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

Pierre-François Loos,[*,†] Anthony Scemama,[†] Aymeric Blondel,[‡] Yann Garniron,[†] Michel Caffarel,[†] and Denis Jacquemin[*,‡]

†Laboratoire de Chimie et Physique Quantiques, Université de Toulouse, CNRS, UPS, 31013 Toulouse Cedex 6, France
‡Laboratoire CEISAM - UMR CNRS 6230, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cedex 3, France

Ⓢ Supporting Information

**ABSTRACT:** Striving to define very accurate vertical transition energies, we perform both high-level coupled cluster (CC) calculations (up to CCSDTQP) and selected configuration interaction (sCI) calculations (up to several millions of determinants) for 18 small compounds (water, hydrogen sulfide, ammonia, hydrogen chloride, dinitrogen, carbon monoxide, acetylene, ethylene, formaldehyde, methanimine, thioformaldehyde, acetaldehyde, cyclopropene, diazomethane, formamide, ketene, nitrosomethane, and the smallest streptocyanine). By systematically increasing the order of the CC expansion, the number of determinants in the CI expansion as well as the size of the one-electron basis set, we have been able to reach near full CI (FCI) quality transition energies. These calculations are carried out on CC3/*aug*-cc-pVTZ geometries, using a series of increasingly large atomic basis sets systematically including diffuse functions. In this way, we define a list of 110 transition energies for states of various characters (valence, Rydberg, $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, singlet, triplet, etc.) to be used as references for further calculations. Benchmark transition energies are provided at the *aug*-cc-pVTZ level as well as with additional basis set corrections, in order to obtain results close to the complete basis set limit. These reference data are used to benchmark a series of 12 excited-state wave function methods accounting for double and triple contributions, namely ADC(2), ADC(3), CIS(D), CIS(D$_\infty$), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSDT-3, CC3, CCSDT., and CCSDTQ. It turns out that CCSDTQ yields a negligible difference with the extrapolated CI values with a mean absolute error as small as 0.01 eV, whereas the coupled cluster approaches including iterative triples are also very accurate (mean absolute error of 0.03 eV). Consequently, CCSDT-3 and CC3 can be used to define reliable benchmarks. This observation does not hold for ADC(3) that delivers quite large errors for this set of small compounds, with a clear tendency to overcorrect its second-order version, ADC(2). Finally, we discuss the possibility to use basis set extrapolation approaches so as to tackle more easily larger compounds.
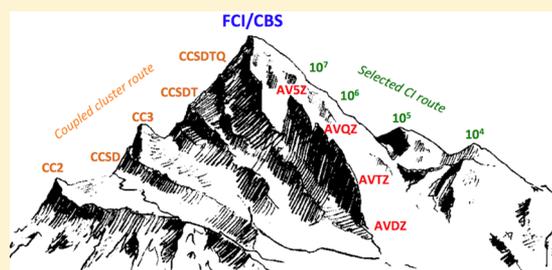
## 1. INTRODUCTION

Defining an effective method reliably providing accurate excited-state energies and properties remains a major challenge in theoretical chemistry. For practical applications, the most popular approaches are the complete active space self-consistent field (CASSCF)[1,2] and the time-dependent density functional theory (TD-DFT)[3,4] methods for systems dominated by static and dynamic electron correlation effects, respectively. When these schemes are not sufficiently accurate, one often uses methods including second-order perturbative corrections. For CASSCF, a natural choice is CASPT2,[5] but this method rapidly becomes impractical for large compounds. If a single-reference method is sufficient, the most popular second-order approaches are probably the second-order algebraic diagrammatic construction, ADC(2),[6] and the second-order coupled cluster, CC2, methods,[7,8] that both offer an attractive $O(N^5)$ scaling (where $N$ is the number of basis functions) allowing applications up to systems compris-

ing ca. 100 atoms. Compared to TD-DFT,[9] these approaches have the indisputable advantage of being free of the choice of a specific exchange-correlation functional. Using ADC(2) or CC2 generally provides more systematic errors with respect to reference values than TD-DFT, although the improvements in terms of error magnitude are often rather moderate (at least for valence singlet states).[10−12] Importantly, both ADC($n$) and CC$n$ offer a systematic pathway for improvement via an increase of the expansion order $n$. For example, using CCSD, CCSDT, CCSDTQ, etc., allows to check the quality of the obtained estimates. However, in practice, one can only contemplate such systematic approach and the ultimate choice of a method for excited-state calculations is often guided by previous benchmarks. These benchmark studies are either performed using experimental or theoretical reference values. While the former approach allows in principle to rely on an

almost infinite pool of reference data, most measurements are performed in solution and provide absorption bands that can be compared to theory only with the use of extra approximations for modeling environmental and vibronic effects. In addition, the most accurate experimental data are obtained for 0−0 energies, whereas obtaining trustworthy experimental estimates of vertical transition energies is an extremely difficult task, generally requiring to back-transform spectroscopic vibronic data through a numerical process,[13] an approach that is typically only applicable to diatomics. Consequently, it is easier to use first-principle reference values as benchmarks, as they allow to assess theoretical methods more consistently (vertical values, same geometries, no environmental effects, etc.). This is well illustrated by the recent contribution of Schwabe and Goerigk,[14] who decided to compute third-order response CC (CC3)[15,16] reference values instead of using the previously collected experimental values for the test set originally proposed by Gordon's group.[17]

While many benchmark sets have been proposed for excited states,[10,11,17−29] the most praised database of theoretical excited state energies is undoubtedly the one set up by Thiel and his co-workers. In 2008, they proposed a large set of theoretical best estimates (TBE) for 28 small and medium CNOH organic compounds.[30] More precisely, using some literature values but mainly their own CC3/TZVP and CASPT2/TZVP results computed on MP2/6-31G(d) geometries, these authors determined 104 singlet and 63 triplet reference excitation energies. The same group soon proposed *aug*-cc-pVTZ TBE for the same set of compounds,[31,32] though some CC3/*aug*-cc-pVTZ reference values were estimated by a basis set extrapolation technique. In their conclusion, they stated that they "*expect this benchmark set to be useful for validation and development purposes, and anticipate future improvements and extensions of this set through further high-level calculations*".[30] The first prediction was soon realized. Indeed, both the TZVP and *aug*-cc-pVTZ TBE were applied to benchmark various computationally effective methods, including semiempirical approaches,[33−35] TD-DFT,[24,25,36−46] the second-order polarization propagator approximation (SOPPA),[47] ADC(2),[48] the second order *N*-electron valence perturbation theory (NEVPT2),[49] the random phase approximation (RPA),[50] as well as several CC variants.[51−56] In contrast, even a decade after the original work appeared, the progresses aiming at improving and/or extending Thiel's set have been much less numerous. To the best of our knowledge, these extensions are limited to the more compact TZVP basis set,[48,52,57,58] but in one case.[59] This diffuse-less basis set offers clear computational advantages and avoids some state mixing. However, it has a clear tendency to overestimate transition energies, especially for Rydberg states, and it makes comparisons between methods more difficult as basis set dependencies are significantly different in wave function-based and density-based methods.[60]

Let us now briefly review these efforts. In 2013, Watson et al. obtained with the TZVP basis set and CCSDT-3—a method employing an iterative approximation of the triples — transition energies very similar to the CC3 values.[57] Nevertheless, as noted the same year by Nooijen and co-workers who also reported CCSDT-3/TZVP values,[52] "*the relative accuracy of EOM-CCSDT-3 versus CC3 compared to full CI (or EOM-CCSDT) is not well established*". In 2014, Dreuw and co-workers performed ADC(3) calculations on Thiel's set and concluded that "*based on the quality of the existing benchmark set*

*it is practically not possible to judge whether ADC(3) or CC3 is more accurate*". The same year, Kannar and Szalay, revisited Thiel's set and proposed CCSDT/TZVP reference energies for 17 singlet states of six molecules.[58] Recently the same group reported CCSDT/*aug*-cc-pVTZ transition energies for valence and Rydberg states of five compact molecules,[59] and used these values to benchmark several simpler CC approaches. To the best of our knowledge, these stand as the highest-level values reported to date. However, it remains difficult to know if these CCSDT transition energies are significantly more accurate than their CC3, CCSDT-3 or ADC(3) counterparts. Indeed, for the $\pi \rightarrow \pi^*$ valence singlet excited state of ethylene, the CC3/TZVP, CCSDT/TZVP and CCSDTQ/TZVP estimates of 8.37, 8.38, and 8.36 eV (respectively) are nearly identical.[58]

Herein, we propose to continue the quest for ultra-accurate excited-state reference energies. First, although this prevents direct comparisons with previously published data, we decided to use more accurate CC3/*aug*-cc-pVTZ geometries for all the compounds considered here. Second, we employ only diffuse-containing Dunning basis sets to be reasonably close from the complete basis set limit. Third, we climb the mountain via two faces following: (i) the CC route (up to the highest computationally possible order) and (ii) the configuration interaction (CI) route with the help of selected CI (sCI) methods. By comparing the results of these two approaches, it is possible to get some reliable information about how far our results are from the full CI (FCI) ones. Fourth, in order not to limit our investigation to vertical absorption, we also report, in a few cases, fluorescence energies. Of course, such extreme choices impose drastic restrictions on the size of the molecules one can treat. However, we claim here that they allow to accurately estimate the FCI result for most excited states.

