Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Benchmarking ionization potentials from the simple pCCD model

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Electronic Supplementary Information

S1 Ionization potentials

Compound	Irrep.	Exp.	CCSDT	RHF(1h)	RHF(2h1p)	PM(1h)	PM(2h1p)	pCCD(1h)	pCCD(2h1p)
C_2F_4	$2b_{3u}$	10.69	10.37	11.40	8.22	11.24	8.10	11.64	8.57
	$4b_{3g}$	15.90	15.78	18.41	13.05	18.54	13.62	19.02	14.22
	$6a_g$	15.90	15.78	18.41	13.49	18.71	13.18	19.11	13.74
	$4b_{2u}$	16.60	16.32	19.00	13.62	19.16	13.74	19.58	14.31
	$1a_u$	15.90	15.78	18.41	13.86	19.56	14.04	19.90	14.54
	$1b_{1g}$	16.60	16.64	19.55	14.05	19.74	14.23	20.07	14.73
	$5b_{1u}$	17.60	17.32	20.16	14.75	20.32	14.89	20.69	15.42
	$1b_{2g}$	18.20	18.02	20.85	15.50	21.04	15.66	21.34	16.11
	$1b_{3u}$	19.40	19.12	21.61	17.01	22.20	17.16	22.50	17.63
	$3b_{3g}$	19.40	19.41	21.99	16.63	21.73	16.72	22.29	17.40
	$3b_{2u}$	21.00	20.76	23.05	18.05	23.17	18.66	24.21	19.29
	$5a_g$	21.00	21.03	23.62	18.57	25.18	19.88	25.68	20.52
HCCF	2π	11.50	11.34	11.76	9.45	11.61	9.31	12.01	9.77
	1π	18.00	17.90	20.86	15.51	20.92	15.51	21.12	15.94
	7σ	18.00	18.12	19.95	16.48	19.93	16.42	20.39	17.04
	6σ	21.20	20.95	23.56	18.48	23.60	18.48	23.96	19.03
	5σ	24.30	24.40	28.68	23.15	28.72	23.14	29.21	23.86
HCCCN	2π	11.75	11.69	11.94	9.49	11.87	9.42	12.37	10.05
	9σ	13.54	13.44	16.22	11.21	16.26	11.16	16.57	11.84
	1π	14.18	14.19	15.09	12.02	15.12	12.00	15.59	12.67
	8σ	18.30	18.53	20.76	16.84	20.79	16.80	21.09	17.46
	7σ	21.30	21.55	24.83	19.69	24.85	19.67	25.13	20.33
	6σ	25.00	25.31	29.87	23.27	29.92	23.26	30.06	23.97
C_2N_2	$1\pi_g$	13.51	13.48	13.85	11.21	13.63	10.97	14.32	11.80
	$5\sigma_g$	14.49	14.40	17.11	13.61	17.09	12.09	17.40	12.84
	$4\sigma_u$	14.86	14.77	17.55	13.61	17.52	12.44	17.83	13.20
	$1\pi_u$	15.60	15.70	16.58	12.42	16.44	13.40	17.04	14.24
	$4\sigma_g$	22.80	23.29	26.91	21.69	26.86	21.56	27.11	22.25
CO	5σ	14.01	13.09	15.49	12.69	15.53	12.73	15.53	12.92
	1π	16.91	16.95	17.78	14.58	17.65	14.45	18.28	15.13
	4σ	19.72	19.54	22.09	17.31	22.12	17.29	22.51	17.81
CO_2	$1\pi_g$	13.79	13.63	15.11	11.13	14.92	10.93	15.35	11.47
	$1\pi_u$	17.60	17.05	19.64	15.49	19.57	15.36	19.97	15.87
	$3\sigma_u$	18.08	17.84	20.33	15.50	20.27	15.38	20.74	15.97
	$4\sigma_g$	19.40	19.08	21.90	16.91	21.85	16.78	22.27	17.33
C_3O_2	$2\pi_u$	10.80	10.62	11.50	8.31	11.31	8.13	11.46	8.49
	$1\pi_g$	15.00	14.92	17.59	12.59	17.65	12.50	18.18	13.15
	$1\pi_u$	16.00	15.72	18.44	13.66	18.51	13.59	18.91	14.07
	$5\sigma_u$	17.30	17.10	20.53	14.75	20.62	14.69	21.04	15.29
	$6\sigma_g$	17.80	17.28	20.84	14.96	20.94	14.90	21.35	15.49
	$4\sigma_u$	21.90	22.22	25.83	20.70	25.82	20.63	26.05	21.08
	$5\sigma_g$	25.60	25.88	30.42	24.06	30.46	23.92	30.62	24.39
OCS	2π	11.24	11.12	11.78	9.34	11.62	9.19	11.80	9.53
	1π	15.53	15.61	18.23	13.56	18.22	13.45	18.86	14.05
	4σ	16.04	15.83	17.50	14.04	17.49	13.99	17.57	14.30
	3σ	17.96	17.89	21.39	15.86	21.43	15.80	21.99	16.32
FCN	2π	13.65	13.50	14.11	11.51	13.98	11.37	14.45	11.91

