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

Supplementary Information for

Configuration Interaction Singles based on Real-Space Numerical Grid Method: Kohn-Sham versus Hartree-Fock Orbitals

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1. KLI virtual orbitals of formaldehyde

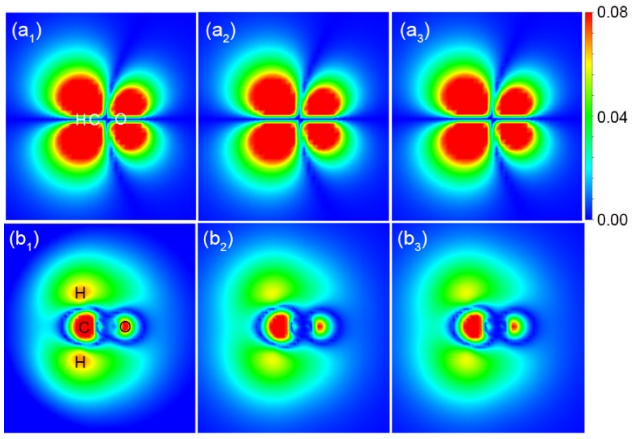

Figure S1. Change in the KLI virtual orbitals of formaldehyde according to the size of simulation box. (a) $\pi^*(2b_1)$ and (b) $\sigma^*(6a_1)$. The radius of simulation box increases from 9 (a_1 and b_1) to 15 (a_2 and b_2) to 21 Bohr (a_3 and b_3). The scaling factor was fixed to 0.3 Bohr.

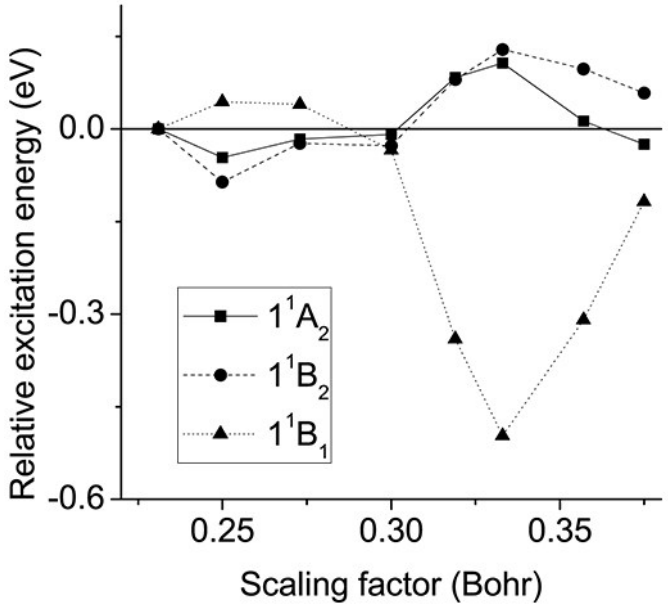

Figure S2. The convergence of the three lowest excitation energies of formaldehyde obtained from KLI-CIS with active space (12, 24) as a function of the scaling factor *h*. The reference values were obtained using h = 0.231 Bohr. All values in the graph were calculated using a spherical simulation box with the radius of 15.0 Bohr.

