

Assessing Excited State Methods by Adiabatic Excitation Energies

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ABSTRACT: We compile a 109-membered benchmark set of adiabatic excitation energies (AEEs) from high-resolution gas-phase experiments. Our data set includes a variety of organic chromophores with up to 46 atoms, radicals, and inorganic transition metal compounds. Many of the 91 molecules in our set are relevant to atmospheric chemistry, photovoltaics, photochemistry, and biology. The set samples valence, Rydberg, and ionic states of various spin multiplicities. As opposed to vertical excitation energies, AEEs are rigorously defined by energy differences of vibronic states, directly observable, and insensitive to errors in equilibrium structures. We supply optimized ground state and excited state structures, which allows fast and convenient evaluation of AEEs with two single-point energy calculations per system. We apply our benchmark set to assess the performance of time-dependent density functional theory using common semilocal functionals and the configuration interaction singles method. Hybrid functionals such as B3LYP and PBE0 yield the best results, with mean absolute errors around 0.3 eV. We also investigate basis set convergence and correlations between different methods and between the magnitude of the excited state relaxation energy and the AEE error. A smaller, 15-membered subset of AEEs is introduced and used to assess the correlated wave function methods CC2 and ADC(2). These methods improve upon hybrid TDDFT for systems with single-reference ground states but perform less well for radicals and small-gap transition metal compounds. None of the investigated methods reaches “chemical accuracy” of 0.05 eV in AEEs.

1. INTRODUCTION

In view of the enormous interest in electronically excited states in analytical, photochemical, and material science applications, the amount of reliable data available to assess and calibrate theoretical excited state treatments is surprisingly small. The most common benchmarks are vertical excitation energies (VEEs) obtained either from higher level theory or from experimental absorption maxima (AM).^{1–22} An extensive VEE benchmark set including a review of previous VEE benchmarks has recently been published by Jacquemin and co-workers.¹⁷

While VEEs are readily obtained in quantum chemistry, they are not observable experimentally. The comparison of computed VEEs to experimental AM is based on three main assumptions: (i) The transition probability is maximized if ground and excited state structures are identical (Franck–Condon approximation). (ii) The transition probability is maximized at the ground state minimum. This is true only if the electronic transition probability is nonzero and does not increase upon geometry distortion, i.e., due to symmetry breaking vibrations. (iii) The absorption maximum is not affected by vibronic or rotational effects. As Herzberg already pointed out,²³ these conditions are not satisfied even in apparently simple cases such as the transition from the ground state to the 1^1B_2 state in CS₂ and the transition from the ground state to the $1^1A''$ state in HCN. The error introduced by comparing VEEs and AM can reach the order of typical method errors, as Dierksen and Grimme illustrated using simulated vibronic spectra: For the $S_0 \rightarrow S_1$ excitations of anthracene, pyrene, and pentacene, the difference between VEEs and AM ranges from 0.25 to 0.33 eV.²⁴

The past decade has seen a number of approaches to improving the accuracy of VEE benchmarks. Thiel and co-workers introduced a large benchmark set based on VEEs with experimental AM

replaced by *best estimates*.^{11,12,21} The latter are obtained from correlated ab initio calculations with large basis sets where available. Otherwise, triple- ζ complete active space second-order perturbation theory (CASPT2) results are used for singlet and triple- ζ approximate third-order coupled cluster (CC3)²⁵ results for triplet excited states. While this method requires only one single-point calculation per system, it is limited to small systems and lacks experimental validation. Jacquemin and co-workers addressed the inherent error of the VEE-AM benchmark by comparing VEEs to Thiel’s *best estimates* and experimental adiabatic excitation energies (AEEs).¹⁷ However, the conclusions are limited since excited state relaxation is neglected in the computed and unknown in the experimental AEEs.

A comprehensive comparison of spectroscopic and computational data is possible by investigating simulated vibronic spectra. Today, such calculations are feasible for fairly large molecules, and the number of vibronic simulations has grown in recent years.^{24,26–29} Simulated vibronic spectra reveal the position of AM, VEEs, and AEEs. These simulations may be systematically improved by including anharmonic corrections, Dushinsky rotation effects, Herzberg–Teller corrections, and hot bands.³⁰ However, such calculations are computationally expensive and demand a high level of expertise. The validity of most approaches is limited to harmonic potential energy surfaces and the existence of an excited state minimum. Currently, a statistically significant assessment of excited state methods using a large number of systems and states is hardly feasible at this level.

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Benchmarks using AEEs represent a compromise between simple VEE-based benchmarks and elaborate vibronic simulations. The AEE is defined as the energy difference between the lowest vibrational level of the excited and ground electronic states. As opposed to VEEs, AEEs are directly observable experimentally, e.g., from 0-0 transitions in high-resolution absorption and fluorescence spectra, and can be measured with high accuracy. On the theoretical side, AEEs require optimized geometries of both the ground and the excited electronic states. Thus, the size and chemical diversity of existing AEE benchmark sets is limited.^{16,31–35} However, with progress in analytical excited state gradient theory,^{31,32} excited state structure optimization is no longer an obstacle, even for systems containing 100 or more atoms. Another significant advantage of AEEs over VEEs is their quadratic dependence on errors in the ground and excited state structures, making them less sensitive to the quality of the structures used. Finally, it is possible to refine computed AEEs to very high accuracy by adding zero-point vibrational energy (ZPVE), relativistic, and diagonal Born–Oppenheimer corrections.³⁶

In this paper, we compile a set of 109 accurate experimental AEEs for benchmark purposes. We include a variety of different systems and states. The benchmark selection procedure is explained in section 2. To the best of our knowledge, this is the largest and most diverse AEE benchmark available so far. Using statistical analysis, we investigate basis set errors (section 4.1) and the performance of time-dependent density functional theory (TDDFT)³⁷ using common hybrid and nonhybrid exchange–correlation (XC) functionals (section 4.2). Configuration interaction singles (CIS)^{38,39} is also considered. We discuss the implications of systematic corrections (section 4.3), correlations between methods (section 4.4), and the influence of large excited state relaxation energies on hybrid TDDFT (section 4.6). Difficult cases for common functionals are discussed in section 5. Section 6 summarizes structural changes observed in the excited state geometry optimizations. A smaller, 15-membered subset of AEEs is introduced in section 7 and used to benchmark the wavefunction-based approximate second-order coupled cluster (CC2)⁴⁰ and the second-order algebraic diagrammatic construction approximation (ADC(2))⁴¹ methods. We present our conclusions in section 8.