	7σ	14.56	14.31	16.54	12.28	16.54	12.22	16.86	12.75
	1π	19.30	19.39	22.35	17.21	22.37	17.18	22.54	17.61
	6σ	22.60	22.79	25.44	20.44	25.39	20.34	25.61	20.80
N_2	$3\sigma_g$	15.58	15.45	17.46	13.65	17.46	13.65	17.63	14.02
	$1\pi_u$	16.93	16.89	17.30	15.13	17.30	15.13	17.56	15.47
	$2\sigma_u$	18.75	18.67	21.48	16.90	21.48	16.90	21.62	17.23
HC_4H	$1\pi_g$	10.30	10.20	10.34	8.04	10.25	7.97	10.78	8.57
	$1\pi_u$	12.71	12.70	13.59	10.59	13.57	10.56	14.02	11.19
	$5\sigma_g$	17.00	17.14	19.30	15.18	19.36	15.17	19.74	15.87
	$4\sigma_u$	17.50	17.82	20.07	16.06	20.16	16.05	20.54	16.81
	$4\sigma_g$	20.00	20.05	23.26	18.11	23.31	18.10	23.63	18.84
	$3\sigma_u$	23.30	23.42	27.80	21.88	27.87	21.09	28.04	22.03
	$3\sigma_g$	25.00	24.76	29.73	22.49	29.80	22.45	29.99	22.61
HCl	2π	12.77	12.58	13.36	11.18	13.20	11.01	13.44	11.30
	5σ	16.60	16.57	17.36	15.13	17.22	14.99	17.55	15.36
	4σ	25.80	26.63	30.51	23.64	30.56	23.56	30.69	23.93
HF	1π	16.19	15.90	17.85	13.54	17.76	13.44	18.19	13.95
	3σ	19.90	19.83	21.03	17.53	20.91	17.40	21.46	18.00
F_2	$1\pi_g$	15.87	15.58	18.34	13.01	18.34	13.01	18.67	13.59
	$1\pi_u$	18.80	18.74	22.21	16.40	22.21	16.40	22.55	17.05
	$3\sigma_g$	21.10	20.96	21.90	18.58	21.90	18.58	22.43	19.14
SiO	7σ	11.61	11.33	12.19	9.28	12.23	9.30	12.57	9.83
	2π	12.19	11.87	13.05	9.23	13.03	9.21	13.57	9.84
	6σ	14.80	14.58	16.69	13.17	16.83	13.33	17.14	13.70
CS	7σ	11.34	11.26	13.09	9.76	13.13	9.77	13.19	10.07
	2π	12.90	12.88	13.05	11.30	12.79	11.06	13.20	11.49
	6σ	18.03	18.08	19.08	15.00	19.15	14.93	19.27	15.32
P_2	$2\pi_u$	10.65	10.51	10.56	9.09	10.56	9.09	10.69	9.26
	$5\sigma_g$	10.84	10.65	11.30	9.13	11.30	9.13	11.28	9.19
H_2CO	$2b_2$	10.90	10.75	12.21	8.37	12.24	8.32	12.83	9.08
	$1b_1$	14.50	14.50	15.12	12.06	14.80	11.77	15.67	12.73
	$5a_1$	16.10	15.96	17.91	13.49	17.87	13.37	18.43	14.15
	$1b_2$	17.00	17.10	19.04	15.61	19.05	15.52	19.54	16.32
	$4a_1$	21.40	21.30	23.86	20.03	23.84	19.92	24.31	20.72
H_2O	$1b_1$	12.62	12.45	14.11	10.29	13.95	10.12	14.40	10.69
	$3a_1$	14.74	14.69	15.99	12.46	15.90	12.34	16.40	12.92
	$1b_2$	18.55	18.84	19.58	16.73	19.45	16.57	20.16	17.36
C_2H_4	$1b_{3u}$	10.68	10.64	10.80	8.82	10.43	8.46	11.14	9.24
	$1b_{3g}$	12.80	13.08	13.95	11.39	13.90	11.27	14.64	12.20
	$3a_g$	14.80	14.79	16.10	12.90	16.04	12.79	16.59	13.54
	$1b_{2u}$	16.00	16.14	17.63	14.43	17.58	14.24	18.24	15.24
	$2b_{1u}$	19.10	19.32	21.68	17.79	21.63	17.58	22.28	18.62
	$2a_g$	23.60	23.87	28.19	22.40	28.20	22.22	28.64	23.12
H_2CS	$3b_2$	9.38	9.25	9.83	7.65	9.76	7.51	10.22	8.05
	$2b_1$	11.76	11.78	11.96	10.14	11.51	9.71	12.20	10.43
	$7a_1$	13.85	13.88	14.86	12.05	14.85	11.98	15.20	12.48
	$2b_2$	15.20	15.61	17.71	13.86	17.69	14.07	18.09	14.96