2. Excitation energies for three valence excited states of formaldehyde, benzene, formamide, and hydrogen molecules

Molecule	Excited state		Best estimation	PBE-CIS										KLI-CIS									
				3	6	9	12	15	30	45	60	75	90	3	6	9	12	15	30	45	60	75	90
Form-aldehyde	$1\ ^1A_2$	$n\rightarrow\pi^*$	3.88	4.61	4.62	4.62	4.61	4.62	4.63	4.62	4.63	4.64	4.64	4.38	4.38	4.38	4.38	4.38	4.37	4.37	4.37	4.37	4.36
	$1\ ^1B_1$	$\sigma\rightarrow\pi^*$	9.10	9.74	9.74	9.75	9.74	9.74	9.75	9.73	9.75	9.76	9.76	9.59	9.59	9.59	9.58	9.59	9.57	9.58	9.57	9.58	9.56
	$2\ ^1A_1$	$\pi\rightarrow\pi^*$	9.30	9.69	9.69	9.64	9.64	9.64	9.63	9.59	9.59	9.59	9.59	11.89	9.59	9.49	9.49	9.41	9.37	9.36	9.35	9.35	9.35
Benzene	$1\ ^1B_{1u}$	$\pi\rightarrow\pi^*$	6.54	7.02	6.98	6.96	6.97	6.97	6.81	6.82	6.76	6.74	6.76	6.93	6.89	6.87	6.80	6.79	6.73	6.71	6.69	6.68	6.68
	$1\ ^1B_{2u}$	$\pi\rightarrow\pi^*$	5.08	6.14	6.14	6.14	6.15	6.16	6.15	6.18	6.17	6.20	6.20	6.14	6.14	6.15	6.15	6.15	6.15	6.17	6.18	6.18	6.19
	$1\ ^1E_{1u}$	$\pi\rightarrow\pi^*$	7.13	9.57	7.15	7.15	7.13	7.13	7.12	7.14	7.15	7.18	7.19	9.49	7.45	7.46	7.43	7.43	7.39	7.40	7.41	7.43	7.43
Form-amide	$1\ ^1A''$	$n\rightarrow\pi^*$	5.63	6.81	6.81	6.80	6.80	6.80	6.80	6.79	6.79	6.80	6.79	6.42	6.42	6.41	6.41	6.42	6.40	6.40	6.40	6.40	6.39
	$2\ ^1A'$	$\pi\rightarrow\pi^*$	7.39	9.17	8.91	8.89	8.89	8.89	8.84	8.82	8.82	8.82	8.82	8.94	8.64	8.63	8.53	8.52	8.50	8.47	8.47	8.45	8.43
	$3\ ^1A'$	$\pi\rightarrow\pi^*$	-	11.15	9.39	9.36	9.35	9.35	9.32	9.28	9.28	9.28	9.28	9.61	9.23	9.16	9.04	9.02	8.99	8.90	8.90	8.89	8.87
Hydrogen molecule	$B\ ^1\Sigma_u^+$	$\sigma_g\rightarrow\sigma_u$	12.32	12.38	12.37	12.37	12.38	12.38	12.38	12.33	12.33	12.33	12.33	12.65	12.36	12.36	12.36	12.36	12.27	12.27	12.27	12.27	12.23
	$EF\ ^1\Sigma_g^+$	$\sigma_g\rightarrow\sigma_g$	12.79	12.69	12.69	12.69	12.62	12.62	12.62	12.62	12.62	12.62	12.62	12.66	12.66	12.66	12.66	12.61	12.61	12.58	12.58	12.58	12.58
	$C\ ^1\Pi_u$	$\sigma_g\rightarrow\pi_u$	12.85	12.86	12.86	12.86	12.63	12.63	12.63	12.63	12.62	12.62	12.62	12.70	12.70	12.70	12.65	12.65	12.65	12.64	12.64	12.64	12.64
MAD				0.81	0.56	0.55	0.58	0.58	0.56	0.55	0.55	0.55	0.56	0.94	0.49	0.48	0.46	0.46	0.44	0.44	0.44	0.44	0.44

Table S1. Excitation energies (eV) of KS-CIS calculations for formaldehyde, benzene, formamide, and hydrogen molecules. The numbers in the second row (with underlines) indicate the number of virtual orbitals comprising active spaces.