2. BENCHMARK SELECTION PROCEDURE

It is impossible to construct a benchmark set that is representative of the entire chemical compound space. Thus, any selection of benchmark data is necessarily biased. It is important to spell out this bias clearly because it intrinsically limits the significance of any benchmark set. Without a well-motivated selection procedure, it must be suspected that a benchmark set has been chosen to favor or disfavor a particular method. This is not our intention.

We chose to bias the present benchmark set toward systems that are expected to be important for a large number of applications. In part, this was accomplished by using experimental reference data only. Experiments are generally more expensive and time-consuming than calculations and are likely more relevant than calculations for systems and states that may not be directly observable. Also, highly accurate calculations of excitation energies are presently feasible for small molecules with 10 or less atoms only. An important selection criterion was the quality of the experimental data: Only vibrationally resolved gas-phase data were included; questionable or controversial results were avoided. Our data set samples important aliphatic, aromatic, and

Table 1. Composition of the Benchmark Set

characteristic	count
molecules	91
excited states	109
organic molecules	64
inorganic molecules	27
transition metal compounds	6
aliphatic molecules	20
aromatic molecules	43
antiaromatic molecules	1
organic radicals	4
singlet excited states	86
triplet excited states	12
spin-unrestricted excited states	11

antiaromatic chromophores; it includes radicals and inorganic main group and selected transition metal compounds (see Table 1). Examples of special interest for applications include coumarin 153, a merocyanine dye, a chromophore model of the photoactive yellow protein, push–pull stilbenes, fluorene, and azaindole. The size of the molecules in our set ranges from 2 to 46 atoms (terylene). Most states are singlets, doublets, or triplets, but a few states of higher spin multiplicity are included as well. The majority of states are of valence type, some have considerable Rydberg character, such as the 3^1A state of aminomethane. Gas-phase results for long-range charge-transfer excitations were not available to us.

3. COMPUTATIONAL DETAILS

All ground and excited state structures were optimized using Becke's three-parameter hybrid functional with Lee–Yang–Parr correlation (B3LYP).⁴² Earlier benchmarks have shown that the excited state minimum structures are similar in accuracy to minimum structures obtained using ground-state density functional theory (DFT) if the Kohn–Sham reference is stable.³¹ The sensitivity of the results to the level of theory used to compute equilibrium structures is further investigated in section 7.3. Excited-state optimizations were started from the ground-state minimum structures. The geometry optimizations employed triple- ζ valence basis sets with one set of polarization functions (def2-TZVP).⁴³ Ground-state energies and density matrices were converged to 10^{-7} au. Fine quadrature grids of size m4⁴⁴ were used in the DFT and TDDFT calculations. The optimized structures were confirmed to be local energy minima by calculating vibrational frequencies. For excited states, second derivatives of the energy were determined by numerical differentiation of analytical gradients using central differences. Energy and density convergence criteria of 10^{-9} au were used for the numerical second derivatives.

For the excitation energy calculations, basis sets of split valence quality with polarization functions except on hydrogen atoms def2-SV(P)⁴³ and of triple- ζ quality (def2-TZVP) were employed. Diffuse-augmented def2-SVPD and def2-TZVPD bases from the newly developed hierarchy of property-optimized basis sets were also investigated.⁴⁵ For Sn, small core pseudopotentials (ECP-28)⁴⁶ were used. AEEs were computed from the total energy difference of ground and excited states at the optimized B3LYP/TZVP structures. The resulting energy differences were corrected by the ZPVEs obtained from vibrational frequency

Table 2. AEEs of All Excited States Contained in the Benchmark Set in eV^a

molecule	state	experiment	B3LYP	reference
1,6-epoxy-10-annulene	1 ¹ B ₁	2.98	3.32	58
2-chloropyrimidine	2 ¹ A'	3.98	3.73	59
2-cyclopenten-1-one	2 ¹ A	3.37	3.28	60
7-azaindole	2 ¹ A	4.29	4.09	61
β -dinaphthyleneoxide	2 ¹ A	3.63	3.25	62
acetaldehyde	2 ¹ A	3.69	3.81	63
acetone	2 ¹ A	3.77	3.87	63
acrolein	1 ¹ A''	3.21	3.02	64
acrolein	1 ³ A''	3.01	2.44	65
aminobenzonitrile	1 ¹ B ₁	4.15	4.25	66
aminoethane	2 ¹ A'	5.21	5.30	67
aminomethane	2 ¹ A'	5.18	5.23	67
aminomethane	3 ¹ A	6.22	6.36	67
aniline	2 ¹ A	4.22	4.34	68
anisole	2 ¹ A	4.51	4.73	69
anthracene	1 ¹ B _{2u}	3.43	2.90	70
AsF	1 ³ Π	3.19	3.10	71
azulene	1 ¹ B ₁	1.77	1.98	72
BeH	1 ² Π	2.48	2.58	71
benzaldehyde	2 ¹ A'	4.36	4.37	73
benzaldehyde	1 ¹ A''	3.34	3.27	74
benzaldehyde	1 ³ A''	3.12	2.71	74
benzene	1 ¹ B _{1u}	4.72	5.14	75
benzonitrile	1 ¹ B ₁	4.53	4.82	76
benzophenone ketyl radical	2 ² A	2.29	2.31	77
BeO	1 ¹ Π	1.17	1.21	71
BF	1 ¹ Π	6.34	6.14	71
BH	1 ¹ Π	2.87	2.70	71
biphenyl	1 ¹ B ₁	4.37	4.24	78
biphenylene	1 ¹ B _{3u}	3.50	3.63	79
C ₂ H ₂	2 ¹ A	5.23	4.72	80
CCl ₂	1 ¹ B ₂	2.14	1.89	81
CH ₂ O	2 ¹ A	3.49	3.62	82
CH ₂ O	1 ³ A	3.12	2.73	82
CH ₂ S	1 ¹ A ₂	2.03	2.07	82
CH ₂ S	1 ³ A	1.80	1.44	82
cinnoline	1 ¹ A''	2.82	2.43	83
CO	1 ¹ Π	8.07	7.99	71
CO	1 ³ Π	6.04	5.58	71
CrF	2 ⁶ Π	1.01	1.24	84
CrH	2 ⁶ Σ^+	1.62	1.78	85
CS ₂	3 ³ A	3.25	3.25	80
Cu ₂	1 ¹ Σ_u^+	2.53	2.75	86
Cu ₂	1 ¹ Π_u	2.71	2.63	86
CuH	2 ¹ Σ^+	2.91	3.06	71
cyanoacetylene	2 ¹ A'	4.77	4.74	23
cyclohexadienyl radical	2 ² A	2.26	2.49	87
DBH ⁸⁸	2 ¹ A	3.66	3.45	89
DCS ⁹⁰	2 ¹ A	3.36	2.95	91
dimethylaminobenzonitrile	1 ¹ B	4.02	4.04	66
DMPD ⁹²	2 ¹ A	3.64	3.68	93
fluorene	2 ¹ A'	4.19	4.19	94
glyoxal	1 ¹ A _u	2.72	2.43	80