	$6a_1$	19.90	19.60	22.28	17.36	22.31	17.15	22.71	17.98
$HCONH_2$	$10a'$	10.40	10.17	11.95	7.60	12.03	7.65	12.67	8.38
	$2a''$	10.70	10.56	11.68	8.06	11.64	8.05	12.09	8.61
	$1a''$	14.10	14.06	15.74	11.93	15.73	11.93	16.26	12.52
	$9a'$	14.80	14.67	16.64	12.15	16.73	12.20	17.33	12.94
	$8a'$	16.30	16.55	18.42	14.70	18.53	14.79	19.03	15.45
	$7a'$	18.80	19.25	20.55	16.81	20.63	16.85	21.08	17.50
	$6a'$	20.70	20.90	23.27	19.18	23.37	19.23	23.81	19.94
HCOOH	$10a'$	11.50	11.33	13.00	8.72	13.07	8.77	13.67	9.46
	$2a''$	12.60	12.47	13.78	9.83	13.72	9.81	14.32	10.45
	$9a'$	14.80	14.79	16.54	12.32	16.64	12.41	17.09	13.02
	$1a''$	15.80	15.71	17.50	13.43	17.55	13.49	18.00	14.11
	$8a'$	17.10	17.06	19.47	14.67	19.57	14.74	20.05	15.34
	$7a'$	17.80	17.81	19.83	15.87	19.91	15.94	20.32	16.59
	$6a'$	22.00	22.08	24.51	20.42	24.59	20.50	25.03	21.18
NSF	$13a'$	11.82	11.62	12.93	9.31	12.87	9.23	13.10	9.68
	$12a'$	13.50	13.30	15.18	11.08	15.26	11.12	15.49	11.56
	$3a''$	13.87	13.74	14.55	11.48	14.32	11.32	14.86	11.89
	$11a'$	15.62	15.24	18.16	12.85	18.29	12.90	18.55	13.36
	$2a''$	16.47	16.11	18.91	14.14	18.95	14.08	19.32	14.57
	$10a'$	17.20	16.35	19.04	14.24	19.14	14.28	19.50	14.81
O_3	$6a_1$	12.73	12.54	15.10	10.06	15.20	9.97	15.42	10.82
	$4b_2$	13.00	12.69	15.45	10.22	15.53	10.09	15.98	11.13
	$1a_2$	13.54	13.46	14.58	10.86	14.00	10.32	15.71	12.01
	$1b_1$	19.99	21.32	21.86	14.93	21.70	14.59	21.67	14.98
$gem-C_2H_2F_2$	$2b_1$	10.70	10.54	11.15	8.56	10.91	8.34	11.54	9.01
