

# A Mountaineering Strategy to Excited States: Highly-Accurate Reference Energies and Benchmarks

## Supporting Information

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## S1 Basis set and frozen-core effects

### S1.1 Water, ammonia and hydrogen chloride

Table S1: CC3 vertical transition energies of water, hydrogen sulfide, ammonia, and hydrogen chloride using various atomic basis sets. FC stands for frozen core (large frozen core for sulfur and chlorine). All values are in eV.

	<i>aug-cc-pVDZ</i>	<i>aug-cc-pVTZ</i>	<i>d-aug-cc-pVTZ</i>	<i>aug-cc-pVQZ</i>	<i>d-aug-cc-pVQZ</i>	<i>t-aug-cc-pVQZ</i>	<i>aug-cc-pV5Z</i>	<i>d-aug-cc-pV5Z</i>
	FC	FC	FC	FC	FC	FC	Full	Full
	Water							
$^1B_1(n \rightarrow 3s)$	7.51	7.60	7.60	7.65	7.66	7.65	7.66	7.67
$^1A_2(n \rightarrow 3p)$	9.29	9.38	9.37	9.43	9.42	9.42	9.42	9.44
$^1A_1(n \rightarrow 3s)$	9.92	9.97	9.89	10.00	9.94	9.93	9.94	10.00
$^3B_1(n \rightarrow 3s)$	7.13	7.23	7.23	7.28	7.29	7.28	7.29	7.31
$^3A_2(n \rightarrow 3p)$	9.12	9.22	9.30	9.26	9.27	9.26	9.26	9.28
$^3A_1(n \rightarrow 3s)$	9.47	9.52	9.52	9.56	9.56	9.56	9.56	9.57
	Hydrogen sulfide							
$^1A_2(n \rightarrow 4p)$	6.29	6.19	6.17	6.16	6.15	6.15	6.14	6.11
$^1B_1(n \rightarrow 4s)$	6.10	6.24	6.24	6.29	6.28	6.29	6.27	6.29
$^3A_2(n \rightarrow 4p)$	5.91	5.82	5.81	5.80	5.79	5.80	5.79	5.75
$^3B_1(n \rightarrow 4s)$	5.75	5.88	5.88	5.93	5.92	5.93	5.92	5.94
	Ammonia							
$^1A_2(n \rightarrow 3s)$	6.46	6.57	6.57	6.61	6.61	6.61	6.61	6.63
$^1E(n \rightarrow 3p)$	8.06	8.15	8.12	8.18	8.18	8.16	8.16	8.17
$^1A_1(n \rightarrow 3p)$	9.66	9.32	8.56	9.11	9.11	8.61	8.60	8.62
$^1A_2(n \rightarrow 4s)$	10.40	9.95	9.12	9.77	9.77	9.16	9.17	9.18
$^3A_2(n \rightarrow 3s)$	6.18	6.29	6.29	6.33	6.34	6.33	6.34	6.35
	Hydrogen chloride							
$^1\Pi(\text{CT})$	7.82	7.84	7.83	7.89	7.87	7.88	7.87	7.87

## S1.2 Dinitrogen and carbon monoxide

Table S2: CC3 vertical transition energies of dinitrogen (top) and carbon monoxide (bottom) using various atomic basis sets. See caption of Table S1 for more details.

	<i>aug-cc-pVDZ</i>	<i>aug-cc-pVTZ</i>	<i>aug-cc-pVQZ</i>	<i>aug-cc-pVQZ</i>	<i>d-aug-cc-pVQZ</i>	<i>t-aug-cc-pVQZ</i>	<i>aug-cc-pV5Z</i>	<i>d-aug-cc-pV5Z</i>	<i>Full</i>
	FC	FC	FC	FC	FC	FC	Full	Full	Full
Dinitrogen									
$^1\Pi_g(V; n \rightarrow \pi^*)$	9.44	9.34	9.33	9.32	9.33	9.32	9.33	9.32	9.32
$^1\Sigma_u^-(V; \pi \rightarrow \pi^*)$	10.06	9.88	9.87	9.87	9.87	9.87	9.87	9.87	9.86
$^1\Delta_u(V; \pi \rightarrow \pi^*)$	10.43	10.29	10.27	10.27	10.27	10.27	10.27	10.27	10.27
$^1\Sigma_g^+(R; n \rightarrow \sigma^*)$	13.23	13.01	12.90	12.91	12.27	12.28	12.27	12.28	12.31
$^1\Pi_u(R)$	13.28	13.22	13.17	13.16	12.89	12.90	12.89	12.90	12.92
$^1\Sigma_u^+(R; n \rightarrow \sigma^*)$	13.14	13.12	13.09	13.10	12.94	12.96	12.94	12.96	12.98
$^1\Pi_u(R)$	13.64	13.49	13.42	13.40	13.34	13.31	13.34	13.31	13.30
$^3\Sigma_u^+(V; \pi \rightarrow \pi^*)$	7.67	7.68	7.71	7.70	7.71	7.70	7.71	7.70	7.71
$^3\Pi_g(V; n \rightarrow \pi^*)$	8.07	8.04	8.04	8.03	8.04	8.03	8.04	8.03	8.04
$^3\Delta_u(V; \pi \rightarrow \pi^*)$	8.97	8.87	8.87	8.86	8.87	8.86	8.87	8.86	8.87
$^3\Sigma_u^-(V; \pi \rightarrow \pi^*)$	9.78	9.68	9.68	9.67	9.68	9.67	9.68	9.67	9.67
Carbon monoxide									
$^1\Pi(V; n \rightarrow \pi^*)$	8.57	8.49	8.47	8.46	8.47	8.45	8.47	8.45	8.45
$^1\Sigma^-(V; \pi \rightarrow \pi^*)$	10.12	9.99	9.99	9.98	9.99	9.98	9.99	9.98	9.98
$^1\Delta(V; \pi \rightarrow \pi^*)$	10.23	10.12	10.12	10.11	10.12	10.11	10.11	10.11	10.11
$^1\Sigma^+(R)$	10.92	10.94	10.90	10.91	10.72	10.72	10.72	10.72	10.74
$^1\Sigma^+(R)$	11.48	11.49	11.46	11.47	11.33	11.34	11.33	11.34	11.35
$^1\Pi(R)$	11.74	11.69	11.63	11.64	11.46	11.46	11.46	11.46	11.48
$^3\Pi(V; n \rightarrow \pi^*)$	6.31	6.30	6.30	6.29	6.30	6.29	6.30	6.29	6.29
$^3\Sigma^+(V; \pi \rightarrow \pi^*)$	8.45	8.45	8.48	8.47	8.48	8.47	8.48	8.47	8.48
$^3\Delta(V; \pi \rightarrow \pi^*)$	9.37	9.30	9.31	9.30	9.31	9.30	9.31	9.30	9.30
$^3\Sigma^-(V; \pi \rightarrow \pi^*)$	9.89	9.82	9.82	9.81	9.81	9.81	9.82	9.81	9.81
$^3\Sigma^-(R)$	10.39	10.45	10.44	10.45	10.33	10.33	10.33	10.34	10.35

### S1.3 Acetylene and ethylene

Table S3: CC3 vertical transition energies determined of acetylene (top) and ethylene (bottom) using various atomic basis sets. See caption of Table S1 for more details.

	<i>aug-cc-pVDZ</i>	<i>aug-cc-pVTZ</i>	<i>aug-cc-pVQZ</i>	<i>aug-cc-pVQZ</i>	<i>d-aug-cc-pVQZ</i>	<i>aug-cc-pV5Z</i>	<i>d-aug-cc-pV5Z</i>	<i>d-aug-cc-pV5Z</i>
	FC	FC	FC	Full	FC	Full	Full	Full
Acetylene								
$^1\Sigma_u^-(\pi \rightarrow \pi^*)$	7.21	7.09	7.09	7.09	7.09	7.09	7.09	7.09
$^1\Delta_u(\pi \rightarrow \pi^*)$	7.51	7.42	7.41	7.42	7.41	7.42	7.42	7.42
$^3\Sigma_u^+(\pi \rightarrow \pi^*)$	5.48	5.50	5.53	5.52	5.53	5.52	5.53	5.53
$^3\Delta_u(\pi \rightarrow \pi^*)$	6.46	6.40	6.40	6.40	6.40	6.40	6.40	6.40
$^3\Sigma_u^-(\pi \rightarrow \pi^*)$	7.13	7.07	7.07	7.07	7.07	7.07	7.08	7.08
$^1A_u[F](\pi \rightarrow \pi^*)$	3.70	3.64	3.63	3.63	3.63	3.63	3.63	3.63
$^1A_2[F](\pi \rightarrow \pi^*)$	3.92	3.84	3.83	3.84	3.84	3.84	3.84	3.84
Ethylene								
$^1B_{3u}(\pi \rightarrow 3s)$	7.29	7.35	7.38	7.39	7.37	7.38	7.39	7.39
$^1B_{1u}(\pi \rightarrow \pi^*)$	7.94	7.91	7.90	7.91	7.90	7.93	7.91	7.90
$^1B_{1g}(\pi \rightarrow 3p)$	7.97	8.03	8.04	8.05	8.03	8.04	8.05	8.05
$^3B_{1u}(\pi \rightarrow \pi^*)$	4.53	4.53	4.54	4.53	4.54	4.53	4.53	4.53
$^3B_{3u}(\pi \rightarrow 3s)$	7.17	7.24	7.27	7.28	7.26	7.28	7.29	7.29
$^3B_{1g}(\pi \rightarrow 3p)$	7.93	7.98	8.00	8.00	7.99	7.99	8.01	8.00

## S1.4 Formaldehyde, methanimine and thioformaldehyde



Table S4: CC3 vertical transition energies determined of formaldehyde (top), methanimine (center), and thioformaldehyde (bottom) using various atomic basis sets. See caption of Table S1 for more details.