Table 2. Continued

molecule	state	experiment	B3LYP	reference
HCN	1 ¹ A''	6.48	5.97	80
HCOOH	2 ¹ A	4.64	4.78	95
HCP	2 ¹ A'	4.31	4.31	97
hexatriene	1 ¹ B _u	4.93	4.32	71
hydroquinone	1 ¹ B _u	4.15	4.28	100
indole	2 ¹ A'	4.37	4.31	101
Li ₂	1 ¹ Σ_u^+	1.74	1.99	71
merocyanine dye ⁹⁹	2 ¹ A	2.58	2.53	100
methyl-4-hydroxycinnamate	2 ¹ A	4.08	3.96	101
Mg ₂	1 ¹ Σ_u^+	3.23	3.44	71
N ₂	1 ¹ Δ_u	8.94	8.32	71
N ₂	1 ¹ Π_g	8.59	8.57	71
N ₂	1 ³ Π_g	7.39	6.94	71
naphthalene	1 ¹ B _{2u}	3.97	3.96	102
NH	1 ³ Π	3.70	3.92	71
NH ₃	1 ¹ A'' ₂	5.73	5.73	103
NH ₃	3 ¹ A	7.34	7.59	103
NO ₃	1 ² E'	1.87	2.13	104
octatetraene	1 ¹ B _u	4.41	3.72	105
o-cyanobenzyl radical	2 ² A	2.50	2.65	106
oxalylfluoride	1 ¹ A _u	4.02	3.72	107
P ₂	1 ¹ Π_g	4.27	4.12	71
p-benzoquinone	2 ¹ A	2.48	2.28	108
p-benzoquinone	1 ¹ B _{1g}	4.07	3.34	109
p-benzoquinone	1 ¹ B _{2g}	2.49	2.26	108
p-diethynylbenzene	1 ¹ B _{2u}	4.25	4.17	110
p-phenylenediamine	2 ¹ A	3.70	3.69	93
PH ₂	2 ² B ₂	2.27	2.37	80
phenol	2 ¹ A	4.51	4.78	111
porphyrin	1 ¹ B _{1u}	2.02	2.20	80
propynal	2 ¹ A	3.24	3.25	112
pyrene	2 ¹ A	3.34	3.40	113
pyridine	2 ¹ A	4.31	4.14	114
pyridone lactam	2 ¹ A	3.70	3.70	115
pyridone lactim	2 ¹ A	4.48	4.60	115
pyrimidine	2 ¹ A	3.85	3.67	116
pyrimidine	4 ¹ A	5.00	5.16	114
quinoline	2 ¹ A	3.99	3.51	116
quinoline	1 ³ A'	2.79	2.26	116
quinoxaline	2 ¹ A ₁	3.97	4.25	116
quinoxaline	2 ¹ A	3.36	3.02	83
quinoxaline	1 ³ A	2.68	2.19	117
ScO	1 ² Π	2.04	2.14	118
SiF ₂	1 ¹ B ₂	5.34	5.35	80
SiO	1 ¹ Π	5.31	5.20	80
SnF ₂	1 ¹ B ₂	5.05	4.65	119
styrene	2 ¹ A	4.31	4.40	120
syn-coumarin 153	2 ¹ A	3.21	2.96	121
terylene	2 ¹ A'	2.39	1.90	122
tetrazine	2 ¹ A	2.25	1.99	123
thioacetone	2 ¹ A	2.33	2.35	124
thioacetone	1 ³ A	2.14	1.85	124
toluene	1 ¹ A''	4.65	5.01	125
t-stilbene	2 ¹ A	4.00	3.51	126

Table 2. Continued

molecule	state	experiment	B3LYP	reference
vinyl radical	2^2A	2.48	2.56	127
VO	$1^4\Pi$	1.56	1.41	118

^aThe calculated zero-point vibrational energy corrected values are compared to experimental values. All theoretical values were obtained using the B3LYP functional and def2-TZVP basis sets.

calculations at the B3LYP/TZVP level. Excited state relaxation energies were computed from the difference of calculated VEEs and AEEs. The fluorescence energies are vertical de-excitation energies computed at the optimized B3LYP/TZVP excited state structure. A complete list of fluorescence and relaxation energies is given as Supporting Information.

The following density functionals were investigated: The Perdew–Wang parametrization of the local spin-density approximation (LSDA);⁴⁷ the generalized gradient approximation (GGA) functionals of Becke and Perdew (BP86)^{48,49} and of Perdew, Burke, and Ernzerhof (PBE);⁵⁰ the meta-GGA functional of Tao, Perdew, Staroverov, and Scuseria (TPSS);⁵¹ and the B3LYP⁴² and PBE0⁵² hybrid GGAs. Wave function methods included CIS,⁵³ the approximate coupled cluster singles and doubles method CC2,⁴⁰ and the second-order algebraic diagrammatic construction approximation (ADC(2)).⁴¹ In the CC2 and ADC(2) calculations, the resolution-of-the-identity approximation is employed along with def2-TZVP basis and auxiliary basis sets.^{54–56} To obtain excited state energies, the ADC(2) excitation energies are added to ground state MP2 energies. All calculations were carried out using the TURBOMOLE program suite.⁵⁷

A correct assignment is vital for comparison of experimental excited state data with theoretical results. We adopted the following procedure to ensure that the computed AEEs correspond to the experimentally observed states:

1. Vertical excitation energies were computed at the optimized ground state minimum, including all excitations with energies close to the experimental AEE.
2. A set of excited states was preselected on the basis of oscillator strength if absorption properties are available from the experiment.
3. The selected excited states were optimized, and the experimental states were assigned using oscillator strengths and further experimental evidence, such as rotational intensities and rotational constants.
4. In diatomic molecules, symmetry information from rovibronic spectra was required to be consistent with the excited state term symbol.