	$5b_2$	14.90	14.96	16.48	13.79	16.46	13.73	17.15	14.56
	$8a_1$	15.80	15.52	17.42	13.05	17.44	13.04	17.94	13.69
	$4b_2$	16.10	15.85	18.28	12.52	18.28	12.47	18.70	13.14
	$1a_2$	16.10	16.02	18.89	13.40	18.90	13.36	19.34	14.04
	$7a_1$	18.20	18.27	20.54	16.09	20.58	16.07	21.04	16.79
	$1b_1$	18.20	18.10	20.88	15.77	20.91	15.73	21.32	16.40
	$3b_2$	19.70	19.63	21.98	17.04	21.99	16.98	22.47	17.71
	$6a_1$	21.50	21.41	24.23	19.17	24.25	19.11	24.72	19.87
	$5a_1$	25.20	25.10	29.24	23.42	29.28	23.35	29.63	24.12
$cis-C_2H_2F_2$	$2b_1$	10.62	10.39	11.04	8.27	10.82	8.10	11.46	8.79
	$7a_1$	14.00	13.88	15.80	11.42	15.92	12.33	16.35	12.13
	$6b_2$	14.90	14.80	16.90	12.21	17.04	11.53	17.51	12.93
	$1a_2$	16.20	16.07	18.81	13.38	18.95	13.50	19.33	14.07
	$5b_2$	17.10	16.85	19.10	14.51	19.25	15.87	19.68	15.33
	$1b_1$	17.10	16.97	19.51	14.47	19.67	14.58	20.07	15.20
	$6a_1$	18.80	18.50	20.60	15.81	20.69	14.61	21.19	16.55
	$5a_1$	18.80	18.88	21.23	16.91	21.37	18.84	21.76	17.66
	$4b_2$	20.90	20.85	23.46	18.79	23.58	16.98	24.05	19.59
	$4a_1$	25.20	24.61	29.05	23.15	29.13	23.10	29.45	24.00
CH_4	$1t_2$	13.60	14.35	15.06	12.78	15.07	12.80	15.67	13.48
	$2a_1$	22.90	23.11	25.80	21.78	25.90	21.88	26.44	22.62
CH_3CCH	$2e$	10.54	10.46	10.63	8.39	10.62	8.39	11.21	9.05
	$1e$	14.60	15.17	16.26	13.42	16.35	13.51	16.86	14.20
	$7a_1$	15.40	15.22	16.85	13.11	16.90	13.15	17.34	13.81
	$6a_1$	17.40	17.65	19.62	15.86	19.71	15.92	20.19	16.69