	<i>aug-cc-pVDZ</i>	<i>aug-cc-pVTZ</i>	<i>aug-cc-pVQZ</i>	<i>d-aug-cc-pVQZ</i>	<i>aug-cc-pV5Z</i>	<i>d-aug-cc-pV5Z</i>	<i>Full</i>
	FC	FC	FC	Full	FC	Full	Full
	Formaldehyde						
$^1A_2(n \rightarrow \pi^*)$	4.00	3.97	3.97	3.96	3.97	3.96	3.96
$^1B_2(n \rightarrow 3s)$	7.05	7.18	7.23	7.23	7.22	7.23	7.25
$^1B_2(n \rightarrow 3p)$	8.02	8.07	8.10	8.11	8.05	8.06	8.08
$^1A_1(n \rightarrow 3p)$	8.08	8.18	8.22	8.23	8.20	8.20	8.22
$^1A_2(n \rightarrow 3p)$	8.65	8.64	8.60	8.61	8.44	8.45	8.47
$^1B_1(\sigma \rightarrow \pi^*)$	9.31	9.19	9.19	9.18	9.19	9.18	9.18
$^1A_1(\pi \rightarrow \pi^*)$	9.59	9.48	9.46	9.46	9.30	9.31	9.31
$^3A_2(n \rightarrow \pi^*)$	3.58	3.57	3.58	3.57	3.58	3.57	3.57
$^3A_1(\pi \rightarrow \pi^*)$	6.09	6.05	6.06	6.06	6.07	6.06	6.06
$^3B_2(n \rightarrow 3s)$	6.91	7.03	7.08	7.09	7.08	7.09	7.11
$^3B_2(n \rightarrow 3p)$	7.84	7.92	7.95	7.96	7.91	7.96	7.94
$^3A_1(n \rightarrow 3p)$	7.97	8.08	8.12	8.12	8.10	8.11	8.13
$^3B_1(n \rightarrow 3d)$	8.48	8.41	8.42	8.41	8.42	8.41	8.41
$^1A''[F](n \rightarrow \pi^*)$	2.87	2.84	2.85	2.84	2.85	2.84	2.84
	Methanimine						
$^1A''(n \rightarrow \pi^*)$	5.26	5.20	5.20	5.18	5.20	5.18	5.18
$^3A''(n \rightarrow \pi^*)$	4.63	4.61	4.62	4.60	4.62	4.60	4.60
	Thioformaldehyde						
$^1A_2(n \rightarrow \pi^*)$	2.27	2.23	2.23	2.21	2.23	2.21	2.21
$^1B_2(n \rightarrow 4s)$	5.80	5.91	5.95	5.95	5.95	5.94	5.96
$^1A_1(\pi \rightarrow \pi^*)$	6.62	6.48	6.46	6.45	6.45	6.45	6.43
$^3A_2(n \rightarrow \pi^*)$	1.97	1.94	1.95	1.94	1.95	1.94	1.93
$^3A_1(\pi \rightarrow \pi^*)$	3.43	3.38	3.40	3.39	3.40	3.39	3.39
$^3B_2(n \rightarrow 4s)$	5.64	5.72	5.75	5.75	5.75	5.74	5.75
$^1A_2[F](n \rightarrow \pi^*)$	2.00	1.97	1.98	1.96	1.97	1.96	1.95

## S1.5 Larger compounds

Table S5: CC3 vertical transition energies of six compounds incorporating three non-hydrogen atoms. See caption of Table S1 for more details.

Molecule state	<i>aug-cc-pVDZ</i>	<i>aug-cc-pVTZ</i>	<i>aug-cc-pVQZ</i>		<i>d-aug-cc-pVQZ</i>	
	FC	FC	FC	Full	Full	
Acetaldehyde	$^1A''(n \rightarrow \pi^*)$	4.34	4.31	4.32	4.31	
	$^3A''(n \rightarrow \pi^*)$	3.96	3.95	3.97	3.96	
Cyclopropene	$^1B_1(\sigma \rightarrow \pi^*)$	6.72	6.68	6.68	6.68	
	$^1B_2(\pi \rightarrow \pi^*)$	6.77	6.73	6.73	6.73	
	$^3B_2(\pi \rightarrow \pi^*)$	4.34	4.34	4.35	4.34	
	$^3B_1(\sigma \rightarrow \pi^*)$	6.43	6.40	6.41	6.40	
Diazomethane	$^1A_2(\pi \rightarrow \pi^*)$	3.10	3.07	3.07	3.06	3.06
	$^1B_1(\pi \rightarrow 3s)$	5.32	5.45	5.49	5.51	5.50
	$^1A_1(\pi \rightarrow \pi^*)$	5.80	5.84	5.85	5.85	5.83
	$^3A_2(\pi \rightarrow \pi^*)$	2.84	2.83	2.82	2.82	2.83
	$^3A_1(\pi \rightarrow \pi^*)$	4.05	4.03	4.04	4.03	4.03
	$^3B_1(\pi \rightarrow 3s)$	5.17	5.31	5.35	5.37	5.36
	$^3A_1(\pi \rightarrow 3p)$	6.83	6.80	6.81	6.80	6.70
	$^1A''[F](\pi \rightarrow \pi^*)$	0.68	0.68	0.68	0.67	0.67
Formamide	$^1A''(n \rightarrow \pi^*)$	5.71	5.66	5.66	5.64	
	$^1A'(n \rightarrow 3s)$	6.65	6.74	6.78	6.79	
	$^1A'(\pi \rightarrow \pi^*)^a$	7.63	7.62	7.63	7.63	
	$^1A'(n \rightarrow 3p)^a$	7.31	7.40	7.43	7.43	
	$^3A''(n \rightarrow \pi^*)$	5.42	5.38	5.39	5.37	
	$^3A'(\pi \rightarrow \pi^*)$	5.83	5.82	5.83	5.82	
Ketene	$^1A_2(\pi \rightarrow \pi^*)$	3.89	3.88	3.88	3.88	3.88
	$^1B_1(n \rightarrow 3s)$	5.83	5.96	6.00	6.01	6.01
	$^1A_2(\pi \rightarrow 3p)$	7.05	7.16	7.19	7.20	7.17
	$^3A_2(n \rightarrow \pi^*)$	3.79	3.78	3.79	3.78	3.78
	$^3A_1(\pi \rightarrow \pi^*)$	5.62	5.61	5.62	5.60	5.60
	$^3B_1(n \rightarrow 3s)$	5.63	5.76	5.81	5.82	5.82
	$^3A_2(\pi \rightarrow 3p)$	7.01	7.12	7.15	7.16	7.14
	$^1A''[F](\pi \rightarrow \pi^*)$	1.00	1.00	1.00	1.00	1.00
Nitrosomethane	$^1A''(n \rightarrow \pi^*)$	2.00	1.96	1.96	1.96	
	$^1A'(n, n \rightarrow \pi^*, \pi^*)$	5.75	5.76	5.74	5.73	
	$^1A'(n \rightarrow 3s/3p)$	6.20	6.31	6.35	6.36	
	$^3A''(n \rightarrow \pi^*)$	1.13	1.14	1.15	1.14	
	$^3A'(\pi \rightarrow \pi^*)$	5.54	5.51	5.52	5.52	
$^1A''[F](n \rightarrow \pi^*)$	1.70	1.69	1.67	1.66		
Streptocyanine-C1	$^1B_2(\pi \rightarrow \pi^*)$	7.14	7.13	7.13	7.12	
	$^3B_2(\pi \rightarrow \pi^*)$	5.48	5.48	5.49	5.48	

<sup>a</sup>Strong state mixing.

## S2 Geometries

Below are given the cartesian coordinates of the compounds investigated in this study. These are provided in atomic units (bohr) and they have been obtained at the CC3(full)/*aug-cc-pVTZ* level of theory.

### S2.1 Acetaldehyde

C	-0.00234503	0.00000000	0.87125063
C	-1.75847785	0.00000000	-1.34973671
O	2.27947397	0.00000000	0.71968028
H	-0.92904537	0.00000000	2.73929404
H	-2.97955463	1.66046488	-1.25209463
H	-2.97955463	-1.66046488	-1.25209463
H	-0.70043433	0.00000000	-3.11066412

### S2.2 Acetylene

Ground state

C	0.00000000	0.00000000	1.14048351
C	0.00000000	0.00000000	-1.14048351
H	0.00000000	0.00000000	3.14009043
H	0.00000000	0.00000000	-3.14009043

*Trans* excited state ( ${}^1A_u$  state in the  $C_{2h}$  point group)

C	1.29567779	0.00000000	-0.01846047
C	-1.29567779	0.00000000	0.01846047
H	2.41938674	0.00000000	1.70881682
H	-2.41938674	0.00000000	-1.70881682

*Cis* excited state ( ${}^1A_2$  state in the  $C_{2v}$  point group)

C	0.00000000	1.26834508	-0.11726146
C	0.00000000	-1.26834508	-0.11726146
H	0.00000000	2.67282325	1.39629264
H	0.00000000	-2.67282325	1.39629264

### S2.3 Ammonia

N	0.12804615	-0.00000000	0.00000000
H	-0.59303935	0.88580079	-1.53425197
H	-0.59303935	-1.77160157	-0.00000000
H	-0.59303935	0.88580079	1.53425197

### S2.4 Carbon monoxide

C	0.00000000	0.00000000	-1.24942055
O	0.00000000	0.00000000	0.89266692

### S2.5 Cyclopropene

C	0.00000000	0.00000000	-1.66820880
C	0.00000000	1.22523906	0.90681419
C	0.00000000	-1.22523906	0.90681419
H	1.72255446	0.00000000	-2.77881149
H	-1.72255446	0.00000000	-2.77881149
H	0.00000000	2.97844519	1.92076771
H	0.00000000	-2.97844519	1.92076771

### S2.6 Diazomethane

Ground state

C	0.00000000	0.00000000	-2.30830005
N	0.00000000	0.00000000	0.14457890
N	0.00000000	0.00000000	2.29923216
H	0.00000000	1.79875201	-3.24272317
H	0.00000000	-1.79875201	-3.24272317

Excited state ( $^1A'$  state in the  $C_s$  point group)

C	1.80206107	0.00000000	-1.03389466
N	-0.01743713	0.00000000	0.84742344
N	-2.25203764	0.00000000	0.54034983
H	3.74280590	0.00000000	-0.44375913
H	1.20115546	0.00000000	-2.98380249

## S2.7 Dinitrogen

N	0.00000000	0.00000000	1.04008632
N	0.00000000	0.00000000	-1.04008632

## S2.8 Ethylene

C	0.00000000	1.26026583	0.00000000
C	0.00000000	-1.26026583	0.00000000
H	0.00000000	2.32345976	1.74287672
H	0.00000000	-2.32345976	1.74287672
H	0.00000000	2.32345976	-1.74287672
H	0.00000000	-2.32345976	-1.74287672

