

TABLE I. Selected singlet excitation energies ΔE (eV) and weights of the corresponding natural transition orbitals (NTOs) for molecules with low-lying Rydberg states and strong valence-Rydberg mixing. The underlined energies correspond to the most valence-like states. Calculated with the def2-TZVP basis. The PBE0 functional was used in the TDDFT, x_α - G_0W_0 -BSE, and evGW-BSE calculations, and $\alpha_{\text{opt}} = 0.65$ was used for G_0W_0 -BSE. Reference values from our CC3/aug-cc-pVTZ calculations (CC3/TZVP for uracil since the aug-cc-pVTZ basis is not feasible). The state numbering here includes Rydberg states.

Molecule	State	TDDFT	CC2	x_α - G_0W_0 -BSE	G_0W_0 -BSE	evGW-BSE	qsGW-BSE	Ref.
Imidazole	1 $^1A''$	99.94% $R_{\pi\sigma^*}$	6.29	99.87% $R_{n\sigma^*}$	6.71	99.87% $R_{\pi\sigma^*}$	6.52	99.86% $R_{\pi\sigma^*}$
	2 $^1A''$	99.70% $V_{n\pi^*}$	6.62	99.56% $V_{n\pi^*}$	6.80	99.65% $V_{n\pi^*}$	6.70	99.71% $R_{\pi\sigma^*}$
	3 $^1A''$							81.48% $R_{\pi\sigma^*}$
Formaldehyde	2 1A_1	68.90% $V_{\pi\pi^*}$	9.29	93.53% $V_{\pi\pi^*}$	8.25	85.83% $V_{\pi\pi^*}$	9.29	99.75% $R_{n\sigma^*}$
	3 1A_1	30.70% $R_{n\sigma^*}$		80.95% $R_{n\sigma^*}$	10.23	13.10% $R_{n\sigma^*}$		83.96% $V_{\pi\pi^*}$
				65.46% $V_{\pi\pi^*}$		14.53% $R_{n\sigma^*}$		13.07% $R_{n\sigma^*}$
Acetone	2 1A_1	67.28% $R_{n\sigma^*}$	8.44	84.58% $R_{n\sigma^*}$	8.81	75.88% $V_{\pi\pi^*}$	8.91	82.98% $V_{\pi\pi^*}$
	3 1A_1	32.33% $V_{\pi\pi^*}$		14.67% $V_{\pi\pi^*}$	9.60	23.40% $R_{n\sigma^*}$		16.50% $R_{n\sigma^*}$
		61.36% $V_{\pi\pi^*}$	9.15	75.57% $V_{\pi\pi^*}$				99.63% $R_{n\sigma^*}$
Formamide	2 $^1A'$	71.22% $R_{n\sigma^*}$	7.21	71.29% $R_{n\sigma^*}$	7.28	68.06% $V_{\pi\pi^*}$	7.52	77.09% $V_{\pi\pi^*}$
	3 $^1A'$	28.68% $V_{\pi\pi^*}$		28.42% $V_{\pi\pi^*}$	8.05	32.07% $R_{n\sigma^*}$		22.99% $R_{n\sigma^*}$
		82.01% $R_{n\sigma^*}$	8.19	59.10% $R_{n\sigma^*}$				68.54% $V_{\pi\pi^*}$
Acetamide	2 $^1A'$	95.46% $R_{n\sigma^*}$	6.92	96.60% $R_{n\sigma^*}$	6.93	85.37% $V_{\pi\pi^*}$	7.54	66.83% $V_{\pi\pi^*}$
	3 $^1A'$	75.71% $V_{\pi\pi^*}$	7.64	82.21% $V_{\pi\pi^*}$	7.67	44.42% $V_{\pi\pi^*}$		33.10% $R_{n\sigma^*}$
		23.96% $R_{n\sigma^*}$	6.96	16.37% $R_{n\sigma^*}$				71.02% $V_{\pi\pi^*}$
Propanamide	2 $^1A'$	95.18% $R_{n\sigma^*}$	6.96	96.38% $R_{n\sigma^*}$	6.94	86.13% $V_{\pi\pi^*}$	7.63	96.68% $R_{n\sigma^*}$
	3 $^1A'$	57.81% $V_{\pi\pi^*}$	7.51	72.52% $V_{\pi\pi^*}$	7.58	61.64% $R_{n\sigma^*}$		65.17% $V_{\pi\pi^*}$
		41.89% $R_{n\sigma^*}$	4.72	26.26% $R_{n\sigma^*}$				33.84% $R_{n\sigma^*}$
Uracil	1 $^1A''$	99.80% $V_{n\pi^*}$	4.72	99.61% $V_{n\pi^*}$	4.86	99.73% $V_{n\pi^*}$	4.92	99.64% $V_{n\pi^*}$
	2 $^1A''$	87.13% $V_{n\pi^*}$	5.91	86.00% $V_{n\pi^*}$	6.19	99.05% $R_{n\sigma^*}$	6.24	98.55% $V_{n\pi^*}$
	3 $^1A''$	12.82% $V_{n\pi^*}$	6.35	13.81% $V_{n\pi^*}$	6.65	97.94% $V_{n\pi^*}$	6.24	93.42% $V_{n\pi^*}$
	3 $^1A''$	67.25% $V_{n\pi^*}$		60.67% $V_{n\pi^*}$		76.65% $V_{n\pi^*}$	6.28	98.21% $R_{n\sigma^*}$
	4 $^1A''$	32.51% $V_{n\pi^*}$		38.93% $V_{n\pi^*}$		21.34% $V_{n\pi^*}$		7.11
								88.88% $V_{n\pi^*}$
								20.34% $V_{n\pi^*}$
								78.86% $V_{n\pi^*}$
								83.88% $V_{n\pi^*}$
								7.33
								15.16% $V_{n\pi^*}$
								28.00% $V_{n\pi^*}$

TABLE II: Singlet excitation energies ΔE (eV) obtained in the def2-TZVP basis. The PBE0 functional was used in the TDDFT, x_α - G_0W_0 -BSE, G_0W_0 -BSE, and evGW-BSE calculations, and $\alpha_{\text{opt}} = 0.65$ was used for G_0W_0 -BSE. The state numbering here is for valence states only. For example, the $1^1A''$ ($\pi \rightarrow \pi^*$) state of imidazole represents the lowest valence $1^1A''$ state with $\pi \rightarrow \pi^*$ character, which is not necessarily the lowest $1^1A''$ state.