## 2. COMPUTATIONAL DETAILS

**2.1. Geometries.** All geometries are obtained at the CC3/*aug*-cc-pVTZ level without applying the frozen core approximation. These geometries are available in the Supporting Information. While several structures are extracted from ref 61 (acetylene, diazomethane, ethylene, formaldehyde, ketene, nitrosomethane, thioformaldehyde and streptocyanine-C1), additional optimizations are performed here following the same protocol as in that earlier work. First, we optimize the structures and compute the vibrational spectra at the CCSD/def2-TZVPP level[62] with Gaussian16.[63] These calculations confirm the minima nature of the obtained geometries.[64] We then reoptimize the structures at the CC3/*aug*-cc-pVTZ level[15,16] using Dalton[65] and/or CFOUR,[66] depending on the size and symmetry of the molecule. CFOUR advantageously provides analytical CC3 gradients for ground-state structures. For the CCSD calculations, the energy and geometry convergence thresholds are systematically tightened to $10^{-10}-10^{-11}$ au for the SCF energy, $10^{-8}-10^{-9}$ au for the CCSD energy, and $10^{-7}-10^{-8}$ au for the EOM-CCSD energy in the case of excited-state geometry optimizations. To check that the structures correspond to genuine minima, the (EOM-)CCSD gradients are differentiated numerically to obtain the vibrational frequencies. The CC3 optimizations are performed with the default convergence thresholds of Dalton or CFOUR without applying the frozen core approximation.

**2.2. Coupled Cluster Calculations.** Unless otherwise stated, the CC transition energies[67] are computed in the frozen-core approximation (large cores for Cl and S). We use several codes to achieve our objectives, namely CFOUR,[66]

**Table 1. Vertical Transition Energies for the Three Lowest Singlet and Three Lowest Triplet Excited States of Water (Top), the Four Lowest Singlet and the Lowest Triplet States of Ammonia (Center), and the Lowest Singlet State of Hydrogen Chloride (Bottom)[m]**

| | water | | | | | | | | | | | | | | |
| | aug-cc-pVDZ | | | | | aug-cc-pVTZ | | | | aug-cc-pVQZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | CCSDTQP | exFCI | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[a] | th.[b] | th.[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1B_1(n \to 3s)$ | 7.51 | 7.50 | 7.53 | 7.53 | 7.53 | 7.60 | 7.59 | 7.62 | 7.62 | 7.65 | 7.64 | 7.68 | 7.41 | 7.81 | 7.57 |
| $^1A_2(n \to 3p)$ | 9.29 | 9.28 | 9.31 | 9.32 | 9.32 | 9.38 | 9.37 | 9.40 | 9.41 | 9.43 | 9.41 | 9.46 | 9.20 | 9.30 | 9.33 |
| $^1A_1(n \to 3s)$ | 9.92 | 9.90 | 9.94 | 9.94 | 9.94 | 9.97 | 9.95 | 9.98 | 9.99 | 10.00 | 9.98 | 10.02 | 9.67 | 9.91 | 9.91 |
| $^3B_1(n \to 3s)$ | 7.13 | 7.11 | 7.14 | 7.14 | 7.14 | 7.23 | 7.22 | 7.24 | 7.25 | 7.28 | 7.26 | 7.30 | 7.20 | 7.42 | 7.21 |
| $^3A_2(n \to 3p)$ | 9.12 | 9.11 | 9.14 | 9.14 | 9.14 | 9.22 | 9.20 | 9.23 | 9.24 | 9.26 | 9.25 | 9.28 | 8.90 | 9.42 | 9.19 |
| $^3A_1(n \to 3s)$ | 9.47 | 9.45 | 9.48 | 9.49 | 9.49 | 9.52 | 9.50 | 9.53 | 9.54 | 9.56 | 9.54 | 9.58 | 9.46 | 9.78 | 9.50 |

| | hydrogen sulfide | | | | | | | | | | | | | | |
| | aug-cc-pVDZ | | | | | aug-cc-pVTZ | | | | aug-cc-pVQZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | CCSDTQP | exFCI | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[d] | exp.[e] | th.[f] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1A_2(n \to 4p)$ | 6.29 | 6.29 | 6.29 | 6.29 | 6.29 | 6.19 | 6.18 | 6.18 | 6.18 | 6.16 | 6.15 | 6.15 | | | 6.12 |
| $^1B_1(n \to 4s)$ | 6.10 | 6.10 | 6.10 | 6.10 | 6.10 | 6.24 | 6.24 | 6.24 | 6.24 | 6.29 | 6.29 | 6.29 | 6.33 | | 6.27 |
| $^3A_2(n \to 4p)$ | 5.91 | 5.90 | 5.90 | 5.90 | 5.90 | 5.82 | 5.81 | 5.81 | 5.81 | 5.80 | 5.79 | 5.79 | | 5.8 | 5.78 |
| $^3B_1(n \to 4s)$ | 5.75 | 5.75 | 5.75 | 5.75 | 5.75 | 5.88 | 5.88 | 5.88 | 5.89 | 5.93 | 5.93 | 5.93 | | 5.4 | 5.92 |

| | ammonia | | | | | | | | | | | | | | |
| | aug-cc-pVDZ | | | | | aug-cc-pVTZ | | | | aug-cc-pVQZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | CCSDTQP | exFCI | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[g] | exp.[h] | th.[i] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1A_2(n \to 3s)$ | 6.46 | 6.46 | 6.48 | 6.48 | 6.48 | 6.57 | 6.57 | 6.59 | 6.59 | 6.61 | 6.61 | 6.64 | 6.38 | 6.39 | 6.48 |
| $^1E(n \to 3p)$ | 8.06 | 8.06 | 8.08 | 8.08 | 8.08 | 8.15 | 8.14 | 8.16 | 8.16 | 8.18 | 8.17 | 8.22 | 7.90 | 7.93 | 8.02 |
| $^1A_1(n \to 3p)$ | 9.66 | 9.66 | 9.68 | 9.68 | 9.68 | 9.32 | 9.31 | | 9.33 | 9.11 | 9.10 | 9.14 | 8.14 | 8.26 | 8.50 |
| $^1A_2(n \to 4s)$ | 10.40 | 10.39 | 10.41 | 10.41 | 10.41 | 9.95 | 9.94 | | 9.96 | 9.77 | 9.77 | | | | 9.03 |
| $^3A_2(n \to 3s)$ | 6.18 | 6.18 | 6.19 | 6.19 | 6.19 | 6.29 | 6.29 | 6.30 | 6.31 | 6.33 | 6.33 | 6.35 | 6.02[j] | | |

| | hydrogen chloride | | | | | | | | | | | | |
| | aug-cc-pVDZ | | | | | aug-cc-pVTZ | | | | aug-cc-pVQZ | | | lit. |
| state | CC3 | CCSDT | CCSDTQ | CCSDTQP | exFCI | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | th.[k] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $^1\Pi$ (CT) | 7.82 | 7.81 | 7.82 | 7.82 | 7.82 | 7.84 | 7.83 | 7.84 | 7.84 | 7.89 | 7.88[l] | 7.88 | 8.23 |

[a]Energy loss experiment from ref 98. [b]MRCI+Q/aug-cc-pVTZ calculations from ref 99. [c]MRCC/aug-cc-pVTZ calculations from ref 100. [d]VUV experiment from ref 101. [e]Electron impact experiment from ref 102. [f]CASPT2/d-aug-cc-pVQZ results from ref 103. [g]Electron impact experiment from ref 104. [h]Electron impact experiment from ref 105. [i]EOM-CCSD($\tilde{T}$)/aug-cc-pVTZ with extra *diffuse* calculations from ref 106. [j]Deduced from the 6.38 eV value of the $^1A_2(n \to 3s)$ state and the −0.36 eV shift reported for the 0−0 energies compared to the corresponding singlet state in ref 107, a splitting consistent with an earlier estimate of −0.39 eV given in ref 108. [k]CC2/cc-pVTZ from ref 22.; [l]The CCSDTQ/aug-cc-pVQZ value is 7.88 eV as well. [m]All states of water and ammonia have a Rydberg character, whereas the lowest state of hydrogen chloride is a charge-transfer state. All values are in eV.

Dalton,[65] Gaussian16,[63] Orca,[68] MRCC,[69,70] and Q-Chem.[71] Globally, we use CFOUR for both CCSDT-3[72,73] and CCSDT[74] calculations, Dalton to perform the CIS(D),[75,76] CC2,[7,8] CCSD,[62] CCSDR(3),[77] and CC3[15,16] calculations, Gaussian for the CIS(D)[75,76] and CCSD,[62] Orca for the similarity-transformed EOM-CCSD (STEOM-CCSD)[56,78] calculations, Q-Chem for ADC(2) and ADC(3) calculations, and MRCC for the CIS(D∞),[79] CCSDT,[74] and CCSDTQ[80] (and higher) calculations. As we mainly report transition energies, it is worth noting that the linear-response (LR) and equation-of-motion (EOM) formalisms provide identical results. Nevertheless, the oscillator strengths characterizing the excited states are obtained at the (LR) CC3 level with Dalton. Default program setting are generally applied, and when modified they are tightened. For the STEOM-CCSD calculations which relies on natural transition orbitals, it was checked that each state is characterized by an active character percentage of 98% or larger (states not matching this criterion are not reported). Nevertheless, the obtained results do slightly depend on the number of states included in the calculations, and we found typical variations of ±0.01−0.05 eV. For all

calculations, we use the well-known Dunning's aug-cc-pVXZ (X = D, T, Q and 5) atomic basis sets, as well as some doubly- and triply augmented basis sets of the same series (d-aug-cc-pVXZ and t-aug-cc-pVXZ).

**2.3. Selected Configuration Interaction Methods.** Alternatively to CC, we also compute transition energies using a selected CI (sCI) approach, an idea that goes back to 1969 in the pioneering works of Bender and Davidson,[81] and Whitten and Hackmeyer.[82] Recently, sCI methods have demonstrated their ability to reach near FCI quality energies for small organic and transition metal-containing molecules.[83−92] To avoid the exponential increase of the size of the CI expansion, we employ the sCI algorithm CIPSI[83,93,94] (Configuration Interaction using a Perturbative Selection made Iteratively) to retain only the energetically relevant determinants. To do so, the CIPSI algorithm uses a second-order energetic criterion to select perturbatively determinants in the FCI space.[83,85,87,92] In the numerical examples presented below, our CI expansions contain typically about a few millions of determinants. We refer the interested readers to refs 92 and

95 for more details about the general philosophy of sCI methods.