## S2.9 Formaldehyde

Ground state

C	0.00000000	0.00000000	-1.13947666
O	0.00000000	0.00000000	1.14402883
H	0.00000000	1.76627623	-2.23398653
H	0.00000000	-1.76627623	-2.23398653

Excited state ( $^1A''$  state in the  $C_s$  point group)

C	-0.09942705	0.00000000	1.27071070
O	0.01987299	0.00000000	-1.23280536
H	0.42778855	1.76729629	2.18470884
H	0.42778855	-1.76729629	2.18470884

## S2.10 Formamide

C	0.00183118	0.00000000	0.79313299
O	2.26817156	0.00000000	0.43918824
N	-1.76886033	0.00000000	-1.06219243
H	-0.84133459	0.00000000	2.68872485
H	-1.21254414	0.00000000	-2.87596907
H	-3.61627502	0.00000000	-0.65031317

## S2.11 Hydrogen chloride

Cl	0.00000000	0.00000000	-0.02489783
H	0.00000000	0.00000000	2.38483140

## S2.12 Hydrogen sulfide

S	0.00000000	0.00000000	-0.50365086
H	0.00000000	1.81828105	1.25212288
H	0.00000000	-1.81828105	1.25212288

## S2.13 Ketene

Ground state

C	0.00000000	0.00000000	-2.44810151
C	0.00000000	0.00000000	0.03498545
O	0.00000000	0.00000000	2.23663914
H	0.00000000	1.77432079	-3.43705988
H	0.00000000	-1.77432079	-3.43705988

Excited state ( $^1A''$  state in the  $C_s$  point group)

C	2.04306304	0.00000000	-0.93056721
C	0.00400918	0.00000000	0.83531393
O	-2.23710378	0.00000000	0.46984584
H	1.63603518	0.00000000	-2.93687368
H	3.96212800	0.00000000	-0.26649149

## S2.14 Methanimine

C	0.10696646	0.00000000	1.11091130
N	0.10764012	0.00000000	-1.29677742
H	-1.59140953	0.00000000	2.27296652
H	1.90475160	0.00000000	2.09393982
H	-1.69956184	0.00000000	-1.96217482

## S2.15 Nitrosomethane

Ground state

C	-1.78426612	0.00000000	-1.07224050
N	-0.00541753	0.00000000	1.08060391
O	2.18814985	0.00000000	0.43452135
H	-0.77343975	0.00000000	-2.86415606
H	-2.97471478	1.66801808	-0.86424584
H	-2.97471478	-1.66801808	-0.86424584

Excited state ( $^1A''$  state in the  $C_s$  point group)

C	1.86306273	0.00000000	-1.06035094
N	0.00638693	0.00000000	1.02546010
O	-2.26923072	0.00000000	0.47699489
H	3.72600129	0.00000000	-0.21094854
H	1.58491147	1.68964774	-2.20977225
H	1.58491147	-1.68964774	-2.20977225

## S2.16 Streptocyanine-C1

C	0.00000000	0.00000000	0.80488833
N	0.00000000	2.19423463	-0.33580561
N	0.00000000	-2.19423463	-0.33580561
H	0.00000000	0.00000000	2.84436959
H	0.00000000	2.36978315	-2.23371976
H	0.00000000	-2.36978315	-2.23371976
H	0.00000000	3.79412648	0.69399206
H	0.00000000	-3.79412648	0.69399206

## S2.17 Thioformaldehyde

Ground state

C	0.00000000	0.00000000	-2.08677304
S	0.00000000	0.00000000	0.97251194
H	0.00000000	1.73657773	-3.17013507
H	0.00000000	-1.73657773	-3.17013507

Excited state ( ${}^1A_2$  state in the  $C_{2v}$  point group)

C	0.00000000	0.00000000	-2.20256705
S	0.00000000	0.00000000	1.02717172
H	0.00000000	1.76634191	-3.21909384
H	0.00000000	-1.76634191	-3.21909384

## S2.18 Water

O	0.00000000	0.00000000	-0.13209669
H	0.00000000	1.43152878	0.97970006
H	0.00000000	-1.43152878	0.97970006



## S3 Benchmark

Table S6: Comparisons between the TBE(FC)/*aug-cc-pVTZ* benchmark (see Table 6) and the results obtained with various computational approaches using the same basis set and approximation. STEOM stands for STEOM-CCSD and CC(3) for CCSDR(3).

Compound	State	TBE	CIS(D)	CIS(D $\infty$ )	CC2	STEOM	CCSD	CC(3)	CCSDT-3	CC3	CCSDT	CCSDTQ	ADC(2)	ADC(3)
Acetaldehyde	$1A''(V; n \rightarrow \pi^*)$	4.31	4.36	4.24	4.41	4.25	4.36	4.31	4.32	4.31	4.29	4.24	4.24	4.29
	$3A''(V; n \rightarrow \pi^*)$	3.97	3.96	3.83	3.98	3.95	3.95	3.95	3.94	3.95	3.94	3.83	3.83	3.89
	$1\Sigma_u^-(V; \pi \rightarrow \pi^*)$	7.10	7.28	7.24	7.26	7.08	7.15	7.09	7.09	7.09	7.09	7.09 <sup>a</sup>	7.24	6.72
Acetylene	$1\Delta_u(V; \pi \rightarrow \pi^*)$	7.44	7.62	7.56	7.59	7.42	7.48	7.43	7.42	7.42	7.43	7.56	7.06	7.06
	$3\Sigma_u^+(V; \pi \rightarrow \pi^*)$	5.53	5.79	5.75	5.76	5.20	5.45	5.45	5.42	5.50	5.51	5.75	5.24	5.24
	$3\Delta_u(V; \pi \rightarrow \pi^*)$	6.40	6.62	6.57	6.60	6.13	6.41	6.41	6.39	6.40	6.39	6.57	6.06	6.06
	$3\Sigma_u^-(V; \pi \rightarrow \pi^*)$	7.08	7.31	7.27	7.29	6.84	7.12	7.12	7.08	7.07	7.08 <sup>b</sup>	7.27	6.72	6.72
	$1A_u[F](V; \pi \rightarrow \pi^*)$	3.64	3.85	3.78	3.94	3.65	3.70	3.70	3.66	3.64	3.64	3.78	2.85	2.85
	$1A_2[F](V; \pi \rightarrow \pi^*)$	3.85	4.06	3.99	4.11	3.85	3.92	3.92	3.85	3.84	3.84	3.99	3.08	3.08
Ammonia	$1A_2(R; n \rightarrow 3s)$	6.59	6.37	6.40	6.39	6.55	6.60	6.57	6.58	6.57	6.57	6.40	6.63	6.63
	$1E(R; n \rightarrow 3p)$	8.16	7.86	7.87	7.85	8.14	8.15	8.15	8.15	8.15	8.14	8.16	7.87	8.21
	$1A_1(R; n \rightarrow 3p)$	9.33	9.04	9.05	9.05	9.33	9.33	9.32	9.32	9.32	9.31	9.05	9.05	9.38
Carbon monoxide	$1A_2(R; n \rightarrow 4s)$	9.96	9.59	9.67	9.65	9.98	9.95	9.94	9.95	9.95	9.94	9.67	10.00	10.00
	$3A_2(R; n \rightarrow 3s)$	6.31	6.18	6.16	6.14	6.31	6.30	6.30	6.29	6.29	6.29	6.16	6.31	6.31
	$1\Pi(V; n \rightarrow \pi^*)$	8.49	8.78	8.69	8.64	8.55	8.59	8.52	8.51	8.49	8.49	8.48	8.24	8.24
	$1\Sigma^-(V; \pi \rightarrow \pi^*)$	9.92	10.13	10.03	10.30	9.90	9.99	9.98	9.98	9.98	9.99	9.94	9.73	9.73
	$1\Delta(V; \pi \rightarrow \pi^*)$	10.06	10.41	10.30	10.60	10.07	10.12	10.12	10.11	10.12	10.12	10.07	10.30	9.82
	$1\Sigma^+(R)$	10.95	11.48	11.32	11.11	11.14	11.22	10.99	11.02	10.94	10.99	10.96	11.32	10.79
Cyclopropene	$1\Sigma^+(R)$	11.52	11.71	11.83	11.63	11.75	11.75	11.53	11.55	11.49	11.54	11.52	11.83	11.33
	$1\Pi(R)$	11.72	12.06	12.03	11.83	12.00	11.96	11.73	11.76	11.69	11.74	11.72	12.03	11.56
	$3\Pi(V; n \rightarrow \pi^*)$	6.28	6.51	6.45	6.42	6.32	6.36	6.36	6.30	6.30	6.30	6.45	5.97	5.97
	$3\Sigma^+(V; \pi \rightarrow \pi^*)$	8.45	8.63	8.54	8.72	8.37	8.34	8.34	8.45	8.45	8.42	8.54	8.21	8.21
	$3\Delta(V; \pi \rightarrow \pi^*)$	9.27	9.44	9.33	9.56	9.21	9.23	9.23	9.30	9.30	9.26	9.33	9.03	9.03
	$3\Sigma^-(V; \pi \rightarrow \pi^*)$	9.80	10.10	10.01	10.27	9.83	9.81	9.81	9.82	9.82	9.82	10.01	9.53	9.53
Diazomethane	$3\Sigma^+(R)$	10.47	10.98	10.83	10.60	10.73	10.71	10.68	10.45	10.50	10.48	10.83	10.29	10.29
	$1B_1(V; \sigma \rightarrow \pi^*)$	6.68	6.90	6.75	6.73	6.94	6.76	6.68	6.70	6.68	6.68	6.75	6.56	6.56
	$1B_2(V; \pi \rightarrow \pi^*)$	6.79	6.90	6.86	6.78	6.94	6.86	6.73	6.76	6.73	6.75	6.86	6.56	6.56
	$3B_2(V; \pi \rightarrow \pi^*)$	4.38	4.55	4.45	4.46	4.36	4.30	4.34	4.35 <sup>b</sup>	4.34	4.35 <sup>b</sup>	4.45	4.09	4.09
	$3B_1(V; \sigma \rightarrow \pi^*)$	6.45	6.49	6.45	6.44	6.57	6.46	6.40	6.40	6.40	6.40	6.45	6.26	6.26
	$1A_2(V; \pi \rightarrow \pi^*)$	3.14	3.55	3.34	3.37	3.20	3.19	3.12	3.10	3.07	3.07	3.34	2.74	2.74
Cyclopropane	$1B_1(R; \pi \rightarrow \pi^*)$	5.54	5.65	5.63	5.53	5.57	5.57	5.48	5.47	5.45	5.48	5.63	5.23	5.23
	$1A_1(V; \pi \rightarrow \pi^*)$	5.90	6.03	5.97	6.00	5.75	5.94	5.87	5.86	5.84	5.86	5.97	5.48	5.48
	$3A_2(V; \pi \rightarrow \pi^*)$	2.79	3.21	3.00	3.08	2.85	3.19	2.83	2.82	2.83	2.82	3.01	2.44	2.44
	$3A_1(V; \pi \rightarrow \pi^*)$	4.05	4.28	4.20	4.25	3.91	3.95	4.03	4.02	4.03	4.02	4.20	3.64	3.64