Molecule	State	TDDFT	CC2	x_α - G_0W_0 -BSE	G_0W_0 -BSE	evGW-BSE	qsGW-BSE	Ref.
Ethene	1^1B_{1u} ($\pi \rightarrow \pi^*$)	7.76	8.26	6.59	7.29	7.75	7.76	7.89 ^a
<i>E</i> -Butadiene	1^1B_u ($\pi \rightarrow \pi^*$)	5.80	6.36	5.09	5.49	5.94	5.93	6.21 ^c
<i>E</i> -Hexatriene	1^1B_u ($\pi \rightarrow \pi^*$)	4.75	5.29	4.25	4.49	4.92	4.91	5.32 ^c
<i>E</i> -Octatetraene	1^1B_u ($\pi \rightarrow \pi^*$)	4.07	4.60	3.72	3.83	4.27	4.26	4.75 ^d
Cyclopropene	1^1B_1 ($\sigma \rightarrow \pi^*$)	6.54	6.86	5.94	6.04	6.56	6.67	6.67 ^a
	1^1B_2 ($\pi \rightarrow \pi^*$)	6.36	6.98	5.58	6.08	6.56	6.63	6.68 ^a
Cyclopentadiene	1^1B_2 ($\pi \rightarrow \pi^*$)	5.07	5.57	4.38	4.64	5.06	5.10	5.49 ^c
Norbornadiene	1^1A_2 ($\pi \rightarrow \pi^*$)	4.88	5.43	4.70	4.71	5.16	5.21	5.37 ^d
	1^1B_2 ($\pi \rightarrow \pi^*$)	5.64	6.23	5.83	5.68	6.16	6.23	6.21 ^d
Benzene	1^1B_{2u} ($\pi \rightarrow \pi^*$)	5.47	5.26	4.84	4.78	5.19	5.22	5.03 ^a
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	6.16	6.55	5.70	5.62	6.03	6.03	6.42 ^a
	1^1E_{1u} ($\pi \rightarrow \pi^*$)	7.12	7.32	6.55	6.44	6.89	6.93	7.14 ^a
Naphthalene	1^1B_{3u} ($\pi \rightarrow \pi^*$)	4.50	4.41	4.14	3.91	4.29	4.33	4.25 ^c
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	4.40	4.81	4.10	3.98	4.37	4.41	4.82 ^c
	1^1B_{1g} ($\pi \rightarrow \pi^*$)	5.74	6.07	5.93	5.41	5.91	5.97	5.75 ^c
	2^1A_g ($\pi \rightarrow \pi^*$)	6.29	6.17	6.33	5.57	6.12	6.14	5.90 ^c
	2^1B_{3u} ($\pi \rightarrow \pi^*$)	5.98	6.15	5.70	5.40	5.83	5.81	6.11 ^c
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	6.18	6.43	6.03	5.61	6.03	6.06	6.36 ^c
	2^1B_{1g} ($\pi \rightarrow \pi^*$)	6.38	6.68	6.42	5.72	6.27	6.28	6.46 ^c
Furan	1^1B_2 ($\pi \rightarrow \pi^*$)	6.21	6.62	5.34	5.66	6.09	6.10	6.26 ^c
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.83	6.80	6.39	6.27	6.78	6.88	6.51 ^c
	3^1A_1 ($\pi \rightarrow \pi^*$)	8.31	8.65	7.75	7.59	8.14	8.24	8.13 ^c
Pyrrole	1^1B_2 ($\pi \rightarrow \pi^*$)	6.46	6.78	5.77	5.90	6.33	6.34	6.20 ^c
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.65	6.56	6.16	6.04	6.51	6.57	6.27 ^c
	3^1A_1 ($\pi \rightarrow \pi^*$)	8.03	8.32	7.50	7.34	7.86	7.94	7.60 ^c
Imidazole	$2^1A'$ ($\pi \rightarrow \pi^*$)	6.53	6.65	5.81	5.96	6.41	6.43	6.32 ^b
	$1^1A''$ ($n \rightarrow \pi^*$)	6.62	6.80	7.00	5.97	6.70	6.73	6.70 ^b
	$3^1A'$ ($\pi \rightarrow \pi^*$)	7.13	7.19	6.60	6.47	6.98	7.03	6.79 ^b
Pyridine	1^1B_1 ($n \rightarrow \pi^*$)	4.85	5.02	5.33	4.28	4.95	4.99	4.95 ^c
	1^1B_2 ($\pi \rightarrow \pi^*$)	5.56	5.30	4.83	4.82	5.23	5.26	5.12 ^c
	1^1A_2 ($n \rightarrow \pi^*$)	5.23	5.31	5.80	4.68	5.37	5.43	5.41 ^c
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.36	6.74	5.87	5.79	6.23	6.24	6.60 ^c
	2^1B_2 ($\pi \rightarrow \pi^*$)	7.36	7.51	6.85	6.63	7.13	7.16	7.33 ^c
	3^1A_1 ($\pi \rightarrow \pi^*$)	7.39	7.60	6.83	6.65	7.14	7.19	7.39 ^c
Pyrazine	1^1B_{3u} ($n \rightarrow \pi^*$)	3.98	4.17	4.23	3.42	4.03	4.07	4.13 ^c
	1^1B_{2u} ($\pi \rightarrow \pi^*$)	5.41	5.11	4.49	4.61	5.01	5.03	4.97 ^c
	1^1A_u ($n \rightarrow \pi^*$)	4.80	4.89	5.23	4.29	4.94	5.02	4.98 ^c
	1^1B_{2g} ($n \rightarrow \pi^*$)	5.63	5.83	6.36	4.87	5.68	5.71	5.65 ^c
	1^1B_{1g} ($n \rightarrow \pi^*$)	6.59	6.65	7.53	5.92	6.76	6.84	6.69 ^c
	1^1B_{1u} ($\pi \rightarrow \pi^*$)	6.55	6.96	5.97	5.95	6.39	6.40	6.83 ^c
	2^1B_{2u} ($\pi \rightarrow \pi^*$)	7.88	7.99	7.48	7.07	7.64	7.68	7.81 ^c
	2^1B_{1u} ($\pi \rightarrow \pi^*$)	7.73	8.00	7.21	6.89	7.44	7.49	7.86 ^c
Pyrimidine	1^1B_1 ($n \rightarrow \pi^*$)	4.33	4.41	4.72	3.75	4.41	4.45	4.43 ^c
	1^1A_2 ($n \rightarrow \pi^*$)	4.70	4.78	5.18	4.14	4.82	4.88	4.85 ^c
	1^1B_2 ($\pi \rightarrow \pi^*$)	5.81	5.50	5.06	5.02	5.46	5.50	5.34 ^c
	2^1A_1 ($\pi \rightarrow \pi^*$)	6.64	6.98	6.14	6.04	6.51	6.52	6.82 ^c
Pyridazine	1^1B_1 ($n \rightarrow \pi^*$)	3.65	3.81	4.10	3.02	3.71	3.76	3.85 ^c
	1^1A_2 ($n \rightarrow \pi^*$)	4.32	4.34	4.91	3.73	4.45	4.52	4.44 ^c
	2^1A_1 ($\pi \rightarrow \pi^*$)	5.66	5.35	4.89	4.86	5.30	5.33	5.20 ^c
	2^1A_2 ($n \rightarrow \pi^*$)	5.52	5.72	5.99	4.96	5.66	5.68	5.66 ^c
<i>s</i> -Triazine	$1^1A_1''$ ($n \rightarrow \pi^*$)	4.56	4.63	4.97	3.98	4.66	4.70	4.70 ^c
	$1^1A_2''$ ($n \rightarrow \pi^*$)	4.62	4.73	5.07	4.09	4.75	4.84	4.71 ^c
	$1^1E''$ ($n \rightarrow \pi^*$)	4.63	4.71	5.06	4.07	4.77	4.80	4.75 ^c

TABLE II (Continued)