In order to treat the electronic states of a given spin manifold on equal footing, a common set of determinants is used for all states. Moreover, to speed up convergence to the FCI limit, a common set of natural orbitals issued from a preliminary (smaller) sCI calculation is employed. All sCI calculations have been performed in the frozen-core approximation. For a given basis set, we estimate the FCI limit using the approach introduced recently by Holmes et al.[90] in the context of the (selected) heat-bath CI method, and used with success, even for challenging chemical situations.[89,91,92] More precisely, we linearly extrapolate the sCI energy $E_{sCI}$ as a function of $E_{PT2}$, which is an estimate of the truncation error in the sCI algorithm, i.e., $E_{PT2} \approx E_{FCI} - E_{sCI}$. When $E_{PT2} = 0$, the FCI limit has effectively been reached. Here, $E_{PT2}$ is efficiently evaluated with a recently proposed hybrid stochastic-deterministic algorithm.[96] Note that we do not report error bars because the statistical errors originating from this algorithm are orders of magnitude smaller than the extrapolation errors. In practice, the extrapolation is based on the two largest sCI wave functions; i.e., we perform a two-point extrapolation, which is justified here because of the quasi-linear behavior of the sCI energy as a function of $E_{PT2}$. Estimating the extrapolation error is a complicated task with no well-defined method to do so. In practice, we have observed that this extrapolation procedure is robust and provides FCI estimates within ±0.02 eV. When the convergence to the FCI limit is too slow to provide reliable estimates, the number of significant digits reported has been reduced accordingly. From herein, the extrapolated FCI results are simply labeled exFCI. Several illustrative examples are reported in Supporting Information where we compare different types of extrapolations for several molecules (see Figure S1 and Table S11). In particular, diazomethane and streptocyanine-C1 can be considered as "difficult" cases (*vide infra*), and the results reported in Supporting Information show that, even in these challenging situations, the two-point linear extrapolation is fairly robust. Moreover, additional points do not significantly alter the exFCI estimates (typically 0.01 eV or less).

All the sCI calculations are performed with the electronic structure software QUANTUM PACKAGE, developed in Toulouse and freely available.[97] Additional information about the sCI wave functions, excitations energies as well as their extrapolated values can be found at the end of the Supporting Information.

## 3. RESULTS AND DISCUSSION

In the discussion below, we first discuss specific molecules of increasing size and compare the results obtained with exFCI and CC approaches, starting with the CC3 method for the latter. This first part is performed applying systematically the frozen-core approximation. We next define two series of TBE, one at the frozen-core aug-cc-pVTZ level, and one close to complete basis set limit by applying corrections for frozen-core and basis set effects. In a following stage, we assess the performances of several popular wave function methods using the former benchmark as reference. Finally, we discuss the performances of basis set extrapolation approaches starting from a compact basis. Unless otherwise stated, we considered the exFCI values as benchmarks.

**3.1. Water, Hydrogen Sulfide, Ammonia, and Hydrogen Chloride.** Because of its small size and ubiquitous role in life, water is often used as a test case for Rydberg excitations. Indeed, it is part of Head−Gordon's,[21] Gordon's[17] and Truhlar−Gagliardi's[29] data sets of compounds, and it has been investigated at many levels of theory.[99,100,103,109] Our results are collected in Table 1. With the aug-cc-pVDZ basis, there is an nearly perfect agreement between the exFCI values and the transition energies obtained with the two largest CC expansions, namely CCSDTQ and CCSDTQP. Indeed, the largest discrepancy is as small as 0.01 eV, and it is therefore reasonable to state that the FCI limit has been reached with that specific basis set. Compared to the exFCI results, the CCSDT values are systematically too low, with an average error of −0.03 eV. The same trend of underestimation is found with CC3, though with smaller absolute deviations for all states. Unsurprisingly, for Rydberg states, increasing the basis set size has a significant impact, and it tends to increase the computed transition energies in water. However, this effect is very similar for all methods listed in Table 1. This means that, on the one hand, the tendency of CCSDT to provide slightly too small transition energies pertains with both aug-cc-pVTZ and aug-cc-pVQZ, and, on the other hand, that estimating the basis set effect with a "cheap" method is possible. Indeed, adding to the exFCI/aug-cc-pVDZ energies, the difference between CC3/aug-cc-pVQZ and CC3/aug-cc-pVDZ results would deliver estimates systematically within 0.01 eV of the actual exFCI/aug-cc-pVQZ values. Such basis set extrapolation approach was already advocated for lower-order CC expansions,[31,110] and it is therefore not surprising that it can be applied with refined models. As it can be seen in Table S1 in the Supporting Information, further extension of the basis set or correlation of the 1s electron have small impacts, except for the Rydberg $^1A_1$ state. Eventually, as evidenced by the data from the rightmost columns of Table 1, the present estimates are in good agreement with previous MRCC values determined on the experimental geometry,[100] whereas the experimental values offer qualitative comparisons only, for reasons discussed elsewhere.[98] We underline that some of the 2013 measurements reported in Table 1 significantly differ from previous electron impact data,[111] that were used previously as references,[17] with, e.g., a 0.2 eV discrepancy between the two experiments for the lowest triplet state.

As water, hydrogen sulfide was also the subject of several high-level theoretical investigations,[103,112−114] which are necessary because there are either no (lowest $^1A_2$ state) or only a few experimental data available for the Rydberg states of $H_2S$,[101,102,115,116] especially as no accurate value could be measured for the first $^1A_2$ state. As can be seen in Table 1, for a given basis set all tested CC methods provide very similar results, systematically within 0.01 eV of the exFCI results. In contrast, the basis set has a significant impact, e.g., the two lowest singlet states switch order when going from aug-cc-pVDZ to aug-cc-pVTZ and the same is true for the two lowest triplet states. Our results are also very consistent with the CASPT2/d-aug-cc-pVQZ values given in ref 103, confirming that a near FCI limit has been reached.

Ammonia is also another popular molecule for evaluating Rydberg excitations, and it was previously investigated at several levels of theory.[14,21,106,117] As in the case of water, we note a nearly perfect match between the CCSDTQ and exFCI estimates with both the aug-cc-pVDZ and aug-cc-pVTZ atomic basis sets, indicating that the FCI limit is reached. Both CC3 and CCSDT are close to this limit, and the former model slightly outperforms the latter. For ammonia, the basis set

**Table 2. Vertical Transition Energies for Various Excited States of Dinitrogen (Top) and Carbon Monoxide (Bottom)[i]**

**dinitrogen**

| state | aug-cc-pVDZ | | | | | aug-cc-pVTZ | | | | aug-cc-pVQZ | | | litt. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CC3 | CCSDT | CCSDTQ | CCSDTQP | exFCI | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[a] | exp.[b] | th.[c] |
| $^1\Pi_g(n \to \pi^*)$ | 9.44 | 9.41 | 9.41 | 9.41 | 9.41 | 9.34 | 9.33 | 9.32 | 9.34 | 9.33 | 9.31 | 9.34 | 9.31 | 9.31 | 9.27 |
| $^1\Sigma_u^-(\pi \to \pi^*)$ | 10.06 | 10.06 | 10.06 | 10.05 | 10.05 | 9.88 | 9.89 | 9.88 | 9.88 | 9.87 | 9.88 | 9.92 | 9.92 | 9.92 | 10.09 |
| $^1\Delta_u(\pi \to \pi^*)$ | 10.43 | 10.44 | 10.43 | 10.43 | 10.43 | 10.29 | 10.30 | | 10.29 | 10.27 | 10.28 | 10.31 | 10.27 | 10.27 | 10.54 |
| $^1\Sigma_g^+(R)$ | 13.23 | 13.20 | 13.18 | 13.18 | 13.18 | 13.01 | 13.00 | 12.97 | 12.98 | 12.90 | 12.89 | 12.89 | | 12.2 | 12.20 |
| $^1\Pi_u(R)$ | 13.28 | 13.17 | 13.13 | 13.13 | 13.12 | 13.22 | 13.14 | 13.09 | 13.03 | 13.17 | | 13.1[d] | 12.78 | 12.90 | 12.84 |
| $^1\Sigma_u^+(R)$ | 13.14 | 13.13 | 13.11 | 13.11 | 13.11 | 13.12 | 13.12 | 13.09 | 13.09 | 13.09 | 13.09 | 13.2[d] | 12.96 | 12.98 | 12.82 |
| $^1\Pi_u(R)$ | 13.64 | 13.59 | 13.56 | 13.56 | 13.56 | 13.49 | 13.45 | 13.42 | 13.46 | 13.42 | 13.37 | 13.7[d] | 13.10 | 13.24 | 13.61 |
| $^3\Sigma_u^+(\pi \to \pi^*)$ | 7.67 | 7.68 | 7.69 | 7.70 | 7.70 | 7.68 | 7.69 | 7.70 | 7.70 | 7.71 | 7.71 | 7.74 | 7.75 | 7.75 | 7.56 |
| $^3\Pi_g(n \to \pi^*)$ | 8.07 | 8.06 | 8.05 | 8.05 | 8.05 | 8.04 | 8.03 | 8.02 | 8.01 | 8.04 | 8.04 | 8.03 | 8.04 | 8.04 | 8.05 |
| $^3\Delta_u(\pi \to \pi^*)$ | 8.97 | 8.96 | 8.96 | 8.96 | 8.96 | 8.87 | 8.87 | 8.87 | 8.87 | 8.87 | 8.87 | 8.88 | 8.88 | 8.88 | 8.93 |
| $^3\Sigma_u^-(\pi \to \pi^*)$ | 9.78 | 9.76 | 9.75 | 9.75 | 9.75 | 9.68 | 9.68 | 9.66 | 9.66 | 9.68 | | 9.66 | 9.67 | 9.67 | 9.86 |