Continued on next page

Compound	State	TBE	CIS(D)	CIS(D <sub>∞</sub> )	CC2	STEOM	CCSD	CC(3)	CCSDT-3	CC3	CCSDT	CCSDTQ	ADC(2)	ADC(3)
Dinitrogen	$^3B_1(R; \pi \rightarrow 3s)$	5.35	5.53	5.50	5.53	5.43	5.42			5.31	5.34	5.50	5.08	
	$^3A_1(R; \pi \rightarrow 3p)$	6.82	7.37	7.09	7.04		6.85			6.80	6.80 <sup>b</sup>	7.09	6.36	
	$^1A''[F](V; \pi \rightarrow \pi^*)$	0.71	1.06	0.80	0.90	0.88	0.81	0.73	0.70	0.68	0.67	0.81	0.24	
	$^1\Pi_g(V; n \rightarrow \pi^*)$	9.34	9.66	9.48	9.44	9.37	9.41	9.36	9.35	9.34	9.33	9.48	9.16	
	$^1\Sigma_u^-(V; \pi \rightarrow \pi^*)$	9.88	10.31	10.26	10.32	10.09	10.00	9.90	9.89	9.88	9.89	10.26	9.33	
	$^1\Delta_u(V; \pi \rightarrow \pi^*)$	10.29	10.85	10.79	10.86	10.56	10.44	10.33	10.31	10.29	10.30	10.29 <sup>a</sup>	10.79	9.74
	$^1\Sigma_g^+(R)$	12.98	13.67	12.99	12.83	13.13	13.15	13.04	13.06	13.01	13.00	12.97	12.99	13.01
	$^1\Pi_u(R)$	13.03	13.64	13.33	13.15	13.43	13.43	13.28	13.27	13.22	13.14	13.09	13.32	12.98
	$^1\Sigma_g^+(R)$	13.09	13.75	13.07	12.89	13.22	13.26	13.14	13.16	13.12	13.12	13.09	13.07	13.09
	$^1\Pi_u(R)$	13.46	14.52	13.99	13.96	13.73	13.67	13.52		13.49	13.45	13.42	14.00	13.40
	$^3\Sigma_u^+(V; \pi \rightarrow \pi^*)$	7.70	8.20	8.15	8.19	7.70	7.66			7.68	7.69	7.70	8.15	7.25
	$^3\Pi_g(V; n \rightarrow \pi^*)$	8.01	8.33	8.20	8.19	8.16	8.09			8.04	8.03	8.02	8.20	7.77
	$^3\Delta_u(V; \pi \rightarrow \pi^*)$	8.87	9.30	9.25	9.30	8.94	8.91			8.87	8.87	8.87	9.25	8.36
	$^3\Sigma_u^-(V; \pi \rightarrow \pi^*)$	9.66	10.29	10.23	10.29	9.90	9.83			9.68	9.68	9.66	10.23	9.14
Ethylene	$^1B_{3u}(R; \pi \rightarrow 3s)$	7.39	7.35	7.34	7.29	7.42	7.42	7.35	7.36	7.35	7.37	7.34	7.17	
	$^1B_{1u}(V; \pi \rightarrow \pi^*)$	7.93	7.95	7.92	7.92		8.02	7.89	7.92	7.91	7.92	7.91	7.69	
	$^1B_{1g}(R; \pi \rightarrow 3p)$	8.08	8.01	7.99	7.95	8.10	8.08	8.02	8.03	8.03	8.04	8.05 <sup>a</sup>	7.99	7.84
	$^3B_{1u}(V; \pi \rightarrow \pi^*)$	4.54	4.62	4.59	4.59	4.36	4.46			4.53	4.53	4.53 <sup>a</sup>	4.59	4.28
	$^3B_{3u}(R; \pi \rightarrow 3s)$	7.23	7.26	7.23	7.19	7.31	7.29			7.24	7.25	7.25 <sup>a</sup>	7.23	7.05
	$^3B_{1g}(R; \pi \rightarrow 3p)$	7.98	7.97	7.95	7.91	8.08	8.03			7.98	7.99	7.99 <sup>a</sup>	7.95	7.80
	$^1A_2(V; n \rightarrow \pi^*)$	3.98	4.04	3.92	4.07	3.91	4.01	3.97	3.98	3.97	3.95	3.96 <sup>a</sup>	3.92	3.90
	$^1B_2(R; n \rightarrow 3s)$	7.23	6.64	6.50	6.56	7.19	7.23	7.18	7.21	7.18	7.16	7.21 <sup>a</sup>	6.50	7.62
	$^1B_2(R; n \rightarrow 3p)$	8.13	7.56	7.53	7.57	8.05	8.12	8.08	8.11	8.07	8.07	8.11 <sup>a</sup>	7.53	8.45
	$^1A_1(R; n \rightarrow 3p)$	8.23	8.16	7.47	7.52	8.18	8.21	8.17	8.21	8.18	8.16	8.21 <sup>a</sup>	7.47	8.61
	$^1A_2(R; n \rightarrow 3p)$	8.67	8.04	7.99	8.04	8.68	8.65	8.63	8.66	8.64	8.61	8.66 <sup>a</sup>	7.99	9.02
	$^1B_1(V; \sigma \rightarrow \pi^*)$	9.22	9.38	9.17	9.32	9.08	9.28	9.20	9.20	9.19	9.17	9.18 <sup>a</sup>	9.17	9.17
	$^1A_1(V; \pi \rightarrow \pi^*)$	9.43	9.08	9.46	9.54		9.67	9.51	9.51	9.48	9.49	9.44 <sup>a</sup>	9.46	9.05
	$^3A_2(V; n \rightarrow \pi^*)$	3.58	3.58	3.46	3.59	3.54	3.56			3.57	3.56	3.57 <sup>a</sup>	3.46	3.48
$^3A_1(V; \pi \rightarrow \pi^*)$	6.06	6.27	6.20	6.30	5.89	5.97			6.05	6.05	6.06 <sup>a</sup>	6.20	5.71	
Formaldehyde	$^3B_2(R; n \rightarrow 3s)$	7.06	6.66	6.39	6.44	7.07	7.08	7.03	7.02	7.03	7.02	6.39	7.44	
	$^3B_2(R; n \rightarrow 3p)$	7.94	7.52	7.41	7.45	7.98	7.94	7.92	7.90	7.92	7.90	7.41	8.23	
	$^3A_1(R; n \rightarrow 3p)$	8.10	7.68	7.40	7.44	8.15	8.09			8.08	8.06	7.40	8.46	
	$^3B_1(R; n \rightarrow 3d)$	8.42	8.57	8.39	8.52	8.36	8.43			8.41	8.40	8.39	8.32	
	$^1A'_1[F](V; n \rightarrow \pi^*)$	2.80	2.90	2.71	2.97	2.81	2.93	2.86	2.86	2.84	2.82	2.71	2.77	
	$^1A''V; (n \rightarrow \pi^*)$	5.65	5.58	5.45	5.69	5.72	5.69	5.66	5.67	5.66	5.63 <sup>b</sup>	5.45	5.75	
	$^1A'(R; n \rightarrow 3s)$	6.77	6.82 <sup>d</sup>	6.26 <sup>d</sup>	6.31 <sup>d</sup>	6.94	6.99	6.83	6.83	6.74	6.74	6.26 <sup>d</sup>	7.20	
Formamide	$^1A'(V; \pi \rightarrow \pi^*)$	7.63	6.84 <sup>d</sup>	7.39 <sup>d</sup>	7.55 <sup>d</sup>		7.44	7.68 <sup>d</sup>	7.68 <sup>d</sup>	7.62 <sup>d</sup>	7.61 <sup>b</sup>	7.39 <sup>d</sup>	7.80 <sup>d</sup>	
	$^1A'(R; n \rightarrow 3p)$	7.38	6.89 <sup>d</sup>	6.83 <sup>d</sup>	6.89 <sup>d</sup>		7.78 <sup>d</sup>	7.65	7.46 <sup>d</sup>	7.40 <sup>d</sup>	7.38 <sup>b</sup>	6.83 <sup>d</sup>	8.12 <sup>d</sup>	
	$^3A''(V; n \rightarrow \pi^*)$	5.38	5.31	5.15	5.36	5.29	5.36	7.65	7.46 <sup>d</sup>	5.38	5.35 <sup>b</sup>	5.15	5.42	