Molecule	State	TDDFT	CC2	x_α - G_0W_0 -BSE	G_0W_0 -BSE	evGW-BSE	qsGW-BSE	Ref.
s-Tetrazine	1 $^1A_2'$ ($\pi \rightarrow \pi^*$)	6.22	5.83	5.58	5.38	5.88	5.91	5.71 ^c
	1 $^1B_{3u}$ ($n \rightarrow \pi^*$)	2.28	2.40	2.38	1.62	2.24	2.30	2.46 ^a
	1 1A_u ($n \rightarrow \pi^*$)	3.65	3.63	4.06	3.08	3.76	3.86	3.78 ^c
	1 $^1B_{1g}$ ($n \rightarrow \pi^*$)	4.84	5.01	5.43	3.99	4.85	4.87	4.87 ^a
	1 $^1B_{2u}$ ($\pi \rightarrow \pi^*$)	5.62	5.18	4.54	4.68	5.13	5.14	5.08 ^a
	1 $^1B_{2g}$ ($n \rightarrow \pi^*$)	5.38	5.46	5.87	4.55	5.36	5.38	5.28 ^a
Formaldehyde	2 1A_u ($n \rightarrow \pi^*$)	5.13	5.42	5.31	4.64	5.29	5.27	5.39 ^c
	1 1A_2 ($n \rightarrow \pi^*$)	3.88	4.05	3.25	3.12	3.83	3.97	3.89 ^b
	1 1B_1 ($\sigma \rightarrow \pi^*$)	8.94	9.26	8.68	8.10	8.96	9.16	9.05 ^b
Acetone	2 1A_1 ($\pi \rightarrow \pi^*$)	9.29	10.23	8.24	8.57	9.29	9.39	9.31 ^b
	1 1A_2 ($n \rightarrow \pi^*$)	4.36	4.50	4.56	3.48	4.25	4.37	4.38 ^b
<i>p</i> -Benzoquinone	2 1A_1 ($\pi \rightarrow \pi^*$)	9.15	9.60	8.71	8.15	8.91	9.05	8.90 ^b
	1 1B_1 ($\sigma \rightarrow \pi^*$)	8.66	9.19	8.93	8.26	9.03	9.05	9.03 ^b
	1 $^1B_{1g}$ ($n \rightarrow \pi^*$)	2.48	2.76	3.15	1.97	2.73	2.85	2.74 ^c
	1 1A_u ($n \rightarrow \pi^*$)	2.66	2.89	3.55	2.03	2.87	3.01	2.86 ^c
	1 $^1B_{3g}$ ($\pi \rightarrow \pi^*$)	3.84	4.57	3.37	3.67	4.09	4.17	4.44 ^c
	1 $^1B_{1u}$ ($\pi \rightarrow \pi^*$)	4.94	5.51	4.67	4.65	5.19	5.22	5.47 ^c
	2 $^1B_{3g}$ ($\pi \rightarrow \pi^*$)	6.74	7.23	6.93	6.40	7.03	7.18	7.16 ^c
Formamide	1 $^1A''$ ($n \rightarrow \pi^*$)	5.60	5.73	5.50	4.75	5.55	5.65	5.56 ^b
Acetamide	1 $^1A''$ ($n \rightarrow \pi^*$)	5.62	5.75	5.88	4.77	5.57	5.70	5.62 ^b
Propanamide	1 $^1A''$ ($n \rightarrow \pi^*$)	5.66	5.77	6.01	4.77	5.56	5.72	5.64 ^b
Cytosine	2 $^1A'$ ($\pi \rightarrow \pi^*$)	4.76	4.77	4.76	4.20	4.76	4.83	4.61 ^e
	1 $^1A''$ ($n \rightarrow \pi^*$)	4.92	4.97	5.98	4.53	5.30	5.28	5.06 ^e
	2 $^1A''$ ($n \rightarrow \pi^*$)	5.34	5.40	6.57	4.97	5.80	5.95	5.42 ^e
Thymine	3 $^1A'$ ($\pi \rightarrow \pi^*$)	5.57	5.67	5.91	5.14	5.76	5.83	5.46 ^e
	1 $^1A''$ ($n \rightarrow \pi^*$)	4.79	4.89	5.74	4.13	4.93	5.05	4.87 ^e
	2 $^1A'$ ($\pi \rightarrow \pi^*$)	5.07	5.29	5.02	4.64	5.16	5.20	5.14 ^e
	3 $^1A'$ ($\pi \rightarrow \pi^*$)	6.14	6.39	6.72	5.77	6.49	6.61	6.14 ^e
Uracil	2 $^1A''$ ($n \rightarrow \pi^*$)	5.99	6.26	7.19	5.41	6.29	6.47	6.28 ^e
	4 $^1A'$ ($\pi \rightarrow \pi^*$)	6.44	6.71	6.88	6.15	6.73	6.77	6.41 ^e
	1 $^1A''$ ($n \rightarrow \pi^*$)	4.72	4.86	5.63	4.10	4.92	5.03	4.80 ^e
	2 $^1A'$ ($\pi \rightarrow \pi^*$)	5.26	5.43	5.08	4.75	5.29	5.35	5.25 ^e
	3 $^1A'$ ($\pi \rightarrow \pi^*$)	6.04	6.36	6.70	5.74	6.44	6.57	6.10 ^e
Adenine	2 $^1A''$ ($n \rightarrow \pi^*$)	5.91	6.19	7.04	5.36	6.24	6.39	6.15 ^e
	4 $^1A'$ ($\pi \rightarrow \pi^*$)	6.64	6.89	6.85	6.30	6.90	6.95	6.54 ^e
	3 $^1A''$ ($n \rightarrow \pi^*$)	6.35	6.65	7.89	6.28	7.17	7.33	6.69 ^e
	2 $^1A'$ ($\pi \rightarrow \pi^*$)	5.11	5.25	5.05	4.66	5.13	5.18	5.10 ^e
	3 $^1A'$ ($\pi \rightarrow \pi^*$)	5.35	5.33	5.26	4.74	5.23	5.23	5.17 ^e
	1 $^1A''$ ($n \rightarrow \pi^*$)	5.08	5.20	5.94	4.59	5.28	5.31	5.20 ^e
	2 $^1A''$ ($n \rightarrow \pi^*$)	5.71	5.82	6.64	5.15	5.86	5.88	5.79 ^e

^aDirect CC3/aug-cc-pVTZ results. Taken from Ref. 1.

^bDirect CC3/aug-cc-pVTZ results. Taken from our own calculations.

^cEstimated CC3/aug-cc-pVTZ results based on CC3/TZVP with basis set correction from CCSDR(3)/aug-cc-pVTZ and CCSDR(3)/TZVP. Taken from Ref. 1.

^dEstimated CC3/aug-cc-pVTZ results based on CC3/TZVP with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP. Taken from Ref. 1.

^eEstimated CC3/aug-cc-pVTZ results based on CC3/TZVP with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP. Derived from Ref. 2 (CC3 results) and Ref. 3 (CC2 results).

TABLE III: Singlet excitation energies ΔE (eV) obtained in the aug-cc-pVTZ basis. The PBE0 functional was used in the TDDFT and evGW-BSE calculations. The state numbering here is for valence states only.