Cases where a clear-cut assignment was not possible were discarded from the benchmark set.

Covariances Σ were computed according to

$$\Sigma(X, Y) = \frac{1}{N-1} \sum_{i=1}^N (E_i^{\text{calc}}(X) - E_i^{\text{exp}}(X))(E_i^{\text{calc}}(Y) - E_i^{\text{exp}}(Y)) \quad (1)$$

where E_i^{calc} and E_i^{exp} are the computed and experimental AEEs and N is the number of excited states in our benchmark set. X and Y denote data sets. Sample standard deviations σ were obtained from Σ according to

$$\sigma(X) = \sqrt{\Sigma(X, X)} \quad (2)$$

Histograms and normalized Gaussians with a mean and SD identical to those of the sample were used to visualize the results.

Table 3. Performance of B3LYP AEEs on the 109 Set Using Different Basis Sets^a

basis	MAE	ME	SD	MaxAE
def2-SV(P)	0.25	−0.07	0.30	0.69
def2-SVPD	0.22	−0.13	0.29	0.78
def2-TZVP	0.21	−0.08	0.28	0.73
def2-TZVPD	0.22	−0.11	0.29	0.74

^aMAE denotes the mean absolute error, ME the mean error, SD the standard deviation, and MaxAE the maximum absolute error. All values are in eV.

Finally, correlation coefficients ρ were computed according to

$$\rho(X, Y) = \frac{\Sigma(X, Y)}{\sigma(X) \sigma(Y)} \quad (3)$$

4. RESULTS

4.1. Basis Set Convergence. The B3LYP AEEs using def2-TZVP basis sets are compared to experimental reference values in Table 2. A statistical analysis of the basis set convergence is presented in Table 3 and illustrated in Figure 1; a complete list of the results is provided as Supporting Information. The basis set convergence of other density functionals and CIS is similar. Higher l -quantum numbers and more diffuse functions are necessary for CC2 and ADC(2), but a systematic assessment of the basis set convergence of these methods is beyond our present scope. Overall, the B3LYP results change very little when going from the smaller def2-SV(P) to the larger def2-TZVP basis set or adding diffuse augmentation. Table 3 suggests that the residual basis set error of the B3LYP/TZVP results is 0.03 eV or less, roughly an order of magnitude less than the method error. Diffuse or triple- ζ basis sets are important for π – π^* excitations as in styrene and for π – σ^* excitations as in aminoethane and diatomic molecules where electrons are excited into diffuse orbitals. Further examples are discussed in section 5.

4.2. Exchange–Correlation Functionals. The performance of different functionals was assessed using def2-TZVP basis sets. A statistical analysis is given in Table 4, and a complete list of results is available as Supporting Information. The hybrid functionals B3LYP and PBE0 have the smallest SD (0.28 eV and 0.30 eV) and a mean error (ME) close to zero (−0.08 eV and 0.01 eV), followed by the TPSS meta-GGA with a SD of 0.41 eV and a ME of −0.20 eV. The GGA functionals PBE and BP86 feature a larger SD of 0.49 eV and a ME of −0.33 eV. LSDA performs just as well as the GGA functionals with a SD of 0.49 eV and a ME of −0.31 eV. CIS strongly overestimates the experimental results as reflected by its large positive ME, and the SD of 1.16 eV is almost 4 times that of B3LYP and PBE0.

The histograms in Figure 2 illustrate that all density functionals except PBE0 underestimate experimental AEEs. The maximum of the distribution lies between zero deviation and the ME. An underestimation by 0.5 eV or more is fairly common for nonhybrid functionals. CIS shows a broad error distribution and seems to have little predictive power for AEEs. The maximum positive and negative deviations for each level are listed in Table 5. The table shows that maximum deviations increase from hybrid GGAs to (meta-)GGAs and to LSDA. The total range of errors increases with the maximum deviations. Again, CIS