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Compound	State	TBE	CIS(D)	CIS(D <sub>∞</sub> )	CC2	STEOM	CCSD	CC(3)	CCSDT-3	CC3	CCSDT	CCSDTQ	ADC(2)	ADC(3)
Hydrogen chloride	$^3A'(V; \pi \rightarrow \pi^*)$	5.81	6.07	5.88	5.99	5.74	5.77			5.82	5.80 <sup>b</sup>	5.88	5.88	5.63
	$^1\Pi(CT)$	7.84	7.98	7.97	7.96	7.91	7.91	7.84	7.85	7.84	7.83	7.84	7.97	7.79
	$^1A_2(R; n \rightarrow 4p)$	6.18	6.38	6.37	6.35	6.23	6.25	6.25	6.23	6.19	6.18	6.18	6.37	6.05
	$^1B_1(R; n \rightarrow 4s)$	6.24	6.33	6.34	6.30	6.31	6.29	6.29	6.28	6.24	6.24	6.24	6.34	6.18
	$^3A_2(R; n \rightarrow 4p)$	5.81	5.94	5.91	5.91	5.96	5.85	5.85		5.82	5.81	5.81	5.91	5.67
Ketene	$^3B_1(R; n \rightarrow 4s)$	5.88	5.99	5.96	5.94	5.98	5.92			5.88	5.88	5.96	5.96	5.81
	$^1A_2(V; \pi \rightarrow \pi^*)$	3.86	4.18	4.11	4.17	3.84	3.97	3.92	3.90	3.88	3.87	4.11	3.67	3.67
	$^1B_1(R; n \rightarrow 3s)$	6.01	6.09	6.03	5.94	6.08	6.09	5.99	5.99	5.96	5.99	6.03	6.03	5.87
	$^1A_2(R; \pi \rightarrow 3p)$	7.18	7.25	7.18	7.09	7.29	7.29	7.19	7.20	7.16	7.20	7.18	7.18	7.07
	$^3A_2(V; n \rightarrow \pi^*)$	3.77	4.00	3.92	3.98	3.82	3.83			3.78	3.78	3.92	3.92	3.56
Methanimine	$^3A_1(V; \pi \rightarrow \pi^*)$	5.61	5.79	5.67	5.72	5.53	5.55			5.61	5.60	5.67	5.67	5.39
	$^3B_1(R; n \rightarrow 3s)$	5.79	5.94	5.85	5.77	5.91	5.89			5.76	5.80	5.85	5.85	5.67
	$^3A_2(R; \pi \rightarrow 3p)$	7.12	7.24	7.15	7.06	7.32	7.25			7.12	7.17	7.15	7.15	7.03
	$^1A'[F](V; \pi \rightarrow \pi^*)$	1.00	1.28	1.20	1.26	1.03	1.13	1.06	1.03	1.00	1.00	1.19	1.19	0.67
	$^1A''(V; n \rightarrow \pi^*)$	5.23	5.38	5.29	5.32	5.20	5.28	5.20	5.22	5.20	5.19	5.20 <sup>a</sup>	5.29	5.05
Nitrosomethane	$^3A''(V; n \rightarrow \pi^*)$	4.65	4.71	4.61	4.65	4.62	4.63			4.61	4.61	4.61	4.61	4.44
	$^1A''(V; n \rightarrow \pi^*)$	1.96	2.03	1.88	1.98	1.80	1.98	1.96	1.96	1.96	1.95	1.88	1.88	1.72
	$^1A'(V; n, n \rightarrow \pi^*, \pi^*)$	4.72												3.00
	$^1A'(R; n \rightarrow 3s/3p)$	6.40	5.89	5.86	5.84	6.51	6.43	6.33	6.38	6.31	6.30	5.86	5.86	6.48
	$^3A''(V; n \rightarrow \pi^*)$	1.16	1.18	1.03	1.12	0.99	1.11			1.14	1.13	1.03	1.03	0.84
Streptocyanine	$^3A'(V; \pi \rightarrow \pi^*)$	5.60	5.89	5.75	5.74	5.04	5.43			5.51	5.51 <sup>b</sup>	5.75	5.75	5.04
	$^1A''[F](V; n \rightarrow \pi^*)$	1.67	1.73	1.55	1.68	1.49	1.68	1.67	1.67	1.69	1.66	1.55	1.55	1.40
	$^1B_2(V; \pi \rightarrow \pi^*)$	7.13	6.99	7.00	7.20	6.76	7.24	7.12	7.16	7.13	7.11	7.00	7.00	7.16
	$^3B_2(V; \pi \rightarrow \pi^*)$	5.47	5.61	5.55	5.60	5.40	5.45			5.48	5.47	5.55	5.55	5.33
	$^1A_2(V; n \rightarrow \pi^*)$	2.22	2.30	2.24	2.34	2.17	2.29	2.22	2.24	2.23	2.21	2.24	2.24	2.05
Thioformaldehyde	$^1B_2(R; n \rightarrow 4s)$	5.96	5.87	5.80	5.82	5.92	5.97	5.90	5.94	5.91	5.89	5.80	5.80	5.94
	$^1A_1(V; \pi \rightarrow \pi^*)$	6.38	6.65	6.57	6.71	6.48	6.63	6.50	6.51	6.48	6.47	6.57	6.57	5.98
	$^3A_2(V; n \rightarrow \pi^*)$	1.94	1.94	1.86	1.94	1.91	1.95			1.94	1.93	1.86	1.86	1.77
	$^3A_1(V; n \rightarrow \pi^*)$	3.43	3.49	3.45	3.48	3.18	3.28			3.38	3.38	3.45	3.45	3.07
	$^3B_2(R; n \rightarrow 4s)$	5.72	5.78	5.62	5.64	5.71	5.76			5.72	5.71	5.62	5.62	5.71
Water	$^1A_2[F](V; n \rightarrow \pi^*)$	1.95	2.00	1.92	2.09	1.92	2.05	1.97	1.98	1.97	1.98	1.92	1.92	1.80
	$^1B_1(R; n \rightarrow 3s)$	7.62	7.17	7.18	7.23	7.56	7.60	7.60	7.61	7.65	7.65	7.62	7.18	7.84
	$^1A_2(R; n \rightarrow 3p)$	9.41	8.92	8.84	8.89	9.37	9.36	9.38	9.38	9.43	9.42	9.40	8.84	9.63
	$^1A_1(R; n \rightarrow 3s)$	9.99	9.52	9.52	9.58	9.92	9.96	9.96	9.97	10.00	9.98	9.98	9.52	10.22
	$^3B_1(R; n \rightarrow 3s)$	7.25	6.92	6.86	6.91	7.24	7.20			7.28	7.28	7.24	6.86	7.41

<sup>a</sup>CCSDTQ/aug-cc-pVDZ value corrected with the difference between CCSDT/aug-cc-pVTZ and CCSDT/aug-cc-pVDZ values; <sup>b</sup>CCSDT/aug-cc-pVDZ

value corrected with the difference between CC3/*aug-cc-pVTZ* and CC3/*aug-cc-pVDZ* values; <sup>c</sup>CCSDTQ/*aug-cc-pVDZ* value corrected with the difference between CC3/*aug-cc-pVTZ* and CC3/*aug-cc-pVDZ* values; <sup>d</sup>Strong state mixing.

## S4 Additional statistical analyses

Table S7: Mean signed and absolute errors for different subsets of electronic transitions. % $T_1$  indicates the single excitation character as given by CC3, see Table 6 in the body of the paper. All values are in eV.

Type	CIS(D)	CIS( $D_\infty$ )	CC2	STEOM	CCSD	CC(3)	CCSDT-3	CC3	CCSDT	CCSDTQ	ADC(2)	ADC(3)
Singlet	MSE	-0.02	0.01	0.03	0.08	0.01	0.01	-0.01	-0.01	-0.01	-0.02	-0.14
	MAE	0.28	0.23	0.09	0.08	0.04	0.03	0.03	0.03	0.01	0.22	0.22
Triplet	MSE	0.12	0.01	0.06	0.01			-0.01	-0.01	0.00	0.01	-0.18
	MAE	0.22	0.19	0.20	0.07			0.02	0.02	0.01	0.19	0.25
Valence	MSE	0.18	0.09	0.17	0.04	0.01	0.01	0.00	-0.01	-0.01	0.09	-0.27
	MAE	0.20	0.15	0.18	0.10	0.03	0.03	0.02	0.02	0.01	0.15	0.28
Rydberg	MSE	-0.01	-0.14	-0.17	0.06	0.00	0.01	-0.01	-0.01	0.00	-0.14	0.01
	MAE	0.32	0.29	0.26	0.09	0.05	0.04	0.03	0.03	0.01	0.29	0.17
$n \rightarrow \pi^*$	MSE	0.11	-0.01	0.08	0.04	0.01	0.02	0.00	-0.01	0.00	-0.01	-0.16
	MAE	0.12	0.12	0.09	0.07	0.02	0.02	0.01	0.02	0.02	0.12	0.18
$\pi \rightarrow \pi^*$	MSE	0.23	0.16	0.24	0.03	0.01	0.01	0.00	-0.01	0.00	0.16	-0.35
	MAE	0.26	0.17	0.24	0.09	0.04	0.03	0.03	0.02	0.01	0.17	0.36
% $T_1 > 95\%$	MSE	0.12	0.03	0.07	0.02	-0.01	-0.01	-0.01	-0.01	0.00	0.03	-0.22
	MAE	0.22	0.19	0.21	0.07	0.03	0.02	0.02	0.02	0.01	0.19	0.28
% $T_1 > 90\%$	MSE	0.08	-0.02	0.02	0.04	0.00	0.01	-0.01	-0.01	-0.01	-0.02	-0.15
	MAE	0.24	0.21	0.22	0.07	0.03	0.03	0.02	0.02	0.01	0.21	0.24
% $T_1 < 90\%$	MSE	0.30	0.11	0.20	0.16	0.06	0.06	0.03	0.01	0.01	0.11	-0.15
	MAE	0.33	0.17	0.20	0.16	0.06	0.06	0.04	0.03	0.03	0.17	0.16

## S5 Basis set extrapolation with 6-31+G(d)

Below we list the CC3/6-31+G(d), CCSDT/6-31+G(d), and CCSDTQ/6-31+G(d) data for the states for which CCSDT/*aug-cc-pVTZ*, and CCSDTQ/*aug-cc-pVTZ* results were obtained.

Table S8: Additional CC results obtained with the compact 6-31+G(d) atomic basis set. All values are in eV.