CH_3CN	$2e$	12.46	12.45	12.72	10.15	12.73	10.16	13.44	10.95
	$7a_1$	13.17	12.97	15.26	10.69	15.31	10.73	15.71	11.41
	$1e$	15.70	16.24	17.33	14.59	17.39	14.65	17.87	15.32
	$6a_1$	17.40	17.38	19.15	15.43	19.21	15.48	19.62	16.11
	$5a_1$	24.90	24.88	28.45	23.58	28.54	23.69	28.93	24.47
CH_3NC	$7a_1$	11.32	11.21	13.02	9.64	13.15	9.79	13.31	10.16
	$2e$	12.50	12.55	13.01	10.23	13.09	10.31	13.69	10.97
	$1e$	16.10	16.59	17.64	14.69	17.74	14.80	18.34	15.52
	$6a_1$	18.20	18.38	20.22	16.16	20.29	16.24	20.85	16.96
	$5a_1$	25.00	25.06	28.02	23.30	28.13	23.43	28.62	24.19
NH_3	$3a_1$	10.80	10.74	11.87	8.80	11.80	8.74	12.24	9.25
	$1e$	16.00	16.48	17.21	14.58	17.20	14.57	17.84	15.29
CH_3F	$2e$	13.10	13.17	14.54	10.76	14.61	10.85	15.21	11.52
	$5a_1$	17.00	17.01	18.47	14.37	18.43	14.34	19.13	15.13
	$1e$	17.00	17.04	18.94	15.10	19.05	15.17	19.56	15.88
	$4a_1$	23.40	23.51	26.07	22.02	26.12	22.07	26.70	22.86
CH_2F_2	$2b_1$	13.30	13.29	14.72	10.98	14.83	11.12	15.38	11.75
	$4b_2$	15.40	14.92	17.27	12.07	17.36	12.18	17.85	12.79
	$6a_1$	15.40	15.20	16.98	12.57	17.10	12.70	17.65	13.33
	$1a_2$	15.80	15.59	18.20	12.87	18.33	13.02	18.75	13.59
	$3b_2$	19.10	18.75	20.62	15.95	20.69	16.03	21.29	16.74
	$5a_1$	19.10	18.97	21.00	16.59	21.11	16.72	21.62	17.38
	$1b_1$	19.10	19.15	21.25	17.29	21.39	17.42	21.84	18.05
CHF_3	$6a_1$	14.80	14.76	16.38	12.38	16.50	12.53	17.03	13.14
	$1a_2$	15.50	15.33	17.84	12.53	17.99	12.70	18.41	13.26
	$5e$	16.20	15.93	18.27	13.12	18.42	13.30	18.88	13.87
	$4e$	17.20	16.99	19.44	14.31	19.61	14.50	20.04	15.05
	$3e$	20.70	20.41	22.59	17.77	22.70	17.90	23.20	18.53
	$5a_1$	20.70	20.93	23.18	18.83	23.32	18.98	23.76	19.59
	$4a_1$	24.40	24.43	27.06	22.50	27.17	22.63	27.67	23.27
C_2H_6	$1e_g$	12.00	12.68	13.36	10.90	13.48	11.03	14.13	11.75
	$3a_{1g}$	12.70	13.06	14.05	11.00	14.06	11.02	14.62	11.65
	$2e_u$	15.00	15.38	16.36	13.62	16.47	13.75	17.05	14.43
	$2b_u$	20.40	20.69	22.97	19.15	23.12	19.31	23.68	20.06
	$2a_{1g}$	23.90	24.15	27.78	22.76	27.91	22.91	28.43	23.66
NNO	2π	12.89	12.74	13.79	10.19	13.65	10.06	13.97	10.43
	7σ	16.38	16.28	19.19	14.43	19.22	14.41	19.60	14.93
	1π	18.23	18.31	21.00	16.38	21.05	16.38	21.33	16.86
	6σ	20.11	19.89	22.81	17.39	22.84	17.34	22.94	17.73
CF_4	$1t_1$	16.20	16.09	18.66	13.37	18.82	13.56	19.22	14.09
	$4t_2$	17.40	17.24	19.42	14.48	19.57	14.66	20.05	15.24
	$1e$	18.50	18.18	20.84	15.67	21.01	15.87	21.39	16.38
	$3t_2$	22.10	21.93	24.31	19.45	24.42	19.59	24.87	20.16
	$4a_1$	25.10	24.85	27.60	22.57	27.70	22.69	28.17	23.28
C_2H_2	$1\pi_u$	11.49	11.42	11.59	9.63	11.34	9.40	11.91	10.06
	$3\sigma_g$	16.70	17.12	18.72	15.44	18.66	15.31	19.14	16.07
	$2\sigma_u$	18.70	19.00	21.09	17.07	21.02	17.23	21.54	18.10
	$2\sigma_g$	23.50	23.70	28.07	22.39	28.08	22.31	28.28	22.86