Molecule	State	TDDFT	CC2	evGW-BSE	qsGW-BSE
Ethene	$1^1 B_{1u} (\pi \rightarrow \pi^*)$	7.50	7.90	7.35	7.52
<i>E</i> -Butadiene	$1^1 B_u (\pi \rightarrow \pi^*)$	5.65	6.13	5.74	5.79
<i>E</i> -Hexatriene	$1^1 B_u (\pi \rightarrow \pi^*)$	4.68	5.18	4.79	4.84
<i>E</i> -Octatetraene	$1^1 B_u (\pi \rightarrow \pi^*)$	4.04	4.53	4.17	4.21
Cyclopropene	$1^1 B_1 (\sigma \rightarrow \pi^*)$	6.34	6.73	6.20	6.59
	$1^1 B_2 (\pi \rightarrow \pi^*)$	6.18	6.72	6.18	6.46
Cyclopentadiene	$1^1 B_2 (\pi \rightarrow \pi^*)$	5.02	5.47	4.90	5.04
Norbornadiene	$1^1 A_2 (\pi \rightarrow \pi^*)$	4.82	5.30	4.92	5.12
	$1^1 B_2 (\pi \rightarrow \pi^*)$	5.57	6.09	5.78	6.14
Benzene	$1^1 B_{2u} (\pi \rightarrow \pi^*)$	5.44	5.22	5.06	5.18
	$1^1 B_{1u} (\pi \rightarrow \pi^*)$	6.10	6.45	5.90	5.96
	$1^1 E_{1u} (\pi \rightarrow \pi^*)$	6.99	7.12	6.68	6.79
Naphthalene	$1^1 B_{3u} (\pi \rightarrow \pi^*)$	4.48	4.38	4.21	4.30
	$1^1 B_{2u} (\pi \rightarrow \pi^*)$	4.38	4.75	4.28	4.37
	$1^1 B_{1g} (\pi \rightarrow \pi^*)$	5.59	5.82	5.54	5.74
	$2^1 A_g (\pi \rightarrow \pi^*)$	6.20	6.07	5.83	6.04
	$2^1 B_{3u} (\pi \rightarrow \pi^*)$	5.89	6.02	5.68	5.73
	$2^1 B_{2u} (\pi \rightarrow \pi^*)$	6.14	6.35	5.90	6.00
	$2^1 B_{1g} (\pi \rightarrow \pi^*)$	6.22	6.44	6.13	6.21
Furan	$1^1 B_2 (\pi \rightarrow \pi^*)$	6.02	6.37	5.81	5.95
	$2^1 A_1 (\pi \rightarrow \pi^*)$	6.73	6.70	6.39	6.77
	$3^1 A_1 (\pi \rightarrow \pi^*)$	7.97	8.13	7.66	7.95
Pyrrole	$1^1 B_2 (\pi \rightarrow \pi^*)$	6.05	6.25	5.77	6.08
	$2^1 A_1 (\pi \rightarrow \pi^*)$	6.50	6.42	5.92	6.44
	$3^1 A_1 (\pi \rightarrow \pi^*)$	7.62	7.81	7.16	7.48
Imidazole	$2^1 A' (\pi \rightarrow \pi^*)$	6.26	6.40	5.93	6.24
	$1^1 A'' (n \rightarrow \pi^*)$	6.56	6.69	6.25	6.66
	$3^1 A' (\pi \rightarrow \pi^*)$	6.93	6.91	6.19	6.86
Pyridine	$1^1 B_1 (n \rightarrow \pi^*)$	4.82	4.97	4.83	4.97
	$1^1 B_2 (\pi \rightarrow \pi^*)$	5.52	5.26	5.12	5.22
	$1^1 A_2 (n \rightarrow \pi^*)$	5.22	5.27	5.25	5.41
	$2^1 A_1 (\pi \rightarrow \pi^*)$	6.31	6.64	6.10	6.17
	$2^1 B_2 (\pi \rightarrow \pi^*)$	7.24	7.32	6.94	7.04
	$3^1 A_1 (\pi \rightarrow \pi^*)$	7.32	7.43	6.94	7.07
Pyrazine	$1^1 B_{3u} (n \rightarrow \pi^*)$	3.96	4.12	3.95	4.05
	$1^1 B_{2u} (\pi \rightarrow \pi^*)$	5.37	5.07	4.91	4.98
	$1^1 A_u (n \rightarrow \pi^*)$	4.80	4.86	4.85	5.00
	$1^1 B_{2g} (n \rightarrow \pi^*)$	5.62	5.79	5.57	5.68
	$1^1 B_{1g} (n \rightarrow \pi^*)$	6.59	6.61	6.65	6.80
	$1^1 B_{1u} (\pi \rightarrow \pi^*)$	6.51	6.86	6.28	6.34
	$2^1 B_{2u} (\pi \rightarrow \pi^*)$	7.76	7.82	7.47	7.57
	$2^1 B_{1u} (\pi \rightarrow \pi^*)$	7.67	7.92	7.18	7.36
Pyrimidine	$1^1 B_1 (n \rightarrow \pi^*)$	4.31	4.37	4.29	4.44
	$1^1 A_2 (n \rightarrow \pi^*)$	4.70	4.75	4.79	4.86
	$1^1 B_2 (\pi \rightarrow \pi^*)$	5.78	5.46	5.41	5.45
	$2^1 A_1 (\pi \rightarrow \pi^*)$	6.59	6.94	6.47	6.45
Pyridazine	$1^1 B_1 (n \rightarrow \pi^*)$	3.65	3.79	3.62	3.76
	$1^1 A_2 (n \rightarrow \pi^*)$	4.31	4.30	4.33	4.50
	$2^1 A_1 (\pi \rightarrow \pi^*)$	5.64	5.32	5.20	5.30
	$2^1 A_2 (n \rightarrow \pi^*)$	5.51	5.70	5.57	5.66
<i>s</i> -Triazine	$1^1 A_1'' (n \rightarrow \pi^*)$	4.55	4.60	4.58	4.69
	$1^1 A_2'' (n \rightarrow \pi^*)$	4.62	4.71	4.70	4.83
	$1^1 E'' (n \rightarrow \pi^*)$	4.62	4.68	4.68	4.79
	$1^1 A_2' (\pi \rightarrow \pi^*)$	6.20	5.80	5.80	5.89
<i>s</i> -Tetrazine	$1^1 B_{3u} (n \rightarrow \pi^*)$	2.29	2.39	2.20	2.31
	$1^1 A_u (n \rightarrow \pi^*)$	3.65	3.61	3.67	3.83

TABLE III (Continued)