**carbon monoxide**

| state | aug-cc-pVDZ | | | | | aug-cc-pVTZ | | | | aug-cc-pVQZ | | | litt. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CC3 | CCSDT | CCSDTQ | CCSDTQP | exFCI | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[e] | th.[f] | th.[g] |
| $^1\Pi(n \to \pi^*)$ | 8.57 | 8.57 | 8.56 | 8.56 | 8.57 | 8.49 | 8.49 | 8.48 | 8.49 | 8.47 | 8.48 | 8.50 | 8.51 | 8.54 | 8.83 |
| $^1\Sigma^-(\pi \to \pi^*)$ | 10.12 | 10.06 | 10.06 | 10.06 | 10.05 | 9.99 | 9.94 | 9.93 | 9.92 | 9.99 | 9.94 | 9.99 | 9.88 | 10.05 | 9.97 |
| $^1\Delta(\pi \to \pi^*)$ | 10.23 | 10.18 | 10.17 | 10.17 | 10.16 | 10.12 | 10.08 | 10.07 | 10.06 | 10.12 | 10.07 | 10.11 | 10.23 | 10.18 | 10.00 |
| $^1\Sigma^+(R)$ | 10.92 | 10.94 | 10.93 | 10.92 | 10.94 | 10.94 | 10.99 | 10.96 | 10.95 | 10.90 | 10.95 | 10.96 | 10.78 | 10.98 | |
| $^1\Sigma^+(R)$ | 11.48 | 11.52 | 11.51 | 11.51 | 11.52 | 11.49 | 11.54 | 11.52 | 11.52 | 11.46 | 11.51 | 11.53 | 11.40 | | |
| $^1\Pi(R)$ | 11.74 | 11.77 | 11.76 | 11.75 | 11.76 | 11.69 | 11.74 | 11.72 | 11.72 | 11.63 | 11.69 | 11.70 | 11.53 | | |
| $^3\Pi(n \to \pi^*)$ | 6.31 | 6.30 | 6.29 | 6.28 | 6.29 | 6.30 | 6.30 | 6.28 | 6.28 | 6.30 | 6.30 | 6.29 | 6.32 | 6.41 | |
| $^3\Sigma^+(\pi \to \pi^*)$ | 8.45 | 8.43 | 8.44 | 8.44 | 8.46 | 8.45 | 8.42 | 8.44 | 8.45 | 8.48 | 8.45 | 8.49 | 8.51 | 8.39 | |
| $^3\Delta(\pi \to \pi^*)$ | 9.37 | 9.33 | 9.34 | 9.34 | 9.33 | 9.30 | 9.26 | 9.26 | 9.27 | 9.31 | 9.26 | 9.29 | 9.36 | 9.23 | |
| $^3\Sigma^-(\pi \to \pi^*)$ | 9.89 | | | | 9.83 | 9.82 | | | 9.80 | 9.82 | | 9.78 | 9.88 | 9.60 | |
| $^3\Sigma^+(R)$ | 10.39 | 10.42 | 10.42 | 10.41 | 10.41 | 10.45 | 10.50 | 10.48 | 10.47 | 10.44 | 10.49 | | 10.4[h] | | |

[a]Experimental vertical values given in ref 13 and computed from the spectroscopic constants of ref 118. [b]Experimental vertical values given in ref 118. [c]MRCCSD/6-311G with one additional d calculations from ref 119. [d]CI convergence too slow to provide estimates to 0.01 eV. [e]Experimental vertical values given in ref 120 and computed from the spectroscopic constants of ref 118. [f]CCSDT/PVTZ+ results from ref 121. [g]CASSCF(10,10)/cc-pVTZ results from ref 122. [h]Only one digit reported for that state, see ref 120. [i]R stands for Rydberg states. All values are in eV.

**Table 3. Vertical (Absorption) Transition Energies for the Five Lowest Low-Lying Valence Excited States of Acetylene (Top) and the Three Lowest Singlet and Triplet Excited States of Ethylene (Bottom)[g]**

| | acetylene | | | | | | | | | |
| | aug-cc-pVDZ | | | | aug-cc-pVTZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[a] | th.[b] | th.[c] |
|---|---|---|---|---|---|---|---|---|---|---|
| $^1\Sigma_u^-$ $(\pi \rightarrow \pi^*)$ | 7.21 | 7.21 | 7.21 | 7.20 | 7.09 | 7.09 | 7.10 | 7.1 | 6.96 | 7.10 |
| $^1\Delta_u(\pi \rightarrow \pi^*)$ | 7.51 | 7.52 | 7.52 | 7.51 | 7.42 | 7.43 | 7.44 | 7.2 | 7.30 | 7.43 |
| $^3\Sigma_u^+(\pi \rightarrow \pi^*)$ | 5.48 | 5.49 | 5.50 | 5.50 | 5.50 | 5.51 | 5.53 | 5.2 | 5.26 | 5.58 |
| $^3\Delta_u(\pi \rightarrow \pi^*)$ | 6.46 | 6.46 | 6.46 | 6.46 | 6.40 | 6.39 | 6.40 | 6.0 | 6.20 | 6.41 |
| $^3\Sigma_u^-(\pi \rightarrow \pi^*)$ | 7.13 | 7.14 | 7.14 | 7.14 | 7.07 | | 7.08 | 7.1 | 6.90 | 7.05 |
| $^1A_u$ [F]$(\pi \rightarrow \pi^*)$ | 3.70 | 3.72 | 3.70 | 3.71 | 3.64 | 3.66 | 3.64 | | | |
| $^1A_2$ [F]$(\pi \rightarrow \pi^*)$ | 3.92 | 3.94 | 3.93 | 3.93 | 3.84 | 3.86 | 3.85 | | | |
| | ethylene | | | | | | | | | |
| | aug-cc-pVDZ | | | | aug-cc-pVTZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[d] | th.[e] | |
| $^1B_{3u}(\pi \rightarrow 3s)$ | 7.29 | 7.29 | 7.30 | 7.31 | 7.35 | 7.37 | 7.39 | 7.11 | 7.45 | |
| $^1B_{1u}(\pi \rightarrow \pi^*)$ | 7.94 | 7.94 | 7.93 | 7.93 | 7.91 | 7.92 | 7.93 | 7.60 | 8.00 | |
| $^1B_{1g}(\pi \rightarrow 3p)$ | 7.97 | 7.98 | 7.99 | 8.00 | 8.03 | 8.04 | 8.08 | 7.80 | 8.06 | |
| $^3B_{1u}(\pi \rightarrow \pi^*)$ | 4.53 | 4.54 | 4.54 | 4.55 | 4.53 | 4.53 | 4.54 | 4.36 | 4.55 | |
| $^3B_{3u}(\pi \rightarrow 3s)$ | 7.17 | 7.18 | 7.18 | 7.16 | 7.24 | 7.25 | f | 6.98 | 7.29 | |
| $^3B_{1g}(\pi \rightarrow 3p)$ | 7.93 | 7.94 | 7.94 | 7.93 | 7.98 | 7.99 | f | 7.79 | 8.02 | |

[a]Electron impact experiment from ref 129. Note that the 7.1 eV value for the $\Sigma_u^-$ singlet and triplet states should be viewed as a tentative assignment. [b]LS-CASPT2/aug-ANO calculations from ref 124. [c]MR-AQCC/extrap. calculations from ref 126. [d]Experimental values collected from various sources from ref 116. (see discussions in refs 30, 130, and 131). [e]Best composite theory from ref 131, close to FCI. [f]CI convergence too slow to provide estimates reliable to 0.01 eV. [g]For acetylene, we also report the vertical emission (denoted [F]) obtained from the lowest trans and cis isomers. All values are in eV.

effects are particularly strong for the third and fourth singlet excited states but these basis set effects are nearly transferrable from one method to another. In fact, as hinted by the large differences between the aug-cc-pVTZ and aug-cc-pVQZ results in Table 1, these two high-lying states require the use of additional diffuse orbitals to attain convergence. The CC3/t-aug-cc-pVQZ values of 8.60 and 9.15 eV (see Table S1 in the Supporting Information), are close from the previous results of Bartlett and co-workers,[106] who also applied extra diffuse orbitals in their calculations relying on approximate triples (see the footnotes in Table 1). As in water, the experimental values do not provide sufficiently clear-cut results to ultimately decide which method is the most accurate. Indeed, the vertical experimental estimates reported in Table 1 differ significantly from the more trustworthy adiabatic values with variations of ca. 0.5 eV.[106] Consequently, a good match between an experimental measurement and a theoretical calculation determined with a compact basis set is, in the present case, a sign of lucky cancellation of errors.

Hydrogen chloride was less frequently used in previous benchmarks, but is included in Tozer's set as an example of charge-transfer (CT) state.[22] Again, the results listed at the bottom of Table 1 demonstrate a remarkable consistency between the various theories. Though large frozen cores are used during the calculations, this does not strongly impact the results, as can be deduced from the data of Table S1. As expected, the absorption band corresponding to this CT state is very broad experimentally (starting at 5.5 eV and peaking at 8.1 eV),[118] making direct comparisons tricky.

