	2493.15	-0.03	0.38	-2.31	7.85	-13.82
$2\nu_4$	2758.31	0.17	-0.27	-1.04	6.43	-17.25
ν_2	2940.96	0.07	0.10	-0.96	-2.09	-1.26
$2\nu_3$	3545.57	-0.05	0.07	-0.47	2.33	-3.48
ν_1	3568.13	0.02	0.26	-1.01	1.13	0.62
MAX	-	0.37	2.94	12.65	25.85	47.69
MAD	-	0.08	0.45	2.18	5.96	11.62

Table S9: Deviations of the vibrational ground state energy as well as fundamental and first overtone excitation energies below 4000 cm^{-1} for *trans*-HCOOH, the 2M[G,V] KEO variant, coefficient screening with a threshold of 10^{-7} and different maximum total polynomial orders of the functions in the fitting basis (FBMO, stated in the column labels) for the fitting of the two-mode coupling terms in G_{ij} and V_{ep}. Deviations are given relative to the full KEO. Calculated with VCC[3]. Wave numbers are reported in cm^{-1}.

state	full	12	10	8	6	4
GS	7328.25	-0.05	-0.03	-0.20	0.34	-0.84
ν_7	624.72	-0.01	0.00	-0.04	0.11	-0.29
ν_9	636.90	-0.03	0.00	-0.32	0.68	-1.58
ν_8	1031.34	-0.03	-0.02	-0.04	0.05	-0.26
ν_6	1106.33	-0.04	0.00	-0.24	0.55	-1.39
$2\nu_9$	1216.49	-0.37	-0.08	-1.34	2.00	-4.71
$2\nu_7$	1268.69	-0.01	0.00	-0.08	0.24	-0.61
ν_5	1300.84	0.29	0.04	0.69	-0.78	1.69
ν_4	1375.47	0.04	-0.01	0.12	-0.13	0.18
ν_3	1775.47	-0.03	-0.02	-0.04	0.03	-0.15
$2\nu_8$	2057.62	-0.07	-0.06	-0.10	0.10	-0.61
$2\nu_6$	2207.71	0.00	0.05	-0.27	0.94	-2.39
$2\nu_5$	2493.15	-0.03	-0.01	-0.17	0.44	-1.24
$2\nu_4$	2758.31	0.17	-0.03	0.49	-0.63	1.33
ν_2	2940.96	0.07	0.02	0.11	0.04	-0.04
$2\nu_3$	3545.57	-0.05	-0.05	-0.07	0.03	-0.25
ν_1	3568.13	0.02	-0.05	-0.05	0.39	-0.84