Molecule	State	TDDFT	CC2	evGW-BSE	qsGW-BSE
Formaldehyde	$1^1B_{1g} (n \rightarrow \pi^*)$	4.85	5.00	4.78	4.89
	$1^1B_{2u} (\pi \rightarrow \pi^*)$	5.60	5.16	5.06	5.13
	$1^1B_{2g} (n \rightarrow \pi^*)$	5.38	5.45	5.29	5.38
	$2^1A_u (n \rightarrow \pi^*)$	5.12	5.40	5.24	5.30
	$1^1A_2 (n \rightarrow \pi^*)$	3.85	4.00	3.61	3.93
	$1^1B_1 (\sigma \rightarrow \pi^*)$	8.91	9.19	8.69	9.11
Acetone	$2^1A_1 (\pi \rightarrow \pi^*)$	9.21	9.78	8.97	9.26
	$1^1A_2 (n \rightarrow \pi^*)$	4.35	4.45	3.99	4.37
<i>p</i> -Benzoquinone	$2^1A_1 (\pi \rightarrow \pi^*)$	8.62	9.31	8.74	9.02
	$1^1B_1 (\sigma \rightarrow \pi^*)$	8.62	9.11	8.76	9.00
	$1^1B_{1g} (n \rightarrow \pi^*)$	2.48	2.76	2.68	2.85
	$1^1A_u (n \rightarrow \pi^*)$	2.67	2.88	2.82	3.00
	$1^1B_{3g} (\pi \rightarrow \pi^*)$	3.82	4.53	4.03	4.14
	$1^1B_{1u} (\pi \rightarrow \pi^*)$	4.91	5.46	5.10	5.18
Formamide	$2^1B_{3g} (\pi \rightarrow \pi^*)$	6.71	7.17	6.89	7.12
Acetamide	$1^1A'' (n \rightarrow \pi^*)$	5.51	5.59	5.23	5.56
	$1^1A'' (n \rightarrow \pi^*)$	5.54	5.61	4.58	5.61
Propanamide	$1^1A'' (n \rightarrow \pi^*)$	5.57	5.62	4.54	5.63
Cytosine	$2^1A' (\pi \rightarrow \pi^*)$	4.71	4.69	4.60	4.75
	$1^1A'' (n \rightarrow \pi^*)$	4.89	4.91	5.15	5.23
Thymine	$2^1A'' (n \rightarrow \pi^*)$	5.32	5.33	5.40	5.88
	$3^1A' (\pi \rightarrow \pi^*)$	5.51	5.56	5.58	5.72
	$1^1A'' (n \rightarrow \pi^*)$	4.76	4.83	4.77	5.00
	$2^1A' (\pi \rightarrow \pi^*)$	5.00	5.19	4.99	5.11
	$3^1A' (\pi \rightarrow \pi^*)$	6.07	6.26	6.29	6.50
	$2^1A'' (n \rightarrow \pi^*)$	5.95	6.16	6.01	6.39
Uracil	$4^1A' (\pi \rightarrow \pi^*)$	6.31	6.50	6.42	6.60
	$1^1A'' (n \rightarrow \pi^*)$	4.70	4.81	4.77	4.99
Adenine	$2^1A' (\pi \rightarrow \pi^*)$	5.20	5.33	5.13	5.26
	$3^1A' (\pi \rightarrow \pi^*)$	5.99	6.24	6.26	6.47
	$2^1A'' (n \rightarrow \pi^*)$	5.87	6.09	6.00	6.32
	$4^1A' (\pi \rightarrow \pi^*)$	6.48	6.66	6.62	6.75
	$3^1A'' (n \rightarrow \pi^*)$	6.29	6.54	6.98	7.25
	$2^1A' (\pi \rightarrow \pi^*)$	5.04	5.20	4.98	5.08
Adenine	$3^1A' (\pi \rightarrow \pi^*)$	5.28	5.20	5.08	5.17
	$1^1A'' (n \rightarrow \pi^*)$	5.05	5.13	5.11	5.26
	$2^1A'' (n \rightarrow \pi^*)$	5.67	5.74	5.71	5.70

TABLE IV: Triplet excitation energies ΔE (eV) obtained in the def2-TZVP basis. The PBE0 functional was used in the TDDFT, x_α - G_0W_0 -BSE, G_0W_0 -BSE, and evGW-BSE calculations, and $\alpha_{\text{opt}} = 0.76$ was used for G_0W_0 -BSE.

Molecule	State	TDDFT	CC2	x_α - G_0W_0 -BSE	G_0W_0 -BSE	evGW-BSE	qsGW-BSE	Ref.
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.81	4.58	3.32	3.31	3.73	3.92	4.50 ^a
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	2.56	3.43	2.43	2.13	2.59	2.74	3.34 ^b
	$1^3A_g (\pi \rightarrow \pi^*)$	4.71	5.30	4.81	3.96	4.58	4.64	5.15 ^a
<i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	1.89	2.81	1.92	1.44	1.95	2.11	2.71 ^b
	$1^3A_g (\pi \rightarrow \pi^*)$	3.78	4.44	4.10	3.02	3.71	3.79	4.33 ^b
<i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	1.48	2.42	1.61	0.96	1.54	1.73	2.32 ^b
	$1^3A_g (\pi \rightarrow \pi^*)$	3.10	3.79	3.50	2.35	3.06	3.16	3.69 ^b
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.52	4.43	3.46	3.24	3.70	3.76	4.28 ^a
	$1^3B_1 (\sigma \rightarrow \pi^*)$	5.99	6.54	6.14	5.48	6.00	6.11	6.40 ^a
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	2.56	3.38	2.55	2.14	2.57	2.65	3.26 ^b
	$1^3A_1 (\pi \rightarrow \pi^*)$	4.62	5.24	4.83	4.02	4.55	4.55	5.09 ^b
Norbornadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	2.93	3.75	3.30	2.61	3.06	3.15	3.68 ^b
	$1^3B_2 (\pi \rightarrow \pi^*)$	3.43	4.27	3.83	3.00	3.48	3.60	4.16 ^b
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.58	4.35	3.76	3.02	3.45	3.52	4.12 ^a
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	4.68	5.08	4.68	4.04	4.43	4.46	4.81 ^a
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	5.06	5.92	4.99	4.32	4.73	4.75	5.78 ^a
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.33	7.98	8.30	6.29	7.15	7.20	7.45 ^a
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	2.54	3.26	2.82	2.05	2.47	2.53	3.09 ^b
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	3.93	4.31	4.13	3.33	3.72	3.75	4.09 ^b
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.07	4.63	4.61	3.42	3.93	3.95	4.42 ^b
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.38	4.83	4.72	3.79	4.19	4.20	4.56 ^b
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	4.20	4.97	4.36	3.56	3.95	3.98	4.92 ^b
	$1^3A_g (\pi \rightarrow \pi^*)$	5.29	5.73	5.95	4.44	5.06	5.06	5.42 ^b
	$2^3B_{1g} (\pi \rightarrow \pi^*)$	5.70	6.28	6.59	5.35	5.88	5.95	6.12 ^b
	$2^3A_g (\pi \rightarrow \pi^*)$	5.98	6.69	6.64	5.23	5.78	5.79	6.17 ^b
	$3^3A_g (\pi \rightarrow \pi^*)$	6.14	6.84	7.31	5.56	6.24	6.30	6.65 ^b
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	6.59	7.18	7.69	5.68	6.45	6.52	6.67 ^b
Furan	$1^3B_2 (\pi \rightarrow \pi^*)$	3.56	4.37	3.32	2.99	3.41	3.50	4.11 ^b
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.14	5.66	5.20	4.43	4.92	4.95	5.43 ^b
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	3.97	4.69	3.85	3.37	3.78	3.85	4.44 ^b
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.24	5.70	5.31	4.54	4.99	5.02	5.42 ^b
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.15	4.89	4.03	3.55	3.97	4.05	4.65 ^b
	$2^3A' (\pi \rightarrow \pi^*)$	5.36	5.96	5.37	4.67	5.14	5.19	5.64 ^b
	$1^3A'' (n \rightarrow \pi^*)$	5.90	6.41	7.11	5.19	5.92	5.96	6.25 ^b
	$3^3A' (\pi \rightarrow \pi^*)$	5.96	6.67	6.24	5.15	5.70	5.77	6.38 ^b
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	3.69	4.49	3.88	3.11	3.57	3.64	4.28 ^b
	$1^3B_1 (n \rightarrow \pi^*)$	4.05	4.49	5.34	3.46	4.14	4.17	4.42 ^b
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.45	4.97	4.26	3.73	4.10	4.13	4.72 ^b
	$2^3A_1 (\pi \rightarrow \pi^*)$	4.82	5.27	4.85	4.13	4.55	4.59	4.96 ^b
	$1^3A_2 (n \rightarrow \pi^*)$	5.05	5.28	6.45	4.50	5.19	5.26	5.35 ^b
	$2^3B_2 (\pi \rightarrow \pi^*)$	5.63	6.39	5.75	4.88	5.35	5.39	6.22 ^b
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.40	1.83	2.40	0.76	1.41	1.45	1.87 ^a
	$1^3A_u (n \rightarrow \pi^*)$	3.18	3.41	4.46	2.62	3.29	3.39	3.49 ^a
	$1^3B_{1g} (n \rightarrow \pi^*)$	3.67	4.26	5.22	2.80	3.69	3.70	4.18 ^a
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.60	4.66	3.82	2.92	3.48	3.49	4.36 ^a
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.96	4.67	3.49	3.11	3.50	3.49	4.39 ^a
	$1^3B_{2g} (n \rightarrow \pi^*)$	4.50	5.00	5.94	3.70	4.52	4.53	4.89 ^a
	$2^3A_u (n \rightarrow \pi^*)$	4.47	4.99	5.53	3.97	4.64	4.62	4.96 ^a
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.21	5.61	5.08	4.38	4.84	4.88	5.32 ^a
Formaldehyde	$1^3A_2 (n \rightarrow \pi^*)$	3.07	3.55	3.39	2.31	3.02	3.18	3.49 ^a
	$1^3A_1 (\pi \rightarrow \pi^*)$	4.96	6.13	4.62	4.20	4.87	5.06	5.86 ^a
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	3.65	4.09	4.76	2.78	3.55	3.66	4.05 ^a
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.24	6.31	5.82	4.57	5.31	5.31	6.07 ^a
<i>p</i> -Benzoquinone	$1^3B_{1g} (n \rightarrow \pi^*)$	1.91	2.45	3.40	1.36	2.14	2.26	2.50 ^b
	$1^3A_u (n \rightarrow \pi^*)$	2.07	2.58	3.82	1.42	2.27	2.41	2.61 ^b