HCN	1π	13.61	13.72	13.98	11.78	13.79	11.61	14.35	12.25
	5σ	14.01	13.84	16.05	11.80	16.05	11.70	16.34	12.26
	4σ	19.86	20.43	22.44	19.10	22.39	18.99	22.72	19.62
SiF_4	$1t_1$	16.40	16.23	18.50	13.60	18.68	13.81	19.12	14.34
	$5t_2$	17.50	17.24	19.39	14.65	19.58	14.87	20.02	15.39
	$1e$	18.10	17.63	19.86	15.16	20.04	15.37	20.46	15.87
	$4t_2$	19.50	19.17	21.30	16.74	21.47	16.95	21.89	17.44
	$5a_1$	21.55	21.27	23.46	18.99	23.60	19.16	24.02	19.64

Table S1: Ionization potentials (IPs) [eV] for selected states determined from various IP-EOM-pCCD methods. IP-EOM-CCSDT and experimental reference data is given for comparison and taken from Ref. 1. All listed IPs were computed using the cc-pVTZ basis set and employing geometries optimized at the CCSD(T)/aug-cc-pVTZ level of theory, as provided in the supplementary information of Ref. 1. Irrep. indicates the leading configuration, where an electron is removed.

S2 Correlation plots

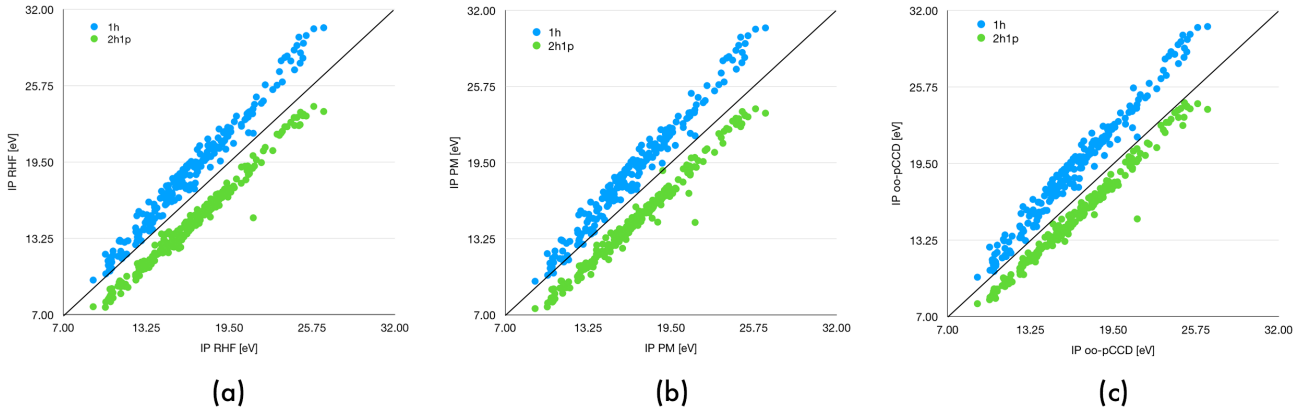

Figure S1: Correlation plots of the vertical ionization energies calculated with the IP-EOM-pCCD method using 1h and 2h1p operators with (a) RHF, (b) PM, and (c) natural orbital-optimized (oo-)pCCD orbitals.