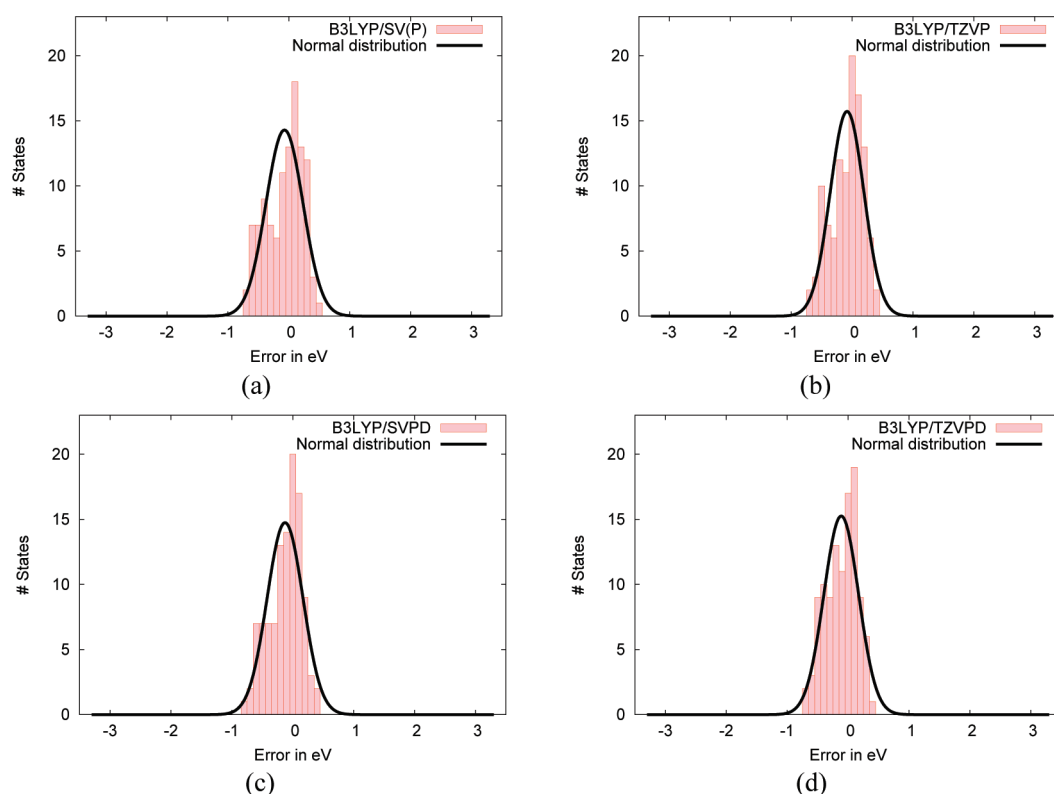


Figure 1. Error histograms of B3LYP AEEs obtained using different basis sets (see insets). Also shown are normal distributions with the computed ME and SD of the sample.

Table 4. Performance of AEEs Obtained from Various Exchange-Correlation Functionals Using def2-TZVP Basis Sets^a

method	MAE	ME	SD	MaxAE
B3LYP	0.21	−0.08	0.28	0.73
PBE0	0.25	0.01	0.30	0.66
TPSS	0.32	−0.20	0.41	1.05
BP86	0.39	−0.32	0.49	1.14
PBE	0.40	−0.33	0.49	1.14
LSDA	0.39	−0.31	0.49	1.19
CIS	0.98	0.90	1.16	3.04

^a See Table 3 for further explanation. All values are in eV.

performs more weakly than the density functional methods, with a total range of errors of almost 4 eV.

4.3. A Posteriori Corrections. Jacquemin and co-workers proposed to use linear regression to correct TDDFT excitation energies in solution and reduce the ME and SD.³⁴ This procedure is useful for samples of similar compounds. In Table 6, we show how the statistical parameters are affected when AEEs are shifted by a constant that makes the ME vanish. CIS benefits most from such a shift, which partially corrects the systematic overestimation of AEEs. LSDA and (meta-)GGAs, which underestimate excitation energies, are considerably improved, with reductions of ~ 0.1 eV in the MAE and SD. As expected from their small MEs, the hybrid results change little: B3LYP and PBE0 still outperform all other functionals, even after application of the shift. Thus, our

gas-phase data support a posteriori corrections for nonhybrid functionals only.

4.4. Correlations. We compare the similarity of the AEEs obtained with two functionals by calculating correlation coefficients and the maximum absolute deviation between two calculated AEEs (Table 7). The thus obtained correlation coefficients deviate from unity in the second to fourth digit. The maximum absolute deviations range from 0.2 to 1.2 eV.

The correlation analysis shows marked differences between LSDA, GGA, meta-GGA, and hybrid functionals. Within each rung of functionals, correlations are higher; e.g., the BP86 and PBE functionals perform very similarly, as indicated by a correlation coefficient of 0.9997 and a maximum deviation of 0.19 eV. Table 7 also shows that LSDA and GGA AEEs are highly correlated, in line with the empirical observation that GGAs tend to improve little upon LSDA for excitation energies. The TPSS results are quite similar to the GGA results, confirming that the improvement from GGAs to meta-GGAs is quite small for excitation energies.¹²⁸ On the other hand, the hybrid functionals PBE0 and B3LYP show lower correlations to other methods. This underlines the fact that hybrid exchange systematically improves over LSDA and GGAs for AEEs, consistent with the results of section 4.2.

4.5. Zero Point Vibrational Energies. The ZPVE corrections to the AEEs in our benchmark set range from -0.30 eV to $+0.26$ eV; they are positive in only eight cases. A complete list of the ZPVE corrections is available as Supporting Information. The largest ZPVE corrections occur when amino groups become planar in the excited state. Examples are aminomethane, aminoethane, and ammonia.