TABLE IV (Continued)

Molecule	State	TDDFT	CC2	x_α - G_0W_0 -BSE	G_0W_0 -BSE	evGW-BSE	qsGW-BSE	Ref.
Formamide	$1^3B_{1u} (\pi \rightarrow \pi^*)$	2.05	3.17	2.30	1.54	2.14	2.30	3.02 ^b
	$1^3B_{3g} (\pi \rightarrow \pi^*)$	2.59	3.48	2.69	2.25	2.71	2.76	3.37 ^b
	$1^3A'' (n \rightarrow \pi^*)$	4.96	5.38	5.79	4.12	4.92	5.02	5.28 ^a
	$1^3A' (\pi \rightarrow \pi^*)$	5.10	5.96	5.29	4.25	4.91	5.05	5.69 ^a
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	5.02	5.43	6.19	4.17	4.97	5.09	5.35 ^b
	$1^3A' (\pi \rightarrow \pi^*)$	5.24	6.08	5.76	4.42	5.09	5.23	5.71 ^b
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	5.06	5.45	6.32	4.18	4.97	5.12	5.38 ^b
	$1^3A' (\pi \rightarrow \pi^*)$	5.27	6.09	5.89	4.42	5.11	5.25	6.08 ^b

^aDirect CC3/aug-cc-pVTZ results. Taken from Ref. 1.

^bEstimated CC3/aug-cc-pVTZ results based on CC3/TZVP with basis set correction from CC2/aug-cc-pVTZ and CC2/TZVP. Taken from Ref. 1.

TABLE V: Triplet excitation energies ΔE (eV) obtained in the aug-cc-pVTZ basis. The PBE0 functional was used in the TDDFT and evGW-BSE calculations.

Molecule	State	TDDFT	CC2	evGW-BSE	qsGW-BSE
Ethene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.81	4.56	3.35	3.87
<i>E</i> -Butadiene	$1^3B_u (\pi \rightarrow \pi^*)$	2.56	3.43	2.40	2.72
	$1^3A_g (\pi \rightarrow \pi^*)$	4.68	5.25	4.12	4.59
<i>E</i> -Hexatriene	$1^3B_u (\pi \rightarrow \pi^*)$	1.90	2.80	1.82	2.09
	$1^3A_g (\pi \rightarrow \pi^*)$	3.77	4.42	3.40	3.76
<i>E</i> -Octatetraene	$1^3B_u (\pi \rightarrow \pi^*)$	1.48	2.42	1.44	1.71
	$1^3A_g (\pi \rightarrow \pi^*)$	3.10	3.78	2.89	3.13
Cyclopropene	$1^3B_2 (\pi \rightarrow \pi^*)$	3.50	4.40	3.34	3.73
	$1^3B_1 (\sigma \rightarrow \pi^*)$	5.93	6.44	5.63	6.05
Cyclopentadiene	$1^3B_2 (\pi \rightarrow \pi^*)$	2.56	3.37	2.42	2.64
	$1^3A_1 (\pi \rightarrow \pi^*)$	4.61	5.22	4.16	4.51
Norbornadiene	$1^3A_2 (\pi \rightarrow \pi^*)$	2.93	3.72	2.68	3.13
	$1^3B_2 (\pi \rightarrow \pi^*)$	3.42	4.25	2.83	3.58
Benzene	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.58	4.33	3.32	3.50
	$1^3E_{1u} (\pi \rightarrow \pi^*)$	4.67	5.05	4.30	4.43
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	5.04	5.86	4.60	4.71
	$1^3E_{2g} (\pi \rightarrow \pi^*)$	7.30	7.92	6.82	7.16
Naphthalene	$1^3B_{2u} (\pi \rightarrow \pi^*)$	2.54	3.25	2.38	2.52
	$1^3B_{3u} (\pi \rightarrow \pi^*)$	3.92	4.28	3.63	3.73
	$1^3B_{1g} (\pi \rightarrow \pi^*)$	4.06	4.59	3.70	3.93
	$2^3B_{2u} (\pi \rightarrow \pi^*)$	4.36	4.81	4.10	4.17
	$2^3B_{3u} (\pi \rightarrow \pi^*)$	4.19	4.93	3.86	3.96
	$1^3A_g (\pi \rightarrow \pi^*)$	5.26	5.67	4.80	5.02
	$2^3B_{1g} (\pi \rightarrow \pi^*)$	5.60	6.07	5.65	5.81
	$2^3A_g (\pi \rightarrow \pi^*)$	5.91	6.53	5.50	5.72
	$3^3A_g (\pi \rightarrow \pi^*)$	6.12	6.80	6.03	6.23
	$3^3B_{1g} (\pi \rightarrow \pi^*)$	6.54	6.74	6.13	6.47
Furan	$1^3B_2 (\pi \rightarrow \pi^*)$	3.54	4.33	3.11	3.46
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.11	5.61	4.55	4.91
Pyrrole	$1^3B_2 (\pi \rightarrow \pi^*)$	3.94	4.64	3.21	3.80
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.20	5.63	4.45	4.98
Imidazole	$1^3A' (\pi \rightarrow \pi^*)$	4.12	4.85	3.47	4.02
	$2^3A' (\pi \rightarrow \pi^*)$	5.29	5.86	4.32	5.13
	$1^3A'' (n \rightarrow \pi^*)$	5.86	6.32	5.38	5.91
	$3^3A' (\pi \rightarrow \pi^*)$	5.92	6.57	5.27	5.72
Pyridine	$1^3A_1 (\pi \rightarrow \pi^*)$	3.69	4.48	3.46	3.63
	$1^3B_1 (n \rightarrow \pi^*)$	4.04	4.46	4.01	4.16
	$1^3B_2 (\pi \rightarrow \pi^*)$	4.43	4.93	4.00	4.09
	$2^3A_1 (\pi \rightarrow \pi^*)$	4.80	5.24	4.45	4.55
	$1^3A_2 (n \rightarrow \pi^*)$	5.04	5.24	5.07	5.24
	$2^3B_2 (\pi \rightarrow \pi^*)$	5.61	6.34	5.23	5.35
<i>s</i> -Tetrazine	$1^3B_{3u} (n \rightarrow \pi^*)$	1.41	1.83	1.36	1.47
	$1^3A_u (n \rightarrow \pi^*)$	3.19	3.39	3.21	3.37
	$1^3B_{1g} (n \rightarrow \pi^*)$	3.69	4.27	3.56	3.73
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	3.60	4.66	3.42	3.52
	$1^3B_{2u} (\pi \rightarrow \pi^*)$	3.94	4.65	3.45	3.49
	$1^3B_{2g} (n \rightarrow \pi^*)$	4.51	4.99	4.44	4.53
	$2^3A_u (n \rightarrow \pi^*)$	4.47	4.98	4.58	4.63
	$2^3B_{1u} (\pi \rightarrow \pi^*)$	5.19	5.59	4.77	4.86
Formaldehyde	$1^3A_2 (n \rightarrow \pi^*)$	3.06	3.52	2.81	3.15
	$1^3A_1 (\pi \rightarrow \pi^*)$	4.96	6.12	4.62	5.06
Acetone	$1^3A_2 (n \rightarrow \pi^*)$	3.66	4.07	3.30	3.68
	$1^3A_1 (\pi \rightarrow \pi^*)$	5.25	6.31	5.06	5.34
<i>p</i> -Benzoquinone	$1^3B_{1g} (n \rightarrow \pi^*)$	1.92	2.46	2.09	2.27
	$1^3A_u (n \rightarrow \pi^*)$	2.09	2.58	2.22	2.41
	$1^3B_{1u} (\pi \rightarrow \pi^*)$	2.06	3.18	2.10	2.30
	$1^3B_{3g} (\pi \rightarrow \pi^*)$	2.58	3.46	2.64	2.74