**3.2. Dinitrogen and Carbon Monoxide.** Dinitrogen is a simple diatomic compound for which the low-lying valence and Rydberg states have been investigated at several levels of theory.[13,22,119,121] With a numerical solution of the nuclear

Schrödinger equation, it is possible to treat the experimental spectroscopic constants,[118] so as to obtain reliable vertical estimates, and this procedure was applied previously.[13,119,123] While such approach is supposedly providing experimental vertical excited-state energies with a ca. 0.01 eV error only, it remains that significant excitation energy differences have been reported for the two lowest $^1\Pi_u$ states (see Table 2). As in the previous cases, we find a remarkable agreement between the CCSDTQ and exFCI estimates for most cases in which both could be determined. The only exceptions are the two $^1\Pi_u$ states with the aug-cc-pVTZ basis, but in these two cases, the CC expansion is also converging more slowly than usual, which is consistent with the relatively small degree of single excitation character in these two states (82.9 and 87.4% according to CC3). In contrast to water and ammonia, CCSDT outperforms CC3 with respective mean absolute deviation (MAD) compared to exFCI of 0.02 and 0.04 eV, when using the aug-cc-pVDZ basis set. As it can be deduced from Table S2 in the Supporting Information, the basis set corrections are negligible for all valence states, but significant for some of the Rydberg states, especially $^1\Sigma_g^+$, that requires two sets of diffuse orbitals to be reasonably close from the basis set limit. Applying CC3/d-aug-cc-pV5Z corrections to the most accurate exFCI data, once can determine TBE values (vide infra) that deviate only by 0.02 eV on (absolute) average compared to the experimental estimates for the seven valence states of dinitrogen. Considering the expected inaccuracy of 0.01 eV of the reference values, chemical accuracy is obviously reached without any experimental input. The deviations are about twice larger for the Rydberg states. Nevertheless, for the two $^1\Pi_u$ states, our TBE values, determined on the basis of exFCI/aug-cc-pVTZ results are 12.73 and 13.27 eV (vide infra). This indicates that for the lowest $^1\Pi_u$ state the estimate of ref 13

**Table 4. Vertical (Absorption) Transition Energies for Various Excited States of Formaldehyde (Top), Methanimine (Center), and Thioformaldehyde (Bottom)[h]**

| | | formaldehyde | | | | | | | | |
| | aug-cc-pVDZ | | | | aug-cc-pVTZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[a] | th.[b] | th.[c] |
|---|---|---|---|---|---|---|---|---|---|---|
| $^1A_2(n \rightarrow \pi^*)$ | 4.00 | 3.99 | 4.00 | 3.99 | 3.97 | 3.95 | 3.98 | 4.07 | 3.98 | 3.88 |
| $^1B_2(n \rightarrow 3s)$ | 7.05 | 7.04 | 7.09 | 7.11 | 7.18 | 7.16 | 7.23 | 7.11 | 7.12 | |
| $^1B_2(n \rightarrow 3p)$ | 8.02 | 8.00 | 8.04 | 8.04 | 8.07 | 8.07 | 8.13 | 7.97 | 7.94 | 8.11 |
| $^1A_1(n \rightarrow 3p)$ | 8.08 | 8.07 | 8.12 | 8.12 | 8.18 | 8.16 | 8.23 | 8.14 | 8.16 | |
| $^1A_2(n \rightarrow 3p)$ | 8.65 | 8.63 | 8.68 | 8.65 | 8.64 | 8.61 | 8.67 | 8.37 | 8.38 | |
| $^1B_1(\sigma \rightarrow \pi^*)$ | 9.31 | 9.29 | 9.30 | 9.29 | 9.19 | 9.17 | 9.22 | | 9.32 | 9.04 |
| $^1A_1(\pi \rightarrow \pi^*)$ | 9.59 | 9.59 | 9.54 | 9.53 | 9.48 | 9.49 | 9.43 | | 9.83 | 9.29 |
| $^3A_2(n \rightarrow \pi^*)$ | 3.58 | 3.57 | 3.58 | 3.58 | 3.57 | 3.56 | 3.58 | 3.50 | | 3.50 |
| $^3A_1(\pi \rightarrow \pi^*)$ | 6.09 | 6.08 | 6.09 | 6.10 | 6.05 | 6.05 | 6.06 | 5.86 | | 5.87 |
| $^3B_2(n \rightarrow 3s)$ | 6.91 | 6.90 | 6.95 | 6.95 | 7.03 | 7.02 | 7.06 | 6.83 | | |
| $^3B_2(n \rightarrow 3p)$ | 7.84 | 7.82 | 7.86 | 7.87 | 7.92 | 7.90 | 7.94 | 7.79 | | |
| $^3A_1(n \rightarrow 3p)$ | 7.97 | 7.95 | 8.00 | 8.01 | 8.08 | 8.06 | 8.10 | 7.96 | | |
| $^3B_1(n \rightarrow 3d)$ | 8.48 | 8.47 | 8.48 | 8.48 | 8.41 | 8.40 | 8.42 | | | |
| $^1A''[F](n \rightarrow \pi^*)$ | 2.87 | 2.84 | 2.86 | 2.86 | 2.84 | 2.82 | 2.80 | | | |
| | | methanimine | | | | | | | | |
| | aug-cc-pVDZ | | | | aug-cc-pVTZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | th.[d] | th.[e] | |
| $^1A''(n \rightarrow \pi^*)$ | 5.26 | 5.24 | 5.25 | 5.25 | 5.20 | 5.19 | 5.23 | 5.32 | 5.18 | |
| $^3A''(n \rightarrow \pi^*)$ | 4.63 | 4.63 | 4.63 | 4.63 | 4.61 | 4.61 | 4.65 | | | |
| | | thioformaldehyde | | | | | | | | |
| | aug-cc-pVDZ | | | | aug-cc-pVTZ | | | lit. | | |
| state | CC3 | CCSDT | CCSDTQ | exFCI | CC3 | CCSDT | exFCI | exp.[a] | exp.[f] | |
| $^1A_2(n \rightarrow \pi^*)$ | 2.27 | 2.25 | 2.26 | 2.26 | 2.23 | 2.21 | 2.22 | | 2.03 | |
| $^1B_2(n \rightarrow 4s)$ | 5.80 | 5.80 | 5.82 | 5.83 | 5.91 | 5.89 | 5.96 | 5.85 | 5.84 | |
| $^1A_1(\pi \rightarrow \pi^*)$ | 6.62 | 6.60 | 6.51 | 6.5[g] | 6.48 | 6.47 | 6.4[g] | 6.2 | 5.54 | |
| $^3A_2(n \rightarrow \pi^*)$ | 1.97 | 1.96 | 1.96 | 1.97 | 1.94 | 1.93 | 1.94 | | 1.80 | |
| $^3A_1(\pi \rightarrow \pi^*)$ | 3.43 | 3.43 | 3.44 | 3.45 | 3.38 | 3.38 | 3.43 | 3.28 | | |
| $^3B_2(n \rightarrow 4s)$ | 5.64 | 5.63 | 5.65 | 5.66 | 5.72 | 5.71 | 5.6[g] | | | |
| $^1A_2[F](n \rightarrow \pi^*)$ | 2.00 | 2.00 | 1.98 | 1.98 | 1.97 | 1.98 | 1.95 | | | |

[a]Various experimental sources, summarized in ref 116. [b]MR-AQCC-LRT calculations from ref 134. [c]CC3/aug-cc-pVQZ calculations from ref 30. [d]DMC results form ref 135. [e]CCSDT/aug-cc-pVTZ calculations from ref 59. [f]0−0 energies collected in ref 136. [g]CI convergence too slow to provide reliable estimates. [h]All values are in eV.

(12.78 eV) is probably more accurate than the one of ref 119 (12.90 eV), whereas the opposite is likely true for the highest $^1\Pi_u$ state that was reported to be located at 13.10 and 13.24 eV in refs 13 and 119, respectively. One could argue that reaching agreement between CI and CC is particularly challenging for these two states. However, performing the basis set extrapolation starting from the CCSDTQP/aug-cc-pVDZ results would yield similar TBE of 12.77 and 13.22 eV.

For the isoelectronic carbon monoxide, experimental vertical energies deduced from rovibronic data[118] using a numerical approach are also available.[22,120] With the aug-cc-pVTZ (aug-cc-pVQZ) atomic basis set, the CCSDT and CC3 results are within 0.02 eV (0.03 eV) and 0.03 eV (0.03 eV) of the exFCI results, whereas the errors made by both CCSDTQ and CCSDTQP are again trifling. As for dinitrogen, all the valence states are rather close from the basis set limit with aug-cc-pVTZ, whereas larger basis sets are required for the Rydberg states (Table S2). By correcting the exFCI/aug-cc-pVQZ (exFCI/aug-cc-pVTZ for the highest triplet state) data with basis set effects determined at the CC3/d-aug-cc-pV5Z level, we obtain TBE values that can be compared to the

experimental estimates. The computed MAD is 0.05 eV, the largest deviations being obtained for the Δ and Σ⁻ excited states of both spin symmetries. The agreement between theory and experiment is therefore very satisfying though slightly less impressive than for N². We note that the CC3/aug-cc-pVTZ C = O bond length (1.134 Å) is 0.006 Å larger than the experimental $r_e$ value of 1.128 Å,[118] whereas the discrepancy is twice smaller for dinitrogen: 1.101 Å for CC3/aug-cc-pVTZ compared to 1.098 Å experimentally. This might partially explained the larger deviations noticed for carbon monoxide.