		CC3	CCSDT	CCSDTQ
Acetaldehyde	$^1A''(V; n \rightarrow \pi^*)$	4.39	4.37	
	$^3A''(V; n \rightarrow \pi^*)$	4.04	4.02	
Acetylene	$^1\Sigma_u^-(V; \pi \rightarrow \pi^*)$	7.40	7.40	7.40
	$^1\Delta_u(V; \pi \rightarrow \pi^*)$	7.72	7.73	7.73
	$^3\Sigma_u^+(V; \pi \rightarrow \pi^*)$	5.49	5.51	
	$^3\Delta_u(V; \pi \rightarrow \pi^*)$	6.57	6.57	6.57
	$^3\Sigma_u^-(V; \pi \rightarrow \pi^*)$	7.28	7.28	7.28
	$^1A_u[F](V; \pi \rightarrow \pi^*)$	3.83	3.85	3.84
	$^1A_2[F](V; \pi \rightarrow \pi^*)$	4.05	4.07	4.06
Ammonia	$^1A_2(R; n \rightarrow 3s)$	6.96	6.95	6.96
	$^1E(R; n \rightarrow 3p)$	8.95	8.95	8.96
	$^1A_1(R; n \rightarrow 3p)$	10.19	10.19	10.20
	$^1A_2(R; n \rightarrow 4s)$	11.65	11.64	11.64
	$^3A_2(R; n \rightarrow 3s)$	6.49	6.49	6.50
Carbon monoxide	$^1\Pi(V; n \rightarrow \pi^*)$	8.66	8.67	8.66
	$^1\Sigma^-(V; \pi \rightarrow \pi^*)$	10.19	10.13	10.12
	$^1\Delta(V; \pi \rightarrow \pi^*)$	10.28	10.23	10.22
	$^1\Sigma^+(R)$	10.89	10.92	10.90
	$^1\Sigma^+(R)$	11.53	11.57	11.56
	$^1\Pi(R)$	11.83	11.86	11.85
	$^3\Pi(V; n \rightarrow \pi^*)$	6.35	6.34	6.32
	$^3\Sigma^+(V; \pi \rightarrow \pi^*)$	8.49	8.47	8.48
	$^3\Delta(V; \pi \rightarrow \pi^*)$	9.44	9.39	9.40
	$^3\Sigma^-(V; \pi \rightarrow \pi^*)$	9.94		
	$^3\Sigma^+(R)$	10.33	10.36	10.35
Cyclopropene	$^1B_1(V; \sigma \rightarrow \pi^*)$	6.86	6.85	
	$^1B_2(V; \pi \rightarrow \pi^*)$	6.98	6.99	
	$^3B_2(V; \pi \rightarrow \pi^*)$	4.37	4.38	
	$^3B_1(V; \sigma \rightarrow \pi^*)$	6.61	6.60	
Diazomethane	$^1A_2(V; \pi \rightarrow \pi^*)$	3.05	3.05	
	$^1B_1(R; \pi \rightarrow 3s)$	5.37	5.40	
	$^1A_1(V; \pi \rightarrow \pi^*)$	5.83	5.86	
	$^3A_2(V; \pi \rightarrow \pi^*)$	2.80	2.80	
	$^3A_1(V; \pi \rightarrow \pi^*)$	4.02	4.01	
	$^3B_1(R; \pi \rightarrow 3s)$	5.20	5.23	
	$^3A_1(R; \pi \rightarrow 3p)$	6.86	6.86	

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		CC3	CCSDT	CCSDTQ	
Dinitrogen	$^1A''[F](V; \pi \rightarrow \pi^*)$	0.62	0.60		
	$^1\Pi_g(V; n \rightarrow \pi^*)$	9.46	9.44	9.43	
	$^1\Sigma_u^-(V; \pi \rightarrow \pi^*)$	10.10	10.10	10.10	
	$^1\Delta_u(V; \pi \rightarrow \pi^*)$	10.47	10.48	10.47	
	$^1\Sigma_g^+(R)$	13.29	13.26	13.23	
	$^1\Pi_u(R)$	13.44	13.32	13.28	
	$^1\Sigma_u^+(R)$	13.51	13.51	13.48	
	$^1\Pi_u(R)$	13.85	13.82	13.79	
	$^3\Sigma_u^+(V; \pi \rightarrow \pi^*)$	7.68	7.68	7.70	
	$^3\Pi_g(V; n \rightarrow \pi^*)$	8.10	8.09	8.08	
	$^3\Delta_u(V; \pi \rightarrow \pi^*)$	8.99	8.99	8.99	
	$^3\Sigma_u^-(V; \pi \rightarrow \pi^*)$	9.80	9.78	9.77	
	Ethylene	$^1B_{3u}(R; \pi \rightarrow 3s)$	7.72	7.73	7.72
		$^1B_{1u}(V; \pi \rightarrow \pi^*)$	8.14	8.15	8.14
$^1B_{1g}(R; \pi \rightarrow 3p)$		8.29	8.30	8.29	
$^3B_{1u}(V; \pi \rightarrow \pi^*)$		4.52	4.53	4.53	
$^3B_{3u}(R; \pi \rightarrow 3s)$		7.49	7.51	7.51	
$^3B_{1g}(R; \pi \rightarrow 3p)$		8.20	8.22	8.22	
Formaldehyde		$^1A_2(V; n \rightarrow \pi^*)$	4.03	4.01	4.02
		$^1B_2(R; n \rightarrow 3s)$	7.24	7.23	7.28
	$^1B_2(R; n \rightarrow 3p)$	8.02	8.01	8.04	
	$^1A_1(R; n \rightarrow 3p)$	8.30	8.29	8.34	
	$^1A_2(R; n \rightarrow 3p)$	8.70	8.68	8.72	
	$^1B_1(V; \sigma \rightarrow \pi^*)$	9.37	9.34	9.35	
	$^1A_1(V; \pi \rightarrow \pi^*)$	9.83	9.83	9.78	
	$^3A_2(V; n \rightarrow \pi^*)$	3.66	3.65	3.66	
	$^3A_1(V; \pi \rightarrow \pi^*)$	6.09	6.09	6.10	
	$^3B_2(R; n \rightarrow 3s)$	7.07	7.06	7.11	
	$^3B_2(R; n \rightarrow 3p)$	7.84	7.82	7.86	
	$^3A_1(R; n \rightarrow 3p)$	8.17	8.15	8.20	
	$^3B_1(R; n \rightarrow 3d)$	8.54	8.52	8.53	
	Formamide	$^1A''[F](V; n \rightarrow \pi^*)$	2.88	2.85	2.86
		$^1A''V; (n \rightarrow \pi^*)$	5.83	5.79	
		$^3A''(V; n \rightarrow \pi^*)$	5.55	5.52	
		$^3A'(V; \pi \rightarrow \pi^*)$	5.92	5.90	
Hydrogen chloride	$^1\Pi(CT)$	7.84	7.84	7.84	
Hydrogen sulfide	$^1A_2(R; n \rightarrow 4p)$	6.47	6.46	6.46	
	$^1B_1(R; n \rightarrow 4s)$	6.05	6.05	6.05	
	$^3A_2(R; n \rightarrow 4p)$	6.01	6.00	6.00	
	$^3B_1(R; n \rightarrow 4s)$	5.66	5.66	5.66	
Ketene	$^1A_2(V; \pi \rightarrow \pi^*)$	3.86	3.85		
	$^1B_1(R; n \rightarrow 3s)$	5.91	5.94		
	$^1A_2(R; \pi \rightarrow 3p)$	7.34	7.38		
	$^3A_2(V; n \rightarrow \pi^*)$	3.78	3.78		
	$^3A_1(V; \pi \rightarrow \pi^*)$	5.63	5.62		
	$^3B_1(R; n \rightarrow 3s)$	5.68	5.70		

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		CC3	CCSDT	CCSDTQ
	${}^3A_2(\text{R}; \pi \rightarrow 3p)$	7.27	7.31	
	${}^1A''[\text{F}](\text{V}; \pi \rightarrow \pi^*)$	0.90	0.90	
Methanimine	${}^1A''(\text{V}; n \rightarrow \pi^*)$	5.34	5.32	5.33
	${}^3A''(\text{V}; n \rightarrow \pi^*)$	4.72	4.71	4.72
Nitrosomethane	${}^1A''(\text{V}; n \rightarrow \pi^*)$	2.02	2.00	
	${}^1A'(\text{R}; n \rightarrow 3s/3p)$	6.49	6.48	
	${}^3A''(\text{V}; n \rightarrow \pi^*)$	1.14	1.13	
	${}^3A'(\text{V}; \pi \rightarrow \pi^*)$	5.55	5.55	
	${}^1A''[\text{F}](\text{V}; n \rightarrow \pi^*)$	1.72	1.70	
Streptocyanine	${}^1B_2(\text{V}; \pi \rightarrow \pi^*)$	7.28	7.25	
	${}^3B_2(\text{V}; \pi \rightarrow \pi^*)$	5.53	5.52	
Thioformaldehyde	${}^1A_2(\text{V}; n \rightarrow \pi^*)$	2.26	2.24	2.25
	${}^1B_2(\text{R}; n \rightarrow 4s)$	5.88	5.88	5.89
	${}^1A_1(\text{V}; \pi \rightarrow \pi^*)$	6.82	6.79	6.71
	${}^3A_2(\text{V}; n \rightarrow \pi^*)$	1.98	1.97	1.97
	${}^3A_1(\text{V}; \pi \rightarrow \pi^*)$	3.38	3.39	3.39
	${}^3B_2(\text{R}; n \rightarrow 4s)$	5.67	5.67	5.69
	${}^1A_2[\text{F}](\text{V}; n \rightarrow \pi^*)$	1.99	1.96	1.96
Water	${}^1B_1(\text{R}; n \rightarrow 3s)$	8.32	8.32	8.33
	${}^1A_2(\text{R}; n \rightarrow 3p)$	10.74	10.73	10.74
	${}^1A_1(\text{R}; n \rightarrow 3s)$	10.84	10.83	10.84
	${}^3B_1(\text{R}; n \rightarrow 3s)$	7.71	7.70	7.71
	${}^3A_2(\text{R}; n \rightarrow 3p)$	10.34	10.33	10.34
	${}^3A_1(\text{R}; n \rightarrow 3s)$	10.16	10.15	10.17

## S6 sCI and exFCI results

Table S9: Vertical excitations (in eV) for various states of the studied molecules computed with a extrapolated sCI method (exFCI). The number of determinants  $N_{\text{det}}$  of the largest sCI wave functions and their corresponding excitation energies are also reported.