TABLE V (Continued)

Molecule	State	TDDFT	CC2	evGW-BSE	qsGW-BSE
Formamide	$1^3A'' (n \rightarrow \pi^*)$	4.90	5.27	4.61	4.95
	$1^3A' (\pi \rightarrow \pi^*)$	5.06	5.88	4.61	5.00
Acetamide	$1^3A'' (n \rightarrow \pi^*)$	4.97	5.33	3.99	5.04
	$1^3A' (\pi \rightarrow \pi^*)$	5.21	6.02	4.12	5.19
Propanamide	$1^3A'' (n \rightarrow \pi^*)$	5.00	5.35	3.96	5.06
	$1^3A' (\pi \rightarrow \pi^*)$	5.24	6.02	4.11	5.21

TABLE VI. Singlet excitation energies ΔE (eV) of selected molecules obtained with PBE0 evGW-BSE in various basis sets.

Molecule	State	def2-SVP	def2-TZVP	def2-QZVP	def2-SVPD	def2-TZVPD	def2-QZVPD	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
Ethene	$1^1B_{1u}(\pi \rightarrow \pi^*)$	8.20	7.75	7.60	7.74	7.58	7.55	7.37	7.35	7.36
	$1^1B_u(\pi \rightarrow \pi^*)$	6.24	5.94	5.85	5.96	5.84	5.82	5.76	5.74	5.74
<i>E</i> -Butadiene	$1^1B_2(\pi \rightarrow \pi^*)$	6.46	6.09	5.98	6.13	5.95	5.90	5.85	5.81	5.79
	$2^1A_1(\pi \rightarrow \pi^*)$	7.07	6.78	6.67	6.74	6.63	6.59	6.41	6.39	6.36
Furan	$3^1A_1(\pi \rightarrow \pi^*)$	8.57	8.14	8.00	8.11	7.94	7.89	7.69	7.66	7.62
	$1^1B_2(\pi \rightarrow \pi^*)$	6.71	6.33	6.20	6.36	6.21	6.16	5.87	5.77	5.66
Pyrrole	$2^1A_1(\pi \rightarrow \pi^*)$	6.81	6.51	6.39	6.47	6.37	6.33	5.98	5.92	5.80
	$3^1A_1(\pi \rightarrow \pi^*)$	8.31	7.86	7.69	7.82	7.65	7.60	7.19	7.16	7.04
Imidazole	$2^1A'(\pi \rightarrow \pi^*)$	6.76	6.41	6.28	6.43	6.29	6.23	5.94	5.93	5.89
	$3^1A''(n \rightarrow \pi^*)$	6.81	6.70	6.60	6.59	6.58	6.56	6.20	6.25	6.21
Formaldehyde	$3^1A'(\pi \rightarrow \pi^*)$	7.32	6.98	6.84	6.96	6.83	6.78	6.31	6.19	6.23
	$1^1A_2(n \rightarrow \pi^*)$	4.00	3.83	3.78	3.80	3.73	3.73	3.60	3.61	3.64
Formaldelyde	$1^1A_2(\sigma \rightarrow \pi^*)$	9.16	8.96	8.88	8.90	8.84	8.82	8.74	8.69	8.75
	$2^1A_1(\pi \rightarrow \pi^*)$	9.61	9.29	9.13	9.32	9.10	9.08	9.01	8.97	8.98
Acetone	$1^1A_2(n \rightarrow \pi^*)$	4.24	4.25	4.23	4.15	4.14	4.16	3.92	3.99	4.04
	$2^1A_1(\pi \rightarrow \pi^*)$	9.27	8.91	8.95	9.11	8.90	8.98	8.72	8.74	8.77
Formamide	$1^1B_1(\sigma \rightarrow \pi^*)$	9.21	9.03	8.98	9.07	8.90	8.91	8.83	8.76	8.77
	$1^1A''(n \rightarrow \pi^*)$	5.70	5.55	5.47	5.41	5.38	5.36	5.24	5.23	5.25
Acetamide	$1^1A''(n \rightarrow \pi^*)$	5.61	5.57	5.47	5.33	5.26	5.22	4.51	4.58	4.63
	$1^1A''(n \rightarrow \pi^*)$	5.64	5.56	5.45	5.33	5.26	5.20	4.43	4.54	4.61
Propanamide	$1^1A''(n \rightarrow \pi^*)$	5.64	5.56	5.45	5.33	5.26	5.20	4.43	4.54	4.61

TABLE VII. Triplet excitation energies ΔE (eV) of selected molecules obtained with PBE0 evGW-BSE in various basis sets.