**3.3. Acetylene and Ethylene.** Acetylene is the smallest conjugated organic molecule possessing stable low-lying excited-state structures, therefore allowing to investigate vertical fluorescence. This molecule has been the subject of previous investigations at the CASPT2,[124] CCSD,[125] CCSDT,[59] and MR-AQCC[126] levels. Our results are collected in Table 3. With the double-ζ basis set, the differences between the CC3, CCSDT, and CCSDTQ results are negligible, and the latter estimates are also systematically within 0.02 eV of the exFCI results. In contrast to water and ammonia, both CC3 and CCSDT provide similar accuracies compared to higher

**Table 5. Vertical (Absorption) Transition Energies for Various Excited States of Diazomethane (Top) and Ketene (Bottom)[v]**

| molecule | state | aug-cc-pVDZ | | | aug-cc-pVTZ | | | lit. | |
|---|---|---|---|---|---|---|---|---|---|
| | | CC3 | CCSDT | exFCI | CC3 | CCSDT | exFCI | exp. | th. |
| acetaldehyde | $^1A''(n \rightarrow \pi^*)$ | 4.34 | 4.32 | 4.34 | 4.31 | 4.29 | 4.31 | 4.27[a] | 4.29[b] |
| | $^3A''(n \rightarrow \pi^*)$ | 3.96 | 3.95 | 3.98 | 3.95 | 3.94 | 4.0[c] | 3.97[a] | 3.97[b] |
| cyclopropene | $^1B_1 (\sigma \rightarrow \pi^*)$ | 6.72 | 6.71 | 6.7[c] | 6.68 | 6.68 | 6.6[c] | 6.45[d] | 6.89[e] |
| | $^1B_2 (\pi \rightarrow \pi^*)$ | 6.77 | 6.78 | 6.82 | 6.73 | 6.75 | 6.7[c] | 7.00[f] | 7.11[e] |
| | $^3B_2 (\pi \rightarrow \pi^*)$ | 4.34 | 4.35 | 4.35 | 4.34 | | 4.38 | 4.16[f] | 4.28[g] |
| | $^3B_1 (\sigma \rightarrow \pi^*)$ | 6.43 | 6.43 | 6.43 | 6.40 | | 6.45 | | 6.40[g] |
| diazomethane | $^1A_2 (\pi \rightarrow \pi^*)$ | 3.10 | 3.10 | 3.09 | 3.07 | 3.07 | 3.14 | 3.14[h] | 3.21[i] |
| | $^1B_1 (\pi \rightarrow 3s)$ | 5.32 | 5.35 | 5.35 | 5.45 | 5.48 | 5.54 | | 5.33[i] |
| | $^1A_1 (\pi \rightarrow \pi^*)$ | 5.80 | 5.82 | 5.79 | 5.84 | 5.86 | 5.90 | 5.9[h] | 5.85[i] |
| | $^3A_2 (\pi \rightarrow \pi^*)$ | 2.84 | 2.84 | 2.81 | 2.83 | 2.82 | 2.8[c] | | 2.92[j] |
| | $^3A_1 (\pi \rightarrow \pi^*)$ | 4.05 | 4.04 | 4.03 | 4.03 | 4.02 | 4.05 | | 3.97[j] |
| | $^3B_1 (\pi \rightarrow 3s)$ | 5.17 | 5.20 | 5.18 | 5.31 | 5.34 | 5.35 | | |
| | $^3A_1 (\pi \rightarrow 3p)$ | 6.83 | 6.83 | 6.81 | 6.80 | | 6.82 | | 7.02[j] |
| | $^1A'' [F] (\pi \rightarrow \pi^*)$ | 0.68 | 0.67 | 0.65 | 0.68 | 0.67 | 0.71 | | |
| formamide | $^1A''(n \rightarrow \pi^*)$ | 5.71 | 5.68 | 5.70 | 5.66 | 5.63 | 5.7[c] | 5.8[k] | 5.63[l] |
| | $^1A'(n \rightarrow 3s)$ | 6.65 | 6.64 | 6.67 | 6.74 | 6.74 | | 6.35[k] | 6.62[l] |
| | $^1A' (\pi \rightarrow \pi^*)^m$ | 7.63 | 7.62 | 7.64 | 7.62 | | 7.63 | 7.37[k] | 7.22[l] |
| | $^1A'(n \rightarrow 3p)^m$ | 7.31 | 7.29 | | 7.40 | 7.38 | | 7.73[k] | 7.66[l] |
| | $^3A''(n \rightarrow \pi^*)$ | 5.42 | 5.39 | 5.42 | 5.38 | | 5.4[c] | 5.2[k] | 5.34[l] |
| | $^3A' (\pi \rightarrow \pi^*)$ | 5.83 | 5.81 | 5.82 | 5.82 | | 5.7[c] | ~6[k] | 5.74[l] |
| ketene | $^1A_2 (\pi \rightarrow \pi^*)$ | 3.89 | 3.88 | 3.84 | 3.88 | 3.87 | 3.86 | 3.7[n] | 3.74[o] |
| | $^1B_1 (n \rightarrow 3s)$ | 5.83 | 5.86 | 5.88 | 5.96 | 5.99 | 6.01 | 5.86[n] | 5.82[o] |
| | $^1A_2 (\pi \rightarrow 3p)$ | 7.05 | 7.09 | 7.08 | 7.16 | 7.20 | 7.18 | | 7.00[o] |
| | $^3A_2 (n \rightarrow \pi^*)$ | 3.79 | 3.78 | 3.79 | 3.78 | 3.78 | 3.77 | 3.8[p] | 3.62[q] |
| | $^3A_1 (\pi \rightarrow \pi^*)$ | 5.62 | 5.61 | 5.64 | 5.61 | 5.60 | 5.61 | 5[p] | 5.42[q] |
| | $^3B_1 (n \rightarrow 3s)$ | 5.63 | 5.66 | 5.68 | 5.76 | 5.80 | 5.79 | 5.8[p] | 5.69[q] |
| | $^3A_2 (\pi \rightarrow 3p)$ | 7.01 | 7.05 | 7.07 | 7.12 | 7.17 | 7.12 | | |
| | $^1A''[F] (\pi \rightarrow \pi^*)$ | 1.00 | 0.99 | 0.96 | 1.00 | 1.00 | 1.00 | | |
| nitrosomethane | $^1A''(n \rightarrow \pi^*)$ | 2.00 | 1.98 | 1.99 | 1.96 | 1.95 | 2.0[c] | 1.83[r] | 1.76[s] |
| | $^1A' (n, n \rightarrow \pi^*,\pi^*)$ | 5.75 | 5.26 | 4.81 | 5.76 | 5.29 | 4.72 | | 4.96[s] |
| | $^1A' (n \rightarrow 3s/3p)$ | 6.20 | 6.19 | 6.29 | 6.31 | 6.30 | 6.4[c] | | 6.54[s] |
| | $^3A''(n \rightarrow \pi^*)$ | 1.13 | 1.12 | 1.15 | 1.14 | 1.13 | 1.16 | | 1.42[t] |
| | $^3A' (\pi \rightarrow \pi^*)$ | 5.54 | 5.54 | 5.56 | 5.51 | | 5.60 | | 5.55[t] |
| | $^1A'' [F] (n \rightarrow \pi^*)$ | 1.70 | 1.69 | 1.70 | 1.69 | 1.66 | 1.7[c] | | |
| streptocyanine-C1 | $^1B_2 (\pi \rightarrow \pi^*)$ | 7.14 | 7.12 | 7.14 | 7.13 | 7.11 | 7.1[c] | | 7.16[u] |
| | $^3B_2 (\pi \rightarrow \pi^*)$ | 5.48 | 5.47 | 5.47 | 5.48 | 5.47 | 5.52 | | |

[a]Electron impact experiment from ref 145. [b]NEVPT-PC from ref 127. [c]CI convergence too slow to provide more reliable estimates. [d]Maximum in the gas UV from ref 146. [e]CCSDT/TZVP from ref 58. [f]Electron impact experiment from ref 147. [g]CC3/aug-cc-pVTZ from ref 32. [h]VUV maxima from ref 148. [i]CCSD/6-311(3+,+)G(d) calculations from ref 149. [j]MR-CC/DZP calculations from ref 150. [k]EELS (singlet) and trapped electron (triplet) experiments from ref 151. [l]nR-SI-CCSD(T) results from ref 142. [m]Strong state mixing. [n]Electron impact experiment from ref 152. [o]CASPT2/6-311+G(d) results from ref 153. [p]Electron impact experiment from ref 116. [q]STEOM-CCSD/Sad+//CCSD/Sad+ results from ref 154. [r]Maximum in the gas UV from ref 155. [s]CASPT2/ANO results from ref 156. [t]CASSCF/cc-pVDZ results from ref 157. [u]exCC3//MP2 result from ref 128. [v]All values are in eV.

levels of theory. As expected, for valence states, going from double- to triple-ζ basis set tends to slightly decrease the computed energies (except for the lowest triplet). Nonetheless, as with the smaller basis set, the same near-perfect methodological match pertains with aug-cc-pVTZ. Estimating the exFCI/aug-cc-pVTZ results from the exFCI/aug-cc-pVDZ values and CC3 basis set effects would yield estimates with absolute errors of 0.00−0.02 eV. One also notices that the exFCI/aug-cc-pVTZ values are all extremely close to the previous MR-AQCC estimates, whereas the published CASPT2 values appear to be too low though closer from the electron impact experiment, underlying once more the difficulty to obtain very accurate experimental estimates for vertical energies. This underestimating trend of standard CASPT2 was reported before for other molecules.[127,128] Although our theoretical vertical energy estimates still slightly vary when passing from the aug-cc-pVDZ to aug-cc-pVTZ basis sets, we claim that these vertical energies are probably more trustworthy for further benchmarks than the available experimental values because basis set effects beyond aug-cc-pVTZ seem rather limited (Table S3).