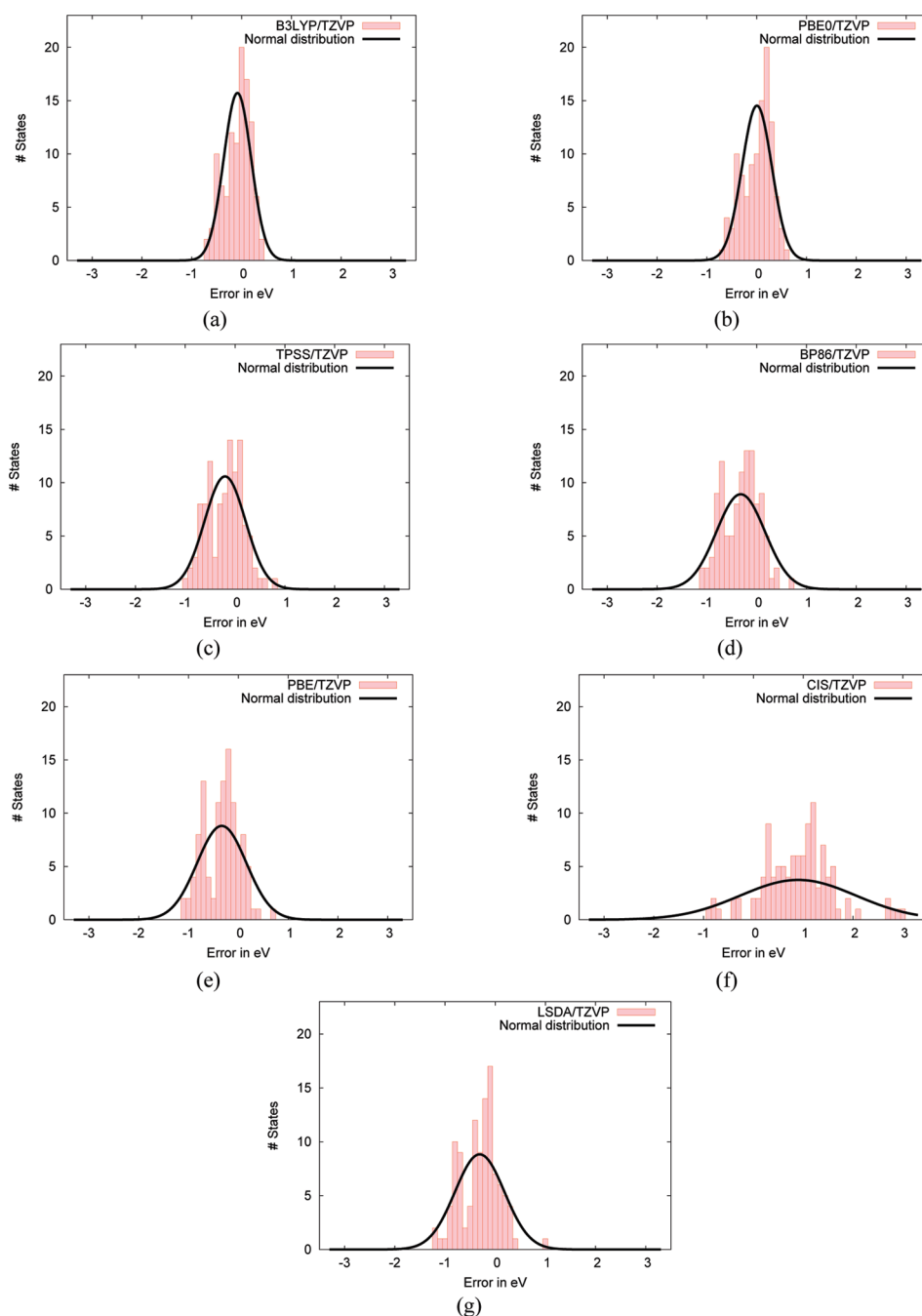


Figure 2. Error histograms of AEEs obtained with different functionals (see insets). Also shown are normal distributions with the computed ME and SD of the sample.

On our data set, the inclusion of ZPVE corrections does not significantly improve the overall accuracy of the B3LYP/TZVP AEEs, see Table 4, but it does not worsen them either. ZPVE corrections are a byproduct of molecular Hessian calculations, which are needed to identify minima. This is particularly important for excited states, where symmetry breaking and saddle point structures are common.

4.6. Excited State Relaxation. Do B3LYP AEEs deteriorate if the molecular structure changes strongly upon excitation? To address this important question, we computed the correlation coefficient between excited state relaxation energies and errors in the corresponding AEEs. If such a correlation existed, it could be

used as a diagnostic for AEEs. However, on our present data set, the correlation coefficient between excited state relaxation energies and AEE errors is -0.29 ; i.e., there is essentially no correlation. This result suggests that the incorrect dissociation behavior of spin-restricted TDDFT potential energy surfaces¹²⁹ has little effect on the AEEs in our benchmark set.

5. DIFFICULT AND NOTEWORTHY CASES

5.1. Aminomethane: 3^1A . Diffuse functions are necessary for an adequate description of the 3^1A state of aminomethane: The B3LYP AEE changes from 6.37 eV to 6.22 eV when the basis set

Table 5. Excited States with Maximum Negative Deviation (MND) and Maximum Positive Deviation (MPD) from the Experimental AEE for Each Level of Theory^a

level	MND	MPD
B3LYP/SV(P)	p-benzoquinone: 1^1B_{1g} −0.69	benzene: 1^1B_{1u} 0.46
B3LYP/SVPD	p-benzoquinone: 1^1B_{1g} −0.78	benzene: 1^1B_{1u} 0.37
B3LYP/TZVP	p-benzoquinone: 1^1B_{1g} −0.73	benzene: 1^1B_{1u} 0.42
B3LYP/TZVPD	p-benzoquinone: 1^1B_{1g} −0.74	benzene: 1^1B_{1u} 0.40
PBE0/TZVP	quinoline: $1^3A'$ −0.66	CuH: $2^1\Sigma^+$ 0.63
TPSS/TZVP	p-benzoquinone: 1^1B_{1g} −1.05	NH: $1^3\Pi$ 0.79
BP86/TZVP	p-benzoquinone: 1^1B_{1g} −1.14	NO ₃ : $1^2E'$ 0.71
PBE/TZVP	p-benzoquinone: 1^1B_{1g} −1.14	NO ₃ : $1^2E'$ 0.74
LSDA/TZVP	quinoline: 2^1A −1.19	NO ₃ : $1^2E'$ 1.00
CIS/TZVP	N ₂ : $1^1\Delta_u$ −0.85	Cu ₂ : $1^1\Pi_u$ 3.04

^a All values are in eV.**Table 6.** Performance of AEEs Obtained from Various Exchange-Correlation Functionals and CIS Using def2-TZVP Basis Sets^a

method	MAE	SD	MaxAE
B3LYP	0.22	0.26	0.64
PBE0	0.25	0.30	0.66
TPSS	0.30	0.36	0.99
BP86	0.30	0.37	1.03
PBE	0.29	0.36	1.07
LSDA	0.30	0.38	1.31
CIS	0.55	0.73	2.14

^a For each method, a constant shift has been applied to make the ME vanish. See Table 3 for further explanation. All values are in eV.

size is increased from the def2-SV(P) basis set to def2-SVPD and from 6.36 eV to 5.97 eV when enlarging the def2-TZVP basis set to def2-TZVPD. This is consistent with a Rydberg $\pi \rightarrow s$ excitation.¹³⁰ The agreement of the nonaugmented basis set result with the experimental value of 6.22 eV⁸⁷ is fortuitous.

5.2. Benzene: 1^1B_{1u} . The excited state potential energy surfaces of benzene are a challenge for excited state methods.^{75,131,132} The PBE0 AEE of 5.26 eV and the CC2 AEE of 4.92 eV⁷⁵ are larger than the experimental AEE of 4.72 eV. The corresponding CASPT2 result of 4.37 eV is too small and might approach the CC2 result when the modified zeroth-order Hamiltonian is used.^{132–134} B3LYP, CC2, and CASPT2 excited state bond lengths agree up to 1 pm.