Molecule	Transition	AVDZ			AVTZ			AVQZ		
		$N_{\text{det}}$	sCI	exFCI	$N_{\text{det}}$	sCI	exFCI	$N_{\text{det}}$	sCI	exFCI
Acetaldehyde	$^1A''(n \rightarrow \pi^*)$	5 803 234	4.37	4.34	1 357 186	4.29	4.31			
	$^3A''(n \rightarrow \pi^*)$	4 151 858	4.07	3.98	1 722 025	3.51	4.01			
Acetylene	$^1\Sigma_u^-(\pi \rightarrow \pi^*)$	4 162 848	7.21	7.20	3 113 480	7.09	7.10			
	$^1\Delta_u(\pi \rightarrow \pi^*)$		7.52	7.51		7.43	7.44			
	$^3\Sigma_u^+(\pi \rightarrow \pi^*)$	8 494 075	5.50	5.50	3 282 690	5.52	5.53			
	$^3\Delta_u(\pi \rightarrow \pi^*)$	4 403 434	6.46	6.46	2 190 673	6.40	6.40			
	$^3\Sigma_u^-(\pi \rightarrow \pi^*)$		7.14	7.14		7.08	7.08			
	$^1A_u(\pi \rightarrow \pi^*)$ [F]	5 943 690	3.71	3.71	3 982 131	3.64	3.64			
	$^1A_2(\pi \rightarrow \pi^*)$ [F]	5 788 835	3.93	3.93	3 967 196	3.85	3.85			
Ammonia	$^1A_2(n \rightarrow 3s)$	2 063 356	6.48	6.48	6 450 032	6.59	6.59	3 608 385	6.64	6.64
	$^1E(n \rightarrow 3p)$		8.08	8.08		8.17	8.16		8.21	8.22
	$^1A_1(n \rightarrow 3p)$		9.68	9.68		9.34	9.33		9.14	9.14
	$^1A_2(n \rightarrow 4s)$		10.41	10.41		9.96	9.96			
	$^3A_1(n \rightarrow 3s)$	2 389 435	6.19	6.19	6 171 274	6.31	6.31	2 698 282	6.34	6.35
Carbon monoxide	$^1\Pi(n \rightarrow \pi^*)$	375 543	8.56	8.57	6 832 118	8.46	8.49	5 809 330	8.41	8.50
	$^1\Sigma(\pi \rightarrow \pi^*)$		10.07	10.05		9.93	9.92		9.92	9.99
	$^1\Delta(\pi \rightarrow \pi^*)$		10.18	10.16		10.06	10.06		10.04	10.11
	$^1\Sigma^+(\text{R})$		10.93	10.94		10.95	10.95		10.89	10.96
	$^1\Sigma^+(\text{R})$		11.52	11.52		11.51	11.52		11.46	11.53
	$^1\Pi(\text{R})$		11.76	11.76		11.70	11.72		11.64	11.70
	$^3\Pi(n \rightarrow \pi^*)$	1 238 764	6.28	6.29	2 221 825	6.28	6.28	4 054 250	6.28	6.29
	$^3\Sigma^+(\pi \rightarrow \pi^*)$	2 117 552	8.46	8.46	7 820 835	8.46	8.45	2 302 698	8.49	8.49
	$^3\Delta(\pi \rightarrow \pi^*)$		9.34	9.33		9.28	9.27		9.29	9.29
	$^3\Sigma^-(\pi \rightarrow \pi^*)$		9.84	9.83		9.78	9.80		9.77	9.78
	$^3\Sigma^+(\text{R})$		10.42	10.41		10.49	10.47			
Cyclopropene	$^1B_1(\sigma \rightarrow \pi^*)$	5 496 693	6.75	6.7 <sup>a</sup>	4 594 382	6.61	6.6 <sup>a</sup>			
	$^1B_2(\pi \rightarrow \pi^*)$		6.82	6.82		6.69	6.7 <sup>a</sup>			
	$^3B_2(\pi \rightarrow \pi^*)$	5 484 297	4.39	4.35	1 762 752	4.38	4.38			
	$^3B_1(\sigma \rightarrow \pi^*)$	4 457 619	6.44	6.43	2 705 402	6.44	6.45			
Diazomethane	$^1A_2(\pi \rightarrow \pi^*)$	8 373 270	3.08	3.09	4 366 276	2.99	3.14			
	$^1B_1(\pi \rightarrow 3s)$		5.38	5.35		5.51	5.54			
	$^1A_1(\pi \rightarrow \pi^*)$		5.82	5.79		5.83	5.90			
	$^3A_2(\pi \rightarrow \pi^*)$	3 407 311	2.81	2.81	1 887 903	2.58	2.8 <sup>a</sup>			
	$^3A_1(\pi \rightarrow \pi^*)$		4.05	4.03		3.81	4.05			
	$^3B_1(\pi \rightarrow 3s)$		5.24	5.18		5.22	5.35			
	$^3A_1(\pi \rightarrow 3p)$		6.85	6.81		6.65	6.82			
$^1A''(\pi \rightarrow \pi^*)$ [F]	10 654 552	0.65	0.65	2 325 176	0.60	0.71				
Dinitrogen	$^1\Pi_g(n \rightarrow 3s)$	2 775 773	9.41	9.41	2 545 210	9.32	9.34	1 728 899	9.28	9.34
	$^1\Sigma_u^-(\pi \rightarrow \pi^*)$		10.05	10.05		9.89	9.88		9.82	9.92
	$^1\Delta_u^-(\pi \rightarrow \pi^*)$		10.43	10.43		10.29	10.29		10.24	10.31
	$^1\Sigma_g^+(\text{R})$		13.19	13.18		12.98	12.98		12.85	12.89
	$^1\Pi_u(\text{R})$		13.12	13.12		13.12	13.03		13.12	13.1 <sup>a</sup>
	$^1\Sigma_u^+(\text{R})$		13.11	13.11		13.10	13.09		13.20	13.2 <sup>a</sup>
	$^1\Pi_u(\text{R})$		13.56	13.56		13.39	13.46		13.23	13.7 <sup>a</sup>
	$^3\Sigma_u^+(\pi \rightarrow \pi^*)$	8 139 401	7.70	7.70	3 302 015	7.70	7.70	4 881 350	7.73	7.74
	$^3\Pi_g(n \rightarrow \pi^*)$	2 705 349	8.05	8.05	6 298 290	8.01	8.01	2 530 197	8.04	8.03

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Molecule	Transition	AVDZ			AVTZ			AVQZ		
		$N_{\text{det}}$	sCI	exFCI	$N_{\text{det}}$	sCI	exFCI	$N_{\text{det}}$	sCI	exFCI
	${}^3\Delta_u(\pi \rightarrow \pi^*)$		8.96	8.96		8.87	8.87		8.88	8.88
	${}^3\Sigma_u^-(\pi \rightarrow \pi^*)$		9.75	9.75		9.66	9.66		9.67	9.66
Ethylene	${}^1B_{3u}(\pi \rightarrow 3s)$	4 158 361	7.32	7.31	11 069 830	7.38	7.39			
	${}^1B_{1u}(\pi \rightarrow \pi^*)$		7.94	7.93		7.90	7.93			
	${}^1B_{1g}(\pi \rightarrow 3p)$		8.01	8.00		8.06	8.08			
	${}^3B_{1u}(\pi \rightarrow \pi^*)$	3 767 429	4.55	4.55	1 709 107	4.55	4.54			
	${}^3B_{3u}(\pi \rightarrow 3s)$	8 479 296	7.23	7.16	4 055 685	7.55	<sup>a</sup>			
	${}^3B_{1g}(\pi \rightarrow 3p)$		8.00	7.93		8.32	<sup>a</sup>			
Formaldehyde	${}^1A_2(n \rightarrow \pi^*)$	2 043 030	4.00	3.99	6 773 751	3.97	3.98			
	${}^1B_2(n \rightarrow 3s)$		7.15	7.11		7.24	7.23			
	${}^1B_2(n \rightarrow 3p)$		8.09	8.04		8.14	8.13			
	${}^1A_1(n \rightarrow 3p)$		8.15	8.12		8.24	8.23			
	${}^1A_2(n \rightarrow 3p)$		8.74	8.65		8.68	8.67			
	${}^1B_1(\sigma \rightarrow \pi^*)$		9.32	9.29		9.20	9.22			
	${}^1A_1(\pi \rightarrow \pi^*)$		9.60	9.53		9.47	9.43			
	${}^3A_2(n \rightarrow \pi^*)$	10 774 489	3.58	3.58	5 289 475	3.58	3.58			
	${}^3A_1(\pi \rightarrow \pi^*)$	4 192 682	6.10	6.10	6 637 572	6.06	6.06			
	${}^3B_2(n \rightarrow 3s)$		6.96	6.95		7.09	7.06			
	${}^3B_2(n \rightarrow 3p)$		7.88	7.87		7.98	7.94			
	${}^3A_1(n \rightarrow 3p)$		8.02	8.01		8.13	8.10			
	${}^3B_1(n \rightarrow 3d)$		8.48	8.48		8.43	8.42			
	${}^1A''(n \rightarrow \pi^*)$ [F]	6 989 511	2.86	2.86	5 289 475	2.83	2.80			
Formamide	${}^1A''(n \rightarrow \pi^*)$	6 392 357	5.74	5.70	5 249 511	5.65	5.7 <sup>a</sup>			
	${}^1A'(n \rightarrow 3s)$		6.76	6.67						
	${}^1A'(n \rightarrow \pi^*)$		7.73	7.64		7.64	7.63			
	${}^3A''(n \rightarrow \pi^*)$	3 958 975	5.44	5.42	1 791 542	5.37	5.4 <sup>a</sup>			
	${}^3A'(\pi \rightarrow \pi^*)$	3 452 920	5.90	5.82	1 791 542	5.65	5.7 <sup>a</sup>			
Hydrogen chloride	${}^1\Pi(\text{CT})$	1 049 127	7.82	7.82	3 546 637	7.84	7.84	6 944 492	7.88	7.88
Hydrogen sulfide	${}^1A_2(n \rightarrow 4p)$	2 005 501	6.29	6.29	5 354 721	6.18	6.18			
	${}^1B_1(n \rightarrow 4s)$		6.10	6.10		6.24	6.24			
	${}^3A_2(n \rightarrow 4p)$	4 293 448	5.90	5.90	5 696 382	5.81	5.81			
	${}^3B_1(n \rightarrow 4s)$	2 401 216	5.75	5.75	3 647 563	5.89	5.89			
Ketene	${}^1A_2(\pi \rightarrow \pi^*)$	6 698 206	3.87	3.84	4 648 503	3.83	3.86			
	${}^1B_1(n \rightarrow 3s)$		5.96	5.88		6.04	6.01			
	${}^1A_2(\pi \rightarrow 3p)$		7.12	7.08		7.22	7.18			
	${}^3A_2(n \rightarrow \pi^*)$	3 293 583	3.81	3.79	1 850 086	3.59	3.77			
	${}^3A_1(\pi \rightarrow \pi^*)$		5.67	5.64		5.44	5.61			
	${}^3B_1(n \rightarrow 3s)$		5.75	5.68		5.70	5.79			
	${}^3A_2(\pi \rightarrow 3p)$		7.11	7.07		7.02	7.12			
	${}^1A''(\pi \rightarrow \pi^*)$ [F]	4 289 184	0.96	0.96	2 798 757	0.94	1.00			
Methanimine	${}^1A''(n \rightarrow \pi^*)$	2 526 499	5.25	5.25	5 096 976	5.20	5.23			
	${}^3A''(n \rightarrow \pi^*)$	1 861 136	4.63	4.63	3 954 983	4.56	4.65			
Nitrosomethane	${}^1A''(n \rightarrow \pi^*)$	3 446 151	2.00	1.99	4 270 321	1.89	2.0 <sup>a</sup>			
	${}^1A'(n, n \rightarrow \pi^*, \pi^*)$		4.82	4.81	5 285 063	4.72	4.72			
	${}^1A'(n \rightarrow 3s/3p)$		6.34	6.29		6.34	6.4 <sup>a</sup>			
	${}^3A''(n \rightarrow \pi^*)$	4 079 674	1.14	1.15	1 607 335	1.09	1.16			
	${}^3A'(\pi \rightarrow \pi^*)$	3 225 628	5.61	5.56	1 792 165	5.60	5.60			
	${}^1A''(n \rightarrow \pi^*)$ [F]	4 509 295	1.70	1.70	2 718 837	1.62	1.7 <sup>a</sup>			
Streptocyanine-C1	${}^1B_2(\pi \rightarrow \pi^*)$	8 620 009	7.17	7.14	5 468 384	7.07	7.1 <sup>a</sup>			
	${}^3B_2(\pi \rightarrow \pi^*)$	6 970 063	5.52	5.47	2 436 373	5.51	5.52			
Thioformaldehyde	${}^1A_2(n \rightarrow \pi^*)$	2 672 140	2.26	2.26	6 036 063	2.21	2.22			
	${}^1B_2(n \rightarrow 4s)$		5.85	5.83		5.97	5.96			