Molecule	Excited state		Best estimation	HF-CIS (grid)										HF-CIS (Gaussian)			
				3	6	9	12	15	30	45	60	75	90	aug-cc-pVQZ	aug-cc-pVDZ	cc-pVQZ	cc-pVDZ
Form-aldehyde	$1\ ^1A_2$	n→π*	3.88	9.50	9.23	9.23	6.32	6.32	5.91	5.91	5.20	5.20	5.16	4.51	4.49	4.52	4.48
	$1\ ^1B_1$	σ→π*	9.10	11.77	11.75	11.04	11.04	11.03	11.03	10.78	10.77	10.77	10.77	9.64	9.69	9.65	9.66
	$2\ ^1A_1$	π→π*	9.30	10.05	10.05	10.04	10.04	10.04	9.69	9.68	9.68	9.58	9.58	9.43	9.49	9.62	9.95
Benzene	$1\ ^1B_{1u}$	π→π*	6.54	11.59	11.53	11.49	8.00	8.00	6.81	6.79	6.79	6.68	6.68	6.15	6.16	6.20	6.35
	$1\ ^1B_{2u}$	π→π*	5.08	11.81	11.78	11.76	7.83	7.83	6.29	6.29	6.29	6.16	6.15	5.99	6.00	6.04	6.18
	$1\ ^1E_{1u}$	π→π*	7.13	11.69	7.59	7.57	7.56	7.56	7.35	7.35	7.34	7.34	7.34	7.51	7.78	8.08	8.36
Formamide	$1\ ^1A''$	n→π*	5.63	8.52	8.51	8.51	8.49	8.49	8.01	7.98	7.97	7.84	7.84	6.45	6.44	6.49	6.48
	$2\ ^1A'$	π→π*	7.39	9.40	9.33	9.33	9.31	9.31	8.92	8.90	8.86	8.76	8.75	8.43	8.46	8.74	9.09
	$3\ ^1A'$	π→π*	-	9.62	9.59	9.58	9.58	9.58	9.28	9.26	9.23	9.18	9.12	8.87	8.89	10.04	11.07
Hydrogen molecule	$B\ ^1\Sigma_u^+$	σ_g→σ_u	12.32	13.31	13.31	13.31	13.31	13.31	12.52	12.52	12.25	12.25	12.25	12.28	12.25	12.89	13.56
	$EF\ ^1\Sigma_g^+$	σ_g→σ_g	12.79	13.06	13.06	13.06	13.06	13.06	12.66	12.66	12.66	12.58	12.58	12.65	12.72	15.76	21.43
	$C\ ^1\Pi_u$	σ_g→π_u	12.85	-	13.51	13.51	13.51	13.51	12.91	12.91	12.91	12.69	12.69	13.62	15.39	20.56	39.89
MAD				-	2.51	2.44	1.50	1.49	0.94	0.91	0.83	0.79	0.79	0.53	0.72	1.56	3.98

Table S2. Excitation energies (eV) of HF-CIS calculations using numerical grid and Gaussian basis sets for formaldehyde, benzene, formamide, and hydrogen molecules. The numbers in the second row (with underlines) indicate the number of virtual orbitals comprising active spaces.