Despite its small size, ethylene remains a challenging molecule and is included in many benchmark sets.[17,26,29,30,75,132] The assignments of the experimental data have been the subject of countless works, and we refer the interested readers to the discussions in refs 30, 91, 116, 130,

131, and 133. On the theoretical side, the most complete and accurate investigation dedicated to the excited states of ethylene is due to Davidson's group, who performed refined CI calculations.[131] They indeed obtained highly accurate transition energies for ethylene, including for the valence yet challenging $^1B_{1u}$ state. From our data, collected in Table 3, one notices that the differences between exFCI/aug-cc-pVDZ and CCSDTQ/aug-cc-pVDZ results are again trifling, the largest deviation being obtained for the $^3B_{3u}$ ($\pi \rightarrow 3s$) Rydberg state (0.02 eV). In addition, given the nice agreement between CC3, CCSDT, and exFCI values, one can directly compare our CC3/aug-cc-pV5Z results (Table S3) to the values of reported in ref 131: a mean absolute deviation (MAD) of 0.03 eV is obtained. The fact that our transition energies tend to be slightly smaller than Davidson's is likely due to geometrical effects. Indeed, our CC3/aug-cc-pVTZ C=C distance is 1.3338 Å, i.e., slightly longer than the best estimate provided in Davidson's work (1.3305 Å). Recently, a stochastic heat-bath CI (SHCI)/ANO-L-pVTZ work reported 4.59 and 8.05 eV values for the $^3B_{1u}$ and $^1B_{1u}$ states, respectively,[91] and we also ascribe the differences with our results to the use of a MP2 geometry in ref 91. Interestingly, these authors found quite large discrepancies between their SHCI and their CC results. Indeed, they reported CR-EOMCC(2,3)D estimates significantly larger than their SHCI results with +0.17 and +0.20 eV upshifts for the triplet and singlet states, respectively. This highlights that only high-level CC schemes are able to recover the exFCI (or SHCI) results for ethylene.

**3.4. Formaldehyde, Methanimine, and Thioformaldehyde.** Similarly to ethylene, formaldehyde is a very popular test molecule,[17,22,26,29,30,59,75,76,132,137−142] and stands as the prototype carbonyl dye with a low-lying n → π* transition. Nevertheless, even for this particular valence state, well-separated from higher-lying excited states, the choice of an experimental reference remains difficult. Indeed, values of 3.94,[22] 4.00,[26,29,138] 4.07,[17,75,139] and 4.1 eV,[137,140] have been used in previous theoretical benchmarks. In contrast to their oxygen cousin, both methanimine and thioformaldehyde were the subject of less attention from the theoretical community.[135,143,144] The results obtained for these three molecules are collected in Table 4. Considering all transitions listed in this table, one obtains a MAD of 0.01 eV between the CCSDTQ/aug-cc-pVDZ and exFCI/aug-cc-pVDZ results, the largest discrepancies of 0.03 eV being observed for two states for which the differences between CCSDT and CCSDTQ are also large (0.05 eV). As in water, using the exFCI/aug-cc-pVDZ values as reference, we found that CC3 delivers slightly more accurate transition energies (MAD of 0.02 eV, maximal deviation of 0.06 eV) than CCSDT (MAD of 0.03 eV, maximal deviation of 0.07 eV). By adding the difference between CC3/aug-cc-pVTZ and CC3/aug-cc-pVDZ results to the exFCI/aug-cc-pVDZ values, we obtain good estimates of the actual exFCI/aug-cc-pVTZ data, with a MAD of 0.02 eV for formaldehyde. Compared to the CC3/aug-cc-pVQZ results of Thiel,[30] the transition energies reported in Table 4 are slightly larger, which is probably due to the influence of the ground-state geometry rather than to basis set effects (see Table S4). Indeed, the carbonyl bond is significantly more contracted with CC3/aug-cc-pVTZ (1.208 Å) than with MP2/6-31G(d) (1.221 Å). In particular, for the hallmark n → π*, our best estimate is 3.97 eV (*vide infra*), nicely matching a previous MR-AQCC value of 3.98 eV,[134] but significantly below the previous DMC/BLYP estimate of 4.24 eV.[135] The

latter discrepancy is probably due to the use of both different structures and pseudopotentials within DMC calculations.

For methanimine and thioformaldehyde, the basis set effects are rather small for the states considered here (see Table S4) and the data reported in the present work are probably the most accurate vertical transition energies reported to date. For the latter molecule, these vertical estimates are systematically larger than the known experimental 0−0 energies,[136] which is the expected trend.

**3.5. Larger Compounds.** Let us now turn our attention to molecules that encompass three heavy (non-hydrogen) atoms. We have treated seven molecules of that family, and all were previously investigated at several levels of theory: acetaldehyde,[26,29,127,138−140,158,159] cyclopropene,[30−32,58,132,160] diazomethane,[149,150,158,161] formamide,[30−32,58,59,162,163] ketene,[150,153,154,164] nitrosomethane,[156,157,165,166] and the shortest streptocyanine.[128,167−170] The results are gathered in Table 5. Note that, for these molecules containing three heavy atoms, it is sometimes challenging to obtain reliable exFCI estimes, especially for the largest basis set.

Experimentally, the lowest singlet and triplet n → π* transitions of acetaldehyde are located 0.3−0.4 eV above their formaldehyde counterparts,[116,145] and this trend is accurately reproduced by theory, which also delivers estimates very close to the NEVPT2 values given in ref 127.

For cyclopropene, the lowest singlet σ → π* and π → π* are close from one another, and both CCSDT and exFCI predict the former to be slightly more stabilized, which is consistent with the large basis set CC3 results obtained by Thiel.[32]

For the isoelectronic diazomethane and ketene molecules (see Table 5), one notes, yet again, consistent results with, however, differences between the exFCI/aug-cc-pVTZ and CCSDT/aug-cc-pVTZ results larger than 0.05 eV for the two lowest singlet states of diazomethane. There is also a reasonable match between our data and previous theoretical results reported for these two molecules.[149,150,153,154] The basis set effects are significant for the Rydberg transitions, especially for the π → 3s states of diazomethane (Table S5).

In formamide, we found strong state mixing between the lowest singlet valence and Rydberg states of A′ symmetry. This is consistent with the CCSDT/TZVP analysis of Kannar and Szalay,[58] who reported, for example, a larger oscillator strength for the lowest Rydberg state than for the π → π* transition. This state-mixing problem pertains with aug-cc-pVTZ, making unambiguous assignments difficult. Consequently, we have decided to classify the three lowest $^1A'$ transitions according to their dominant orbital character, which gives a picture consistent with the computed oscillator strengths (*vide infra*) but yields state inversions compared to Thiel's and Szalay's assignments.[31,58] This strong state mixing also prevented the convergence of several state energies with the exFCI/aug-cc-pVTZ approach. Despite these uncertainties, we obtained transition energies for the Rydberg states that are much closer from experiment[151] as well as from previous multireference CC estimates,[142] than the TZVP ones.[58]

Nitrosomethane is an interesting test molecule for three reasons: (i) it presents very low-lying n → π* states of A″ symmetry, close to ca. 2.0 eV (singlet) and 1.2 eV (triplet), among the smallest absorption energies found in a compact molecule;[171] (ii) it changes from an eclipsed to a staggered conformation of the methyl group when going from the ground to the lowest singlet state;[157,172,173] (iii) the lowest-lying singlet A′ state corresponds to an almost pure double