Continued on next page

Molecule	Transition	AVDZ			AVTZ			AVQZ		
		$N_{\text{det}}$	sCI	exFCI	$N_{\text{det}}$	sCI	exFCI	$N_{\text{det}}$	sCI	exFCI
	$^1A_1(\pi \rightarrow \pi^*)$		6.54	6.5 <sup>a</sup>		6.40	6.4 <sup>a</sup>			
	$^3A_2(n \rightarrow \pi^*)$	1 841 330	1.96	1.97	4 611 888	1.93	1.94			
	$^3A_1(\pi \rightarrow \pi^*)$	8 450 984	3.43	3.45	4 169 151	3.40	3.43			
	$^3B_2(n \rightarrow 4s)$		5.68	5.66		5.66	5.6 <sup>a</sup>			
	$^1A_2(n \rightarrow \pi^*)$ [F]	245 005	1.98	1.98	6 108 383	1.94	1.95			
Water	$^1B_1(n \rightarrow 3s)$	5 869 449	7.53	7.53	5 589 200	7.63	7.62	1 139 302	7.69	7.68
	$^1A_2(n \rightarrow 3p)$		9.32	9.32		9.41	9.41		9.46	9.46
	$^1A_1(n \rightarrow 3s)$		9.94	9.94		9.99	9.99		10.04	10.02
	$^3B_1(n \rightarrow 3s)$	1 985 139	7.14	7.14	5 950 423	7.25	7.25	2 342 816	7.30	7.30
	$^3A_2(n \rightarrow 3p)$	4 566 873	9.14	9.14	3 760 373	9.24	9.24	525 499	9.28	9.28
	$^3A_1(n \rightarrow 3s)$		9.49	9.49		9.54	9.54		9.58	9.58

<sup>a</sup>CI convergence too slow to provide reliable estimate.

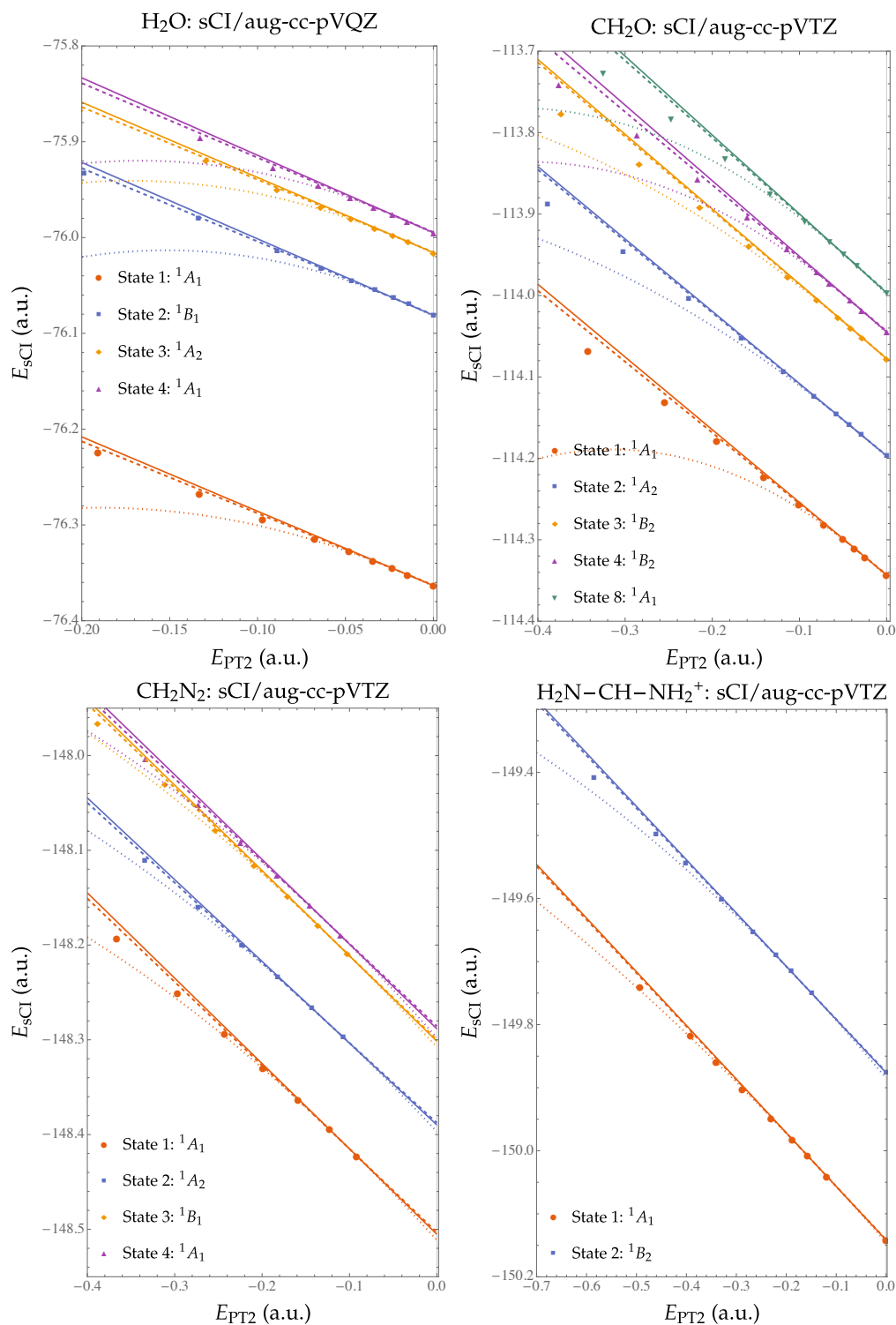


Figure S1: sCI energy  $E_{\text{sCI}}$  (in a.u.) as a function of the second-order perturbative correction  $E_{\text{PT2}}$  (in a.u.) for various singlet states of water ( $\text{H}_2\text{O}$ ), formaldehyde ( $\text{CH}_2\text{O}$ ), diazomethane ( $\text{CH}_2\text{N}_2$ ) and streptocyanine-C1 ( $\text{H}_2\text{N}-\text{CH}-\text{NH}_2^+$ ). The extrapolation to the FCI limit corresponds to  $E_{\text{PT2}} = 0$ . Several extrapolations are reported: i) two-point linear fit (solid slides), ii) three-point linear fit (dashed lines), and iii) three-point quadratic fit (dotted lines). The raw data are reported in Table S10.

Table S10: Total energies (in a.u.) and excitation energies (in eV) of several singlet states of water, formaldehyde, diazomethane and streptocyanine-C1 for various extrapolations: i) two-point linear fit, ii) three-point linear fit, and iii) three-point quadratic fit.

Molecule	Basis	State	Total energies (a.u.)			Excitation energies (eV)		
			2-point linear	3-point linear	3-point quadratic	2-point linear	3-point linear	3-point quadratic
Water	aug-cc-pVQZ	$^1A_1$	-76.363 312	-76.362 851	-76.364088	—	—	—
		$^1B_1$	-76.081 152	-76.080 586	-76.082105	7.68	7.68	7.67
		$^1A_2$	-76.015 753	-76.015 753	-76.016592	9.46	9.46	9.46
		$^1A_1$	-75.994 943	-75.994 943	-75.995900	10.02	10.01	10.02
Formaldehyde	aug-cc-pVTZ	$^1A_1$	-114.343 322	-114.342 705	-114.342924	—	—	—
		$^1A_2$	-114.196 920	-114.196 578	-114.197313	3.98	3.98	3.96
		$^1B_2$	-114.077 546	-114.077 213	-114.078352	7.23	7.22	7.20
		$^1B_2$	-114.044 721	-114.043 658	-114.034962	8.13	8.14	8.38
		$^1A_1$	-114.041 033	-114.039 965	-114.044155	8.23	8.24	8.13
		$^1A_2$	-114.024 737	-114.024 398	-114.025248	8.67	8.66	8.64
		$^1B_1$	-114.004 606	-114.004 206	-114.004960	9.22	9.21	9.20
		$^1A_1$	-113.996 698	-113.995 874	-113.998357	9.43	9.44	9.38
Diazomethane	aug-cc-pVTZ	$^1A_1$	-148.505 218	-148.503 165	-148.511381	—	—	—
		$^1A_2$	-148.389 825	-148.387 654	-148.396857	3.14	3.14	3.12
		$^1B_1$	-148.301 533	-148.299 769	-148.307723	5.54	5.53	5.54
		$^1A_1$	-148.288 384	-148.285 649	-148.297847	5.90	5.92	5.81
Strepto- cyanine-C1	aug-cc-pVTZ	$^1A_1$	-150.141 796	-150.141 081	-150.145 289	—	—	—
		$^1B_2$	-149.876 489	-149.875 113	-149.884 967	7.22	7.24	7.08