Molecule	State	def2-SVP	def2-TZVP	def2-QZVP	def2-SVPD	def2-TZVPD	def2-QZVPD	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ
Ethene	$1^3B_{1u}(\pi \rightarrow \pi^*)$	3.87	3.73	3.62	3.65	3.60	3.58	3.33	3.35	3.35
<i>E</i> -Butadiene	$1^3B_u(\pi \rightarrow \pi^*)$	2.67	2.59	2.54	2.55	2.52	2.51	2.40	2.40	2.40
	$1^3A_g(\pi \rightarrow \pi^*)$	4.74	4.58	4.47	4.49	4.43	4.41	4.13	4.12	4.09
Furan	$1^3B_2(\pi \rightarrow \pi^*)$	3.59	3.41	3.32	3.38	3.28	3.23	3.12	3.11	3.10
	$1^3A_1(\pi \rightarrow \pi^*)$	5.10	4.92	4.84	4.86	4.80	4.77	4.56	4.55	4.52
Pyrrrole	$1^3B_2(\pi \rightarrow \pi^*)$	3.93	3.78	3.68	3.74	3.68	3.64	3.27	3.21	3.11
	$1^3A_1(\pi \rightarrow \pi^*)$	5.17	4.99	4.90	4.95	4.89	4.85	4.50	4.45	4.33
Imidazole	$1^3A'$	4.14	3.97	3.87	3.95	3.89	3.84	3.56	3.47	3.41
	$2^3A'$	5.41	5.14	5.00	5.09	4.99	4.93	4.31	4.32	4.40
	$1^3A''(n \rightarrow \pi^*)$	5.97	5.92	5.83	5.79	5.80	5.77	5.29	5.38	5.41
	$3^3A'$	5.89	5.70	5.61	5.66	5.60	5.57	5.19	5.27	5.24
Formaldehyde	$1^3A_2(n \rightarrow \pi^*)$	3.16	3.02	2.97	2.99	2.92	2.92	2.79	2.81	2.84
	$1^3A_1(n \rightarrow \pi^*)$	4.98	4.87	4.79	4.82	4.77	4.74	4.61	4.62	4.66
	$1^3A_2(n \rightarrow \pi^*)$	3.50	3.55	3.54	3.45	3.45	3.47	3.23	3.30	3.35
Acetone	$1^3A_1(\pi \rightarrow \pi^*)$	5.30	5.31	5.28	5.28	5.21	5.21	5.05	5.06	5.08
	$1^3A_1(\pi \rightarrow \pi^*)$	5.02	4.92	4.84	4.78	4.75	4.73	4.61	4.61	4.62
Formamide	$1^3A''(n \rightarrow \pi^*)$	4.95	4.91	4.85	4.77	4.75	4.73	4.59	4.61	4.62
	$1^3A'$	4.97	4.97	4.88	4.73	4.67	4.63	3.92	3.99	4.04
Acetamide	$1^3A''(n \rightarrow \pi^*)$	5.05	5.09	5.01	4.88	4.79	4.75	4.04	4.12	4.15
	$1^3A'$	5.01	4.97	4.86	4.74	4.67	4.62	3.85	3.96	4.03
Propanamide	$1^3A''(n \rightarrow \pi^*)$	5.10	5.11	5.00	5.33	4.80	4.75	3.98	4.11	4.16

II. RYDBERG STATES

TABLE VIII. Singlet excitation energies ΔE (eV) of the Rydberg states in benzene and naphthalene obtained with extra molecule-centered diffuse functions. CCSDR(3) results taken from Ref. 4 as reference.

Molecule	State	evGW@PBE0-BSE		qsGW-BSE		CCSDR(3)
		def2-TZVP	def2-TZVPD	def2-TZVP	def2-TZVPD	ANO1
Benzene	$1^1E_{1g} (\pi \rightarrow \sigma^*)$	6.18	5.99	6.56	6.49	6.45
	$1^1A_{2u} (\pi \rightarrow \sigma^*)$	6.80	6.52	7.21	7.10	6.98
	$1^1E_{2u} (\pi \rightarrow \sigma^*)$	6.90	6.63	7.27	7.18	7.04
	$1^1A_{1u} (\pi \rightarrow \sigma^*)$	7.00	6.75	7.34	7.26	7.12
	$1^1B_{1g} (\pi \rightarrow \sigma^*)$	7.45	7.27	7.77	7.63	7.65
	$1^1B_{2g} (\pi \rightarrow \sigma^*)$	7.45	7.25	7.78	7.63	7.66
	$1^1E_{2g} (\pi \rightarrow \pi^*)$	7.79	7.71	7.97	7.94	7.85
	$2^1A_{1g} (\pi \rightarrow \pi^*)$	7.82	7.74	7.98	7.96	7.86
	$1^1A_{2g} (\pi \rightarrow \pi^*)$	7.82	7.75	7.99	7.97	7.88
	Naphthalene	$1^1A_u (\pi \rightarrow \sigma^*)$	5.10	5.01	5.66	5.64
$1^1B_{2g} (\pi \rightarrow \pi^*)$		5.53	5.39	6.12	6.07	5.99
$1^1B_{3g} (\pi \rightarrow \pi^*)$		5.53	5.41	6.13	6.09	6.00
$1^1B_{1u} (\pi \rightarrow \sigma^*)$		5.81	5.72	6.36	6.32	6.24
$2^1B_{1g} (\pi \rightarrow \sigma^*)$		6.49	6.45	6.53	6.51	6.39
$2^1A_u (\pi \rightarrow \pi^*)$		6.39	6.05	6.75	6.61	6.57
$2^1B_{1u} (\pi \rightarrow \pi^*)$		6.48	6.20	6.79	6.70	6.61
$2^1B_{2g} (\pi \rightarrow \pi^*)$		6.22	6.10	6.81	6.76	6.67
$2^1B_{3g} (\pi \rightarrow \pi^*)$		6.32	6.19	6.87	6.82	6.72
$3^1B_{2u} (\pi \rightarrow \pi^*)$		6.77	6.70	6.94	6.94	6.80
$3^1B_{3u} (\pi \rightarrow \pi^*)$		6.79	6.73	6.97	6.97	6.84
$3^1A_g (\pi \rightarrow \sigma^*)$		7.15	7.10	7.04	7.01	6.91
$4^1B_{2u} (\pi \rightarrow \pi^*)$		7.33	7.31	7.47	7.50	7.35

III. CHARGE-TRANSFER STATES

TABLE IX. Singlet excitation energies ΔE (eV) of charge-transfer (CT) states.

Molecule	State	CC3/TZVP	CC2/TZVP	CC2/aug-cc-pVTZ	Estimated CC3/aug-cc-pVTZ
<i>p</i> NA	2^1A_1	4.57	4.62	4.44	4.39
DMABN (C_{2v})	2^1A_1	4.98	4.90	4.78	4.86
DMABN (C_s)	$2^1A'$	4.94	4.83	4.64	4.75
PP	2^1B_2	5.48	5.56	5.29	5.21
	3^1A_1	5.96	6.05	5.78	5.69

¹ Silva-Junior, M. R.; Schreiber, M.; Sauer, S. P. A.; Thiel, W. *J. Chem. Phys.* **2010**, *133*, 174318.

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⁴ Falden, H. H.; Falster-Hansen, K. R.; Bak, K. L.; Rettrup, S.; Sauer, S. P. A. *J. Phys. Chem. A* **2009**, *113*, 11995.

FIG. 1. Dominating occupied-virtual pairs of natural transition orbitals (NTOs) obtained from the qsGW-BSE calculations.