3. CIS coefficients for three valence excited states of formaldehyde, benzene, formamide, and hydrogen molecules

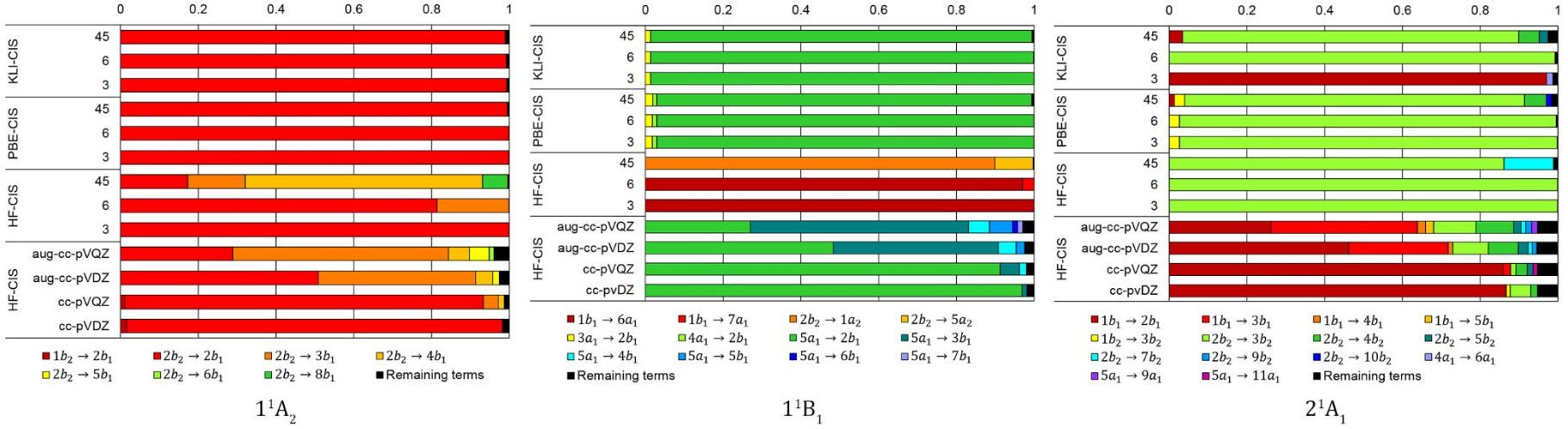

Figure S3. CIS coefficients for the 1^1A_2, 1^1B_1, and 2^1A_1 states of formaldehyde.

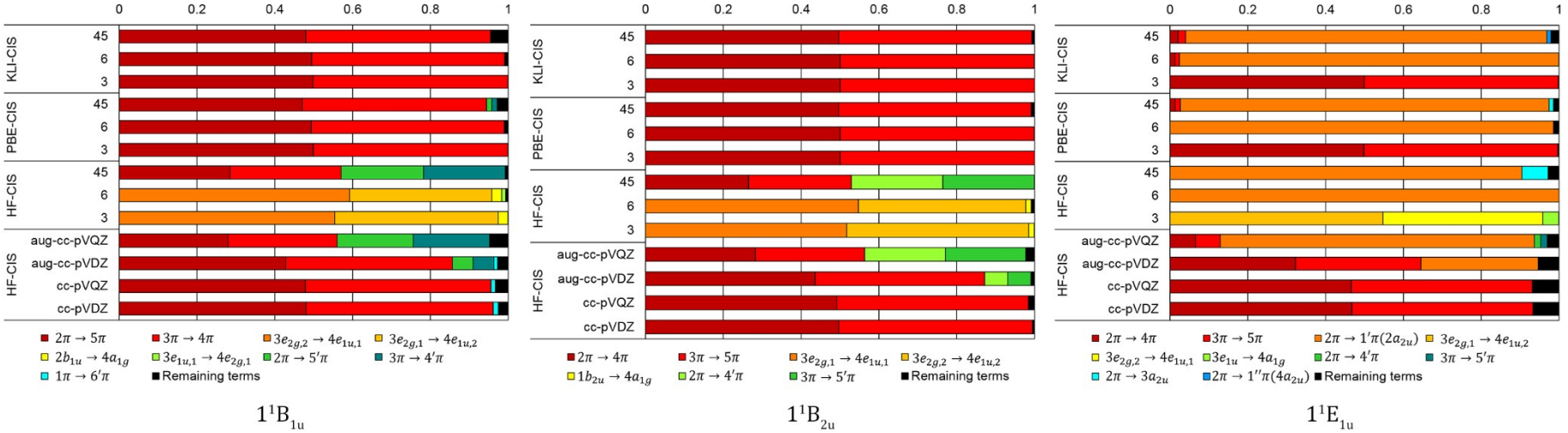

Figure S4. CIS coefficients for the 1^1B_{1u}, 1^1B_{2u}, and 1^1E_{1u} states of benzene.