5.3. CuH: $2^1\Sigma^+$. The ground state of CuH has $1^1\Sigma^+$ symmetry and is dominated by a $2s(sd^{10})$ configuration of the copper atom.^{135,136} For the $2^1\Sigma^+$ state, multireference configuration interaction calculations show a mixed d^9-d^{10} character at the equilibrium bond lengths and strong spin–orbit coupling to the $1^3\Pi$ state.¹³⁵ Within TDDFT, all functionals yield AEEs within 0.1 eV of the experiment. An exception is PBE0 with an AEE too large by 0.63 eV. Diffuse augmentation is necessary but deteriorates the agreement with experimental results. Upon excitation, the dipole moment increases by ~ 2.4 D in the B3LYP calculation. The charge-transfer character of the excitation, the multiconfiguration character of the ground state, and the large spin–orbit coupling make this system difficult for response methods.^{135,137}

Table 7. Correlation Coefficients ρ and Maximum Absolute Deviations $|\Delta_{\max}|$ (in eV) between AEEs Computed with Different Density Functionals

(a) correlation matrix						
	B3LYP	PBE0	TPSS	BP86	PBE	LSDA
B3LYP	1	0.9983	0.9909	0.9888	0.9881	0.9832
PBE0	0.9983	1	0.9880	0.9849	0.9836	0.9781
TPSS	0.9909	0.9880	1	0.9979	0.9971	0.9912
BP86	0.9888	0.9849	0.9979	1	0.9997	0.9964
PBE	0.9881	0.9836	0.9971	0.9997	1	0.9975
LSDA	0.9832	0.9781	0.9912	0.9964	0.9975	1

(b) maximum absolute deviations matrix						
	B3LYP	PBE0	TPSS	BP86	PBE	LSDA
B3LYP	0	0.48	0.69	0.93	0.94	0.91
PBE0	0.48	0	0.95	1.16	1.17	1.14
TPSS	0.69	0.95	0	0.77	0.79	0.81
BP86	0.93	1.16	0.77	0	0.19	0.40
PBE	0.94	1.17	0.79	0.19	0	0.36
LSDA	0.91	1.14	0.81	0.40	0.36	0

5.4. Cu₂: $1^1\Pi_u$. For the $1^1\Pi_u$ state of Cu₂, large basis sets are essential to reproduce the experimental result of 2.71 eV.⁸⁶ The AEEs change from 2.02 eV to 2.15 eV and to 2.63 eV when going from def2-SV(P) to def2-SVPD¹³⁸ and to def2-TZVP. There is little further change when the basis set is increased to def2-TZVPD (2.62 eV) or QZVP⁴³ (2.60 eV). The TDDFT excitation vectors are dominated by one single-electron excitation, whereas the CIS excitation vector shows a multiconfigurational state 3.04 eV above the experimental AEE. The Hartree–Fock and hybrid functional ground state place the bonding $4s \sigma_g$ orbital above all antibonding $3d$ orbitals.¹³⁹ The results are stable with respect to tightened ground state convergence criteria.

5.5. p-Benzoquinone: 1^1B_{1g} . The AEE of p-benzoquinone is underestimated by more than 0.6 eV at the TDDFT level and overestimated by 0.8 eV at the CIS level. While the optimized ground state has C–C bond lengths between 134 and 148 pm, the optimized excited state has C–C bond lengths between 141 and 144 pm. This indicates a reduction of the quinoidal character upon excitation, and an excitation into a hydroquinone like state, in agreement with CASPT2 results of Weber and co-workers.¹⁴⁰

5.6. Quinoline: $1^3A'$. The ground state of quinoline shows a near triplet instability¹⁴¹ at the B3LYP level. This is reflected in the weak performance of the density functional methods for the lowest triplet state $1^3A'$. The quality of the singlet excitations appears to be unaffected by nearby triplet instabilities.

5.7. NO₃: $1^2E'$. The AEE predicted by CIS is lower than the experimental value of 1.87 eV¹⁰⁴ by 0.76 eV. Since CIS usually overestimates excitation energies, this underestimation indicates a multiconfigurational ground state. The underestimation of the CIS AEE is in line with the strong vibronic coupling between the ground and $1^2E'$ excited state.¹⁴² Inclusion of double and higher excitations will mostly lower the ground state energy and increase the AEE. Multireference contributions are noticeable but not dominant in the excited state.¹⁴³ Nonhybrid functionals overestimate the AEE by 0.71–1.00 eV, indicating that NO₃ is too electron-rich for a reliable description by semilocal functionals.

Table 8. Composition of the 15-Membered Subset and Computed AEEs in eV

molecule	state	experiment	CC2/TZVPD	B3LYP/TZVP	reference
acetaldehyde	2 ¹ A	3.69	3.70	3.81	63
anisole	2 ¹ A	4.51	4.60	4.73	69
benzene	1 ¹ B _{1u}	4.72	4.94	5.14	75
benzophenone ketyl radical	2 ² A	2.29	2.84	2.31	77
BF	1 ¹ Π	6.34	6.39	6.14	71
C ₂ H ₂	2 ¹ A	5.23	5.36	4.72	80
cinnoline	1 ¹ A''	2.82	2.77	2.43	83
CO	1 ¹ Π	8.07	7.99	7.99	71
glyoxal	1 ¹ A _u	2.72	2.72	2.43	80
p-diethynylbenzene	1 ¹ B _{2u}	4.25	4.59	4.17	110
propynal	2 ¹ A	3.24	3.27	3.25	112
pyridone lactim	2 ¹ A	4.48	4.70	4.60	115
quinoline	2 ¹ A	3.99	3.66	3.51	116
ScO	1 ² Π	2.04	2.02	2.14	118
VO	1 ⁴ Π	1.56	1.96	1.41	118

5.8. Tetrazine: 2¹A. Hybrid functionals underestimate the AEE by ~0.26 eV and slightly outperform the CASPT2 result of 1.94 eV of Schütz et al.¹⁴⁴ The TDDFT excitation vectors tend to converge to solutions dominated by many different single excitations with default convergence settings. Excitation vectors dominated by one single excitation in agreement with experimental results are obtained with tighter energy and density convergence criteria in the ground state calculation (10⁻⁸ au).