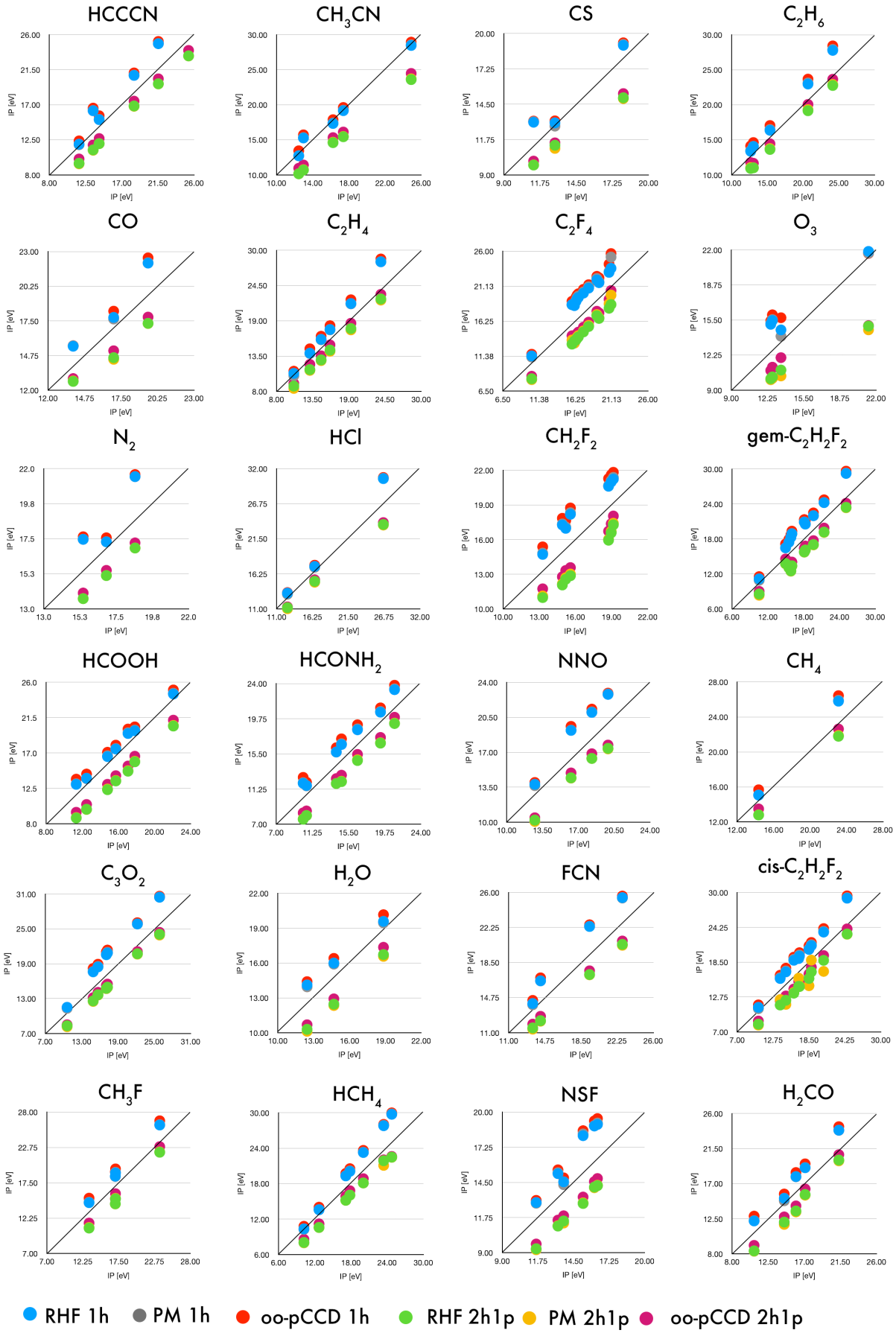

Figure S2: Correlation plots of the vertical ionization energies calculated with the IP-EOM-pCCD method using 1h and 2h1p operators with RHF, PM, and natural orbital-optimized (oo-)pCCD orbitals for individual molecules.