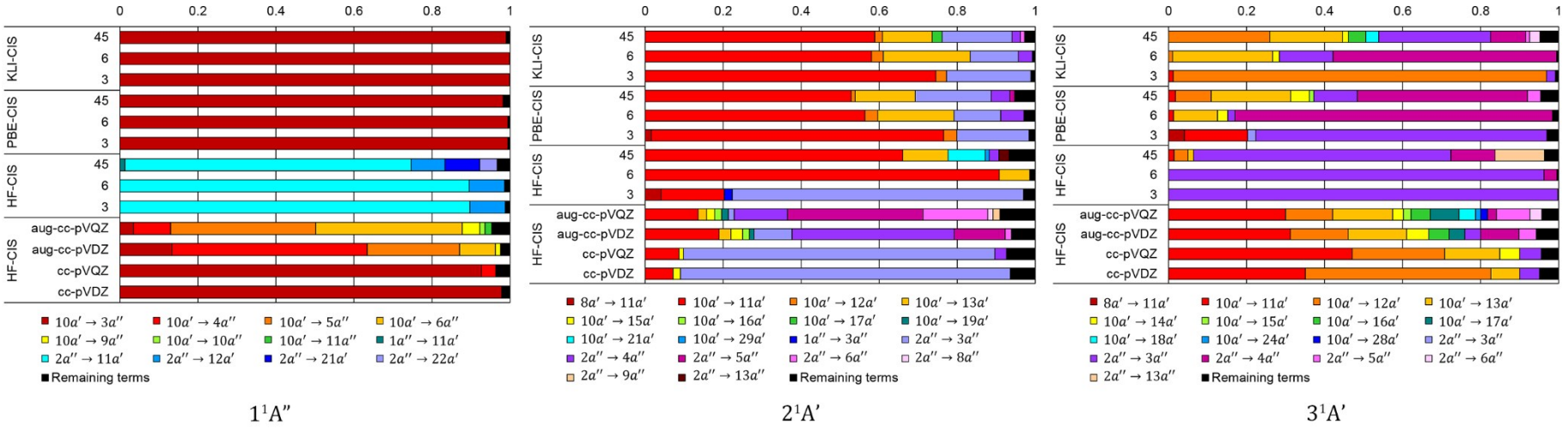

Figure S5. CIS coefficients for the $1^1A''$, $2^1A'$, and $3^1A'$ states of formamide.

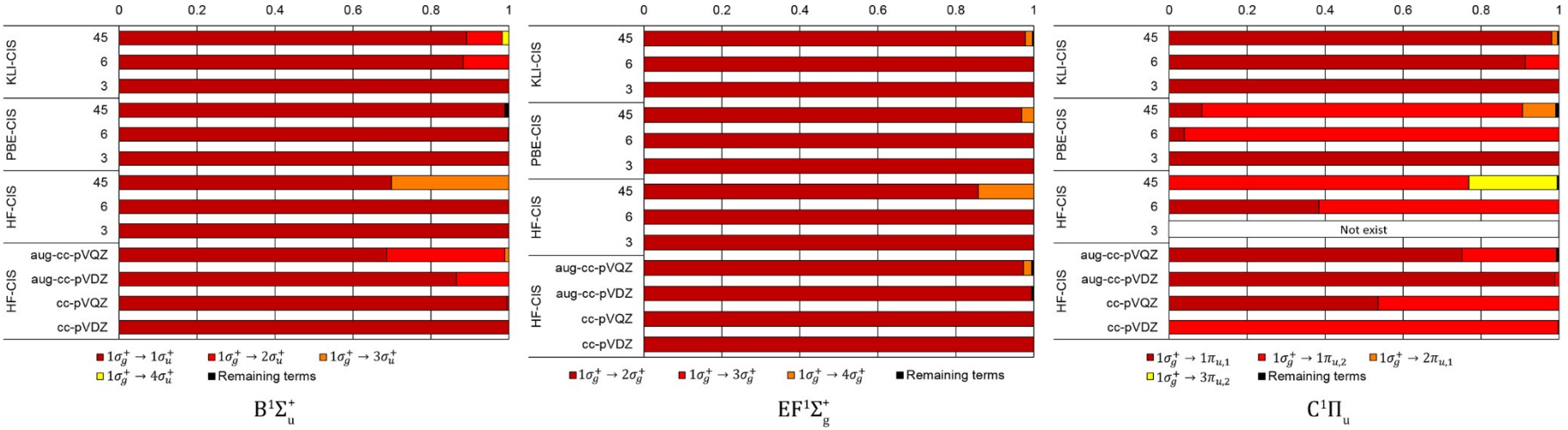

Figure S6. CIS coefficients for the $B^1\Sigma_u^+$, $EF^1\Sigma_g^+$, and $C^1\Pi_u$ states of hydrogen molecule.