6. STRUCTURAL CHANGES

The main symmetry breaking structural changes encountered upon excited state relaxation fall into three groups:

- (1) out-of-plane bending of a C=O or C=S group
- (2) planarization of an amino group
- (3) others

In group 1 systems, a $\pi \rightarrow \pi^*$ excitation of a C=O or C=S chromophore leads to a $sp^2 \rightarrow sp^3$ rehybridization of the carbon atom. In group 2 molecules, planarization is caused by $s \rightarrow p$ promotion of an electron occupying a nitrogen lone pair orbital. The nonplanarity of excited ketyl groups and the planarity of excited ammonia is discussed by Herzberg.²³ The four other cases are the twisted intermolecular charge-transfer state of dimethylaminobenzonitrile,³² the bend excited states of HCN and C₂H₂,²³ and biphenyl. In biphenyl, the ground state is nonplanar due to the steric repulsion of hydrogen atoms in the adjacent rings. The excitation to the 1¹B₁ state takes place from an orbital that is antibonding between the rings to an orbital that is bonding between the rings. This causes the phenyl–phenyl bond to shorten by 7 pm to 141 pm upon excitation and a twist of the rings to a nearly planar structure.¹⁴⁵

7. REDUCED DATA SET

7.1. Composition. Out of the original 109-membered set, we generated a reduced set containing only 15 states. The reduced set was required to approximately reproduce the B3LYP/TZVP ME, MAE, and SD of the original set and cover a variety of different chromophores and states but was randomly chosen otherwise. The resulting reduced data set is shown in Table 8,

Table 9. Performance of Computed AEEs on the Reduced 15-Membered Subset^a

(a) full subset			
method	MAE	ME	SD
B3LYP/TZVP	0.21	−0.08	0.28
CC2/TZVP	0.21	0.16	0.29
CC2/TZVPD	0.17	0.10	0.24
ADC(2)/TZVP	0.23	0.14	0.34

(b) subset after exclusion of VO and benzophenone ketyl radical			
method	MAE	ME	SD
B3LYP/TZVP	0.23	−0.08	0.30
CC2/TZVP	0.16	0.10	0.20
CC2/TZVPD	0.12	0.05	0.17
ADC(2)/TZVP	0.15	0.04	0.20

^a See Table 3 for further explanation. All values are in eV.

and results for density functionals other than B3LYP and CIS are available as Supporting Information.

Due to its small sample size, the reduced set cannot replace the original 109 set. The aim of the reduced set is to provide a convenient and fast initial screening test for new methods, which is desirable for computationally demanding theories.

7.2. Performance of CC2 and ADC(2). To illustrate the use of the reduced data set, we investigate the performance of the correlated wave function methods CC2 and ADC(2) on the reduced set (Table 9). CC2 and ADC(2) behave similarly. On average, CC2 overestimates excitation energies, as reflected in a positive ME. However, the addition of diffuse functions considerably lowers the CC2 ME, MAE, and SD,^{22,146} and CC2/TZVPD outperforms all other methods on the reduced data set.

Scrutiny of the results in Table 8 shows that the largest CC2 errors occur for the benzophenone ketyl radical and for the 1⁴Π state of VO. It can be argued that CC2 and ADC(2) are not expected to work for these open-shell systems whose ground states show some amount of multireference character. Diagnostic criteria to identify such cases are available,^{118,147} and thus it can

Table 10. Comparison of Errors in AEEs Obtained from Various Exchange-Correlation Functionals and CIS Using def2-TZVP Basis Sets on the 15-Membered Subset for B3LYP and PBE0 Equilibrium Structures^a

	Structure	B3LYP	PBE0	TPSS	BP86	PBE	LSDA	CIS
ME	B3LYP	−0.08	−0.01	−0.21	−0.34	−0.35	−0.36	0.97
ME	PBE0	−0.08	−0.01	−0.20	−0.33	−0.34	−0.35	1.00
MAE	B3LYP	0.21	0.22	0.26	0.38	0.38	0.42	1.07
MAE	PBE0	0.21	0.22	0.26	0.37	0.38	0.41	1.09
SD	B3LYP	0.28	0.28	0.38	0.50	0.51	0.57	1.24
SD	PBE0	0.28	0.28	0.38	0.49	0.51	0.56	1.24

^a See Table 3 for further explanation. All values are in eV.

be justified to consider a “single-reference” subset which does not contain VO and benzophenone ketyl. Whereas the B3LYP errors are essentially unchanged, CC2/TZVPD performs very well on the single-reference subset, yielding a MAE of 0.12 eV.

7.3. Sensitivity to Equilibrium Structures. To evaluate the sensitivity of our results to errors in the B3LYP ground and excited state structures, the reduced data set was evaluated using fully optimized PBE0 structures. Table 10 compares the mean errors, mean absolute errors, and standard deviations for B3LYP and PBE0 structures on the reduced data set. The results are virtually identical, with maximum deviations of 0.03 eV for CIS and 0.01 eV for density functional methods. This relative insensitivity to the molecular structure reflects the quadratic dependence of adiabatic excitation energies on nuclear displacements, because both the ground and the excited state are in a minimum for adiabatic excitations. Thus, errors in the underlying equilibrium structures are less of a concern here than for vertical excitation energies, which depend linearly on nuclear displacements.

8. CONCLUSION

“There are lies, damned lies, and statistics.” — It is possible to construct excited state “benchmarks” that (dis)favor a particular method or conclusion. For example, a data set containing mostly Rydberg and charge-transfer excitations will make common density functionals look bad, while single-reference wave function methods will perform poorly for transition metal compounds and radicals with multireference ground states. This is consistent with the work of Jacquemin and co-workers,¹⁷ who observe a significant dependence of their statistical error measures on the subset of molecules or states considered. We have biased the present benchmark set toward systems and states where accurate spectroscopic data are available. A central new aspect is the focus on adiabatic rather than vertical excitation energies which are rigorously defined by differences of observable vibronic energy levels. The main remaining sources of inaccuracies on the theoretical side are the quality of the B3LYP/TZVP structures used and the neglect of relativistic and beyond-Born–Oppenheimer corrections. We estimate^{148,149} that these effects are 0.05 eV or less on average.

None of the methods tested here comes close to the desirable “chemical accuracy” of ~0.05 eV in excitation energies. Clearly, there is ample room for improvement. We hope that the present work will catalyze the development of excited state methods by providing a critical, accurate, and easy to use benchmark.

■ ASSOCIATED CONTENT

S Supporting Information. Tables of AEEs calculated with different functionals and basis sets. Table of the ZPVE for the ground and excited states including the ZPVE correction. Table with VEEs calculated at the ground state minimum, fluorescence energies, and excited state relaxation energies. Statistical parameters of the reduced data set. Figure with the structures of all molecules (Lewis notation). Coordinates of all ground and excited state structures. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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