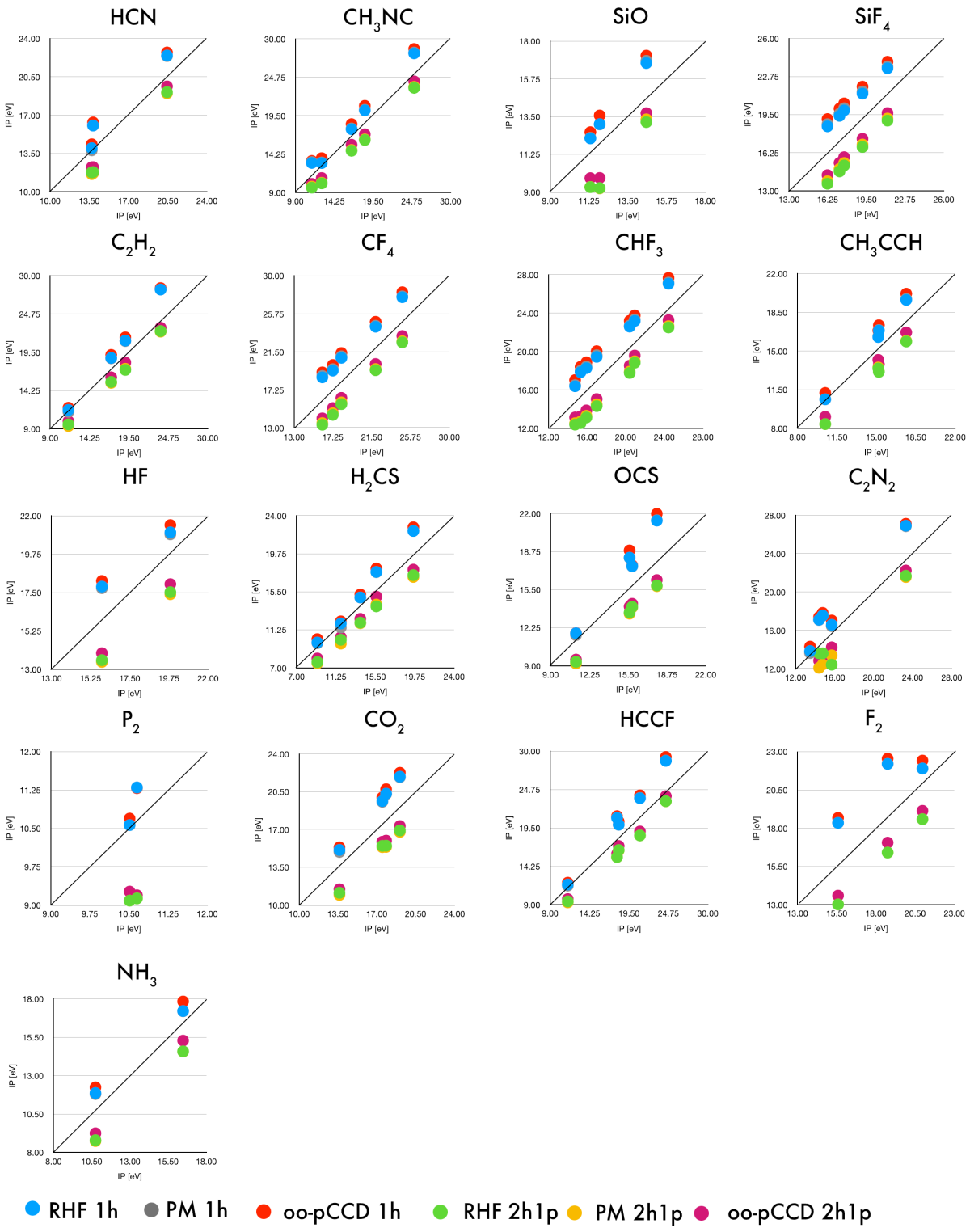

Figure S3: Correlation plots of the vertical ionization energies calculated with the IP-EOM-pCCD method using 1h and 2h1p operators with RHF, PM, and natural orbital-optimized (oo-)pCCD orbitals for individual molecules.

References

[1] D. S. Ranasinghe, J. T. Margraf, A. Perera, and R. J. Bartlett. Vertical valence ionization potential benchmarks from equation-of-motion coupled cluster theory and qtp functionals. *J. Chem. Phys.*, 150(7):074108, 2019.