## Table 6. TBE (in eV) for Various States and Wave Function Approaches[e]

| | state | $f$ | % $T_1$ | TBE(FC) AVTZ | corrected TBE method | corr. | value |
|---|---|---|---|---|---|---|---|
| acetaldehyde | $^1A''$(V; n → π*) | 0.000 | 91.3 | 4.31 | exFCI/AVTZ | AVQZ | 4.31 |
| | $^3A''$(V; n → π*) | | 97.9 | 3.97[a] | exFCI/AVDZ | AVQZ | 3.98 |
| acetylene | $^1\Sigma_u^-$(V; π → π*) | | 96.5 | 7.10 | exFCI/AVTZ | dAV5Z | 7.10 |
| | $^1\Delta_u$(V; π → π*) | | 93.3 | 7.44 | | | 7.44 |
| | $^3\Sigma_u^+$(V; π → π*) | | 99.2 | 5.53 | | | 5.56 |
| | $^3\Delta_u$(V; π → π*) | | 99.0 | 6.40 | | | 6.40 |
| | $^3\Sigma_u^-$(V; π → π*) | | 98.8 | 7.08 | | | 7.09 |
| | $^1A_u$ [F](V; π → π*) | | 95.6 | 3.64 | | | 3.63 |
| | $^1A_2$ [F](V; π → π*) | | 95.5 | 3.85 | | | 3.85 |
| ammonia | $^1A_2$ (R; n → 3s) | 0.086 | 93.5 | 6.59 | exFCI/AVQZ | dAV5Z | 6.66 |
| | $^1E$(R; n → 3p) | 0.006 | 93.7 | 8.16 | | | 8.21 |
| | $^1A_1$ (R; n → 3p) | 0.003 | 94.0 | 9.33 | | | 8.65 |
| | $^1A_2$ (R; n → 4s) | 0.008 | 93.6 | 9.96 | exFCI/AVTZ | dAV5Z | 9.19 |
| | $^3A_2$ (R; n → 3s) | | 98.2 | 6.31 | exFCI/AVQZ | dAV5Z | 6.37 |
| carbon monoxide | $^1\Pi$(V; n → π*) | 0.084 | 93.1 | 8.49 | exFCI/AVQZ | dAV5Z | 8.48 |
| | $^1\Sigma^-$(V; π → π*) | | 93.3 | 9.92 | | | 9.98 |
| | $^1\Delta$(V; π → π*) | | 91.8 | 10.06 | | | 10.10 |
| | $^1\Sigma^+$ (R) | 0.003 | 91.5 | 10.95 | | | 10.80 |
| | $^1\Sigma^+$ (R) | 0.200 | 92.9 | 11.52 | | | 11.42 |
| | $^1\Pi$(R) | 0.053 | 92.4 | 11.72 | | | 11.55 |
| | $^3\Pi$(V; n → π*) | | 98.7 | 6.28 | | | 6.28 |
| | $^3\Sigma^+$ (V; π → π*) | | 98.7 | 8.45 | | | 8.49 |
| | $^3\Delta$(V; π → π*) | | 98.4 | 9.27 | | | 9.28 |
| | $^3\Sigma^-$(V; π → π*) | | 97.5 | 9.80 | | | 9.77 |
| | $^3\Sigma^+$ (R) | | 98.0 | 10.47 | exFCI/AVTZ | dAV5Z | 10.37 |
| cyclopropene | $^1B_1$ (V;σ → π*) | 0.001 | 92.8 | 6.68[b] | CCSDT/AVTZ | AVQZ | 6.68 |
| | $^1B_2$ (V; π → π*) | 0.071 | 95.1 | 6.79[a] | exFCI/AVDZ | AVQZ | 6.78 |
| | $^3B_2$ (V; π → π*) | | 98.0 | 4.38 | exFCI/AVTZ | AVQZ | 4.38 |
| | $^3B_1$ (V;σ → π*) | | 98.9 | 6.45 | | | 6.45 |
| diazomethane | $^1A_2$ (V; π → π*) | | 90.1 | 3.14 | exFCI/AVTZ | dAVQZ | 3.13 |
| | $^1B_1$ (R; π → 3s) | 0.002 | 93.8 | 5.54 | | | 5.59 |
| | $^1A_1$ (V; π → π*) | 0.210 | 91.4 | 5.90 | | | 5.89 |
| | $^3A_2$ (V; π → π*) | | 97.7 | 2.79[a] | exFCI/AVDZ | dAVQZ | 2.80 |
| | $^3A_1$ (V; π → π*) | | 98.6 | 4.05 | exFCI/AVTZ | dAVQZ | 4.05 |
| | $^3B_1$ (R; π → 3s) | | 98.0 | 5.35 | | | 5.40 |
| | $^3A_1$ (R; π → 3p) | | 98.5 | 6.82 | | | 6.72 |
| | $^1A''$ [F](V; π → π*) | | 87.4 | 0.71 | | | 0.70 |
| dinitrogen | $^1\Pi_g$(V; n → π*) | | 92.6 | 9.34 | exFCI/AVQZ | dAV5Z | 9.33 |
| | $^1\Sigma_u^-$(V; π → π*) | | 97.2 | 9.88 | | | 9.91 |
| | $^1\Delta_u$ (V; π → π*) | 0.000 | 95.9 | 10.29 | | | 10.31 |
| | $^1\Sigma_g^+$ (R) | | 92.2 | 12.98 | | | 12.30 |
| | $^1\Pi_u$ (R) | 0.229 | 82.9 | 13.03 | exFCI/AVTZ | dAV5Z | 12.73 |
| | $^1\Sigma_u^+$ (R) | 0.296 | 92.8 | 13.09 | | | 12.95 |
| | $^1\Pi_u$ (R) | 0.000 | 87.4 | 13.46 | | | 13.27 |
| | $^3\Sigma_u^+$ (V; π → π*) | | 99.3 | 7.70 | exFCI/AVQZ | dAV5Z | 7.74 |
| | $^3\Pi_g$ (V; n → π*) | | 98.4 | 8.01 | | | 8.03 |
| | $^3\Delta_u$ (V; π → π*) | | 99.3 | 8.87 | | | 8.88 |
| | $^3\Sigma_u^-$ (V; π → π*) | | 98.8 | 9.66 | | | 9.65 |
| ethylene | $^1B_{3u}$(R; π → 3s) | 0.078 | 95.1 | 7.39 | exFCI/AVTZ | dAV5Z | 7.43 |
| | $^1B_{1u}$(V; π → π*) | 0.346 | 95.8 | 7.93 | | | 7.92 |
| | $^1B_{1g}$(R; π → 3p) | | 95.3 | 8.08 | | | 8.10 |
| | $^3B_{1u}$(V; π → π*) | | 99.1 | 4.54 | | | 4.54 |
| | $^3B_{3u}$(R; π → 3s) | | 98.5 | 7.23[a] | exFCI/AVDZ | dAV5Z | 7.28 |
| | $^3B_{1g}$(R; π → 3p) | | 98.4 | 7.98[a] | | | 8.00 |
| formaldehyde | $^1A_2$ (V; n → π*) | | 91.5 | 3.98 | exFCI/AVTZ | dAV5Z | 3.97 |
| | $^1B_2$ (R; n → 3s) | 0.021 | 91.7 | 7.23 | | | 7.30 |

## Table 6. continued

| state | $f$ | % $T_1$ | TBE(FC) AVTZ | corrected TBE method | corr. | value |
|---|---|---|---|---|---|---|
| $^1B_2$ (R; n → 3p) | 0.037 | 92.4 | 8.13 | | | 8.14 |
| $^1A_1$ (R; n → 3p) | 0.052 | 91.9 | 8.23 | | | 8.27 |
| $^1A_2$ (R; n → 3p) | | 91.7 | 8.67 | | | 8.50 |
| $^1B_1$ (V;σ → π*) | 0.001 | 90.8 | 9.22 | | | 9.21 |
| $^1A_1$ (V; π → π*) | 0.135 | 90.4 | 9.43 | | | 9.26 |
| $^3A_2$ (V; n → π*) | | 98.1 | 3.58 | | | 3.58 |
| $^3A_1$ (V; π → π*) | | 99.0 | 6.06 | | | 6.07 |
| $^3B_2$ (R; n → 3s) | | 97.1 | 7.06 | | | 7.14 |
| $^3B_2$ (R; n → 3p) | | 97.4 | 7.94 | | | 7.96 |
| $^3A_1$ (R; n → 3p) | | 97.2 | 8.10 | | | 8.15 |
| $^3B_1$ (R; n → 3d) | | 97.9 | 8.42 | | | 8.42 |
| $^1A''$ [F] (V; n → π*) | | 87.8 | 2.80 | | | 2.80 |
| formamide $^1A''$ (V; n → π*) | 0.000 | 90.8 | 5.65[a] | exFCI/AVDZ | AVQZ | 5.63 |
| $^1A'$ (R; n → 3s) | 0.001 | 88.6 | 6.77[a] | | | 6.81 |
| $^1A'$ (V; π → π*) | 0.251 | 89.3 | 7.63 | exFCI/AVTZ | AVQZ | 7.64 |
| $^1A'$ (R; n → 3p) | 0.111 | 89.6 | 7.38[b] | CCSDT/AVTZ | AVQZ | 7.41 |
| $^3A''$(V; n → π*) | | 97.7 | 5.38[c] | exFCI/AVDZ | AVQZ | 5.37 |
| $^3A'$ (V; π → π*) | | 98.2 | 5.81[c] | | | 5.81 |
| hydrogen chloride $^1\Pi$(CT) | 0.056 | 94.3 | 7.84 | exFCI/AVQZ | dAV5Z | 7.86 |
| hydrogen sulfide $^1A_2$ (R; n → 4p) | | 94.6 | 6.18 | exFCI/AVQZ | dAV5Z | 6.10 |
| $^1B_1$ (R; n → 4s) | 0.063 | 94.3 | 6.24 | | | 6.29 |
| $^3A_2$ (R; n → 4p) | | 98.7 | 5.81 | | | 5.74 |
| $^3B_1$ (R; n → 4s) | | 98.4 | 5.88 | | | 5.94 |
| ketene $^1A_2$ (V; π → π*) | | 91.0 | 3.86 | exFCI/AVTZ | dAVQZ | 3.86 |
| $^1B_1$ (R; n → 3s) | 0.035 | 93.9 | 6.01 | | | 6.06 |
| $^1A_2$ (R; π → 3p) | | 94.4 | 7.18 | | | 7.19 |
| $^3A_2$ (V; n → π*) | | 91.0 | 3.77 | | | 3.77 |
| $^3A_1$ (V; π → π*) | | 98.6 | 5.61 | | | 5.60 |
| $^3B_1$ (R; n → 3s) | | 98.1 | 5.79 | | | 5.85 |
| $^3A_2$ (R; π → 3p) | | 94.4 | 7.12 | | | 7.14 |
| $^1A''$ [F] (V; π → π*) | | 87.9 | 1.00 | | | 1.00 |
| methanimine $^1A''$(V; n → π*) | 0.003 | 90.7 | 5.23 | exFCI/AVTZ | dAVQZ | 5.21 |
| $^3A''$(V; n → π*) | | 98.1 | 4.65 | | | 4.64 |
| nitrosomethane $^1A''$(V; n → π*) | 0.000 | 93.0 | 1.96[a] | exFCI/AVDZ | AVQZ | 1.95 |
| $^1A'$ (V; n, n → π*,π*) | 0.000 | 2.5 | 4.72 | exFCI/AVTZ | AVQZ | 4.69 |
| $^1A'$ (R; n → 3s/3p) | 0.006 | 90.8 | 6.40[a] | exFCI/AVDZ | AVQZ | 6.42 |
| $^3A''$(V; n → π*) | | 98.4 | 1.16 | | | 1.16 |
| $^3A'$ (V; π → π*) | | 98.9 | 5.60 | | | 5.61 |
| $^1A''$ [F] (V; n → π*) | | 92.7 | 1.67[a] | exFCI/AVDZ | AVQZ | 1.66 |
| streptocyanine-C1 $^1B_2$ (V; π → π*) | 0.347 | 88.7 | 7.13[a] | exFCI/AVDZ | AVQZ | 7.12 |
| $^3B_2$ (V; π → π*) | | 98.3 | 5.52 | exFCI/AVTZ | AVQZ | 5.52 |
| thioformaldehyde $^1A_2$ (V; n → π*) | | 89.3 | 2.22 | exFCI/AVTZ | dAVQZ | 2.20 |
| $^1B_2$ (R; n → 4s) | 0.012 | 92.3 | 5.96 | | | 5.99 |
| $^1A_1$ (V; π → π*) | 0.178 | 90.8 | 6.38[d] | CCSDTQ/AVDZ | dAVQZ | 6.34 |
| $^3A_2$ (V; n → π*) | | 97.7 | 1.94 | exFCI/AVTZ | dAVQZ | 1.94 |
| $^3A_1$ (V; π → π*) | | 98.9 | 3.43 | | | 3.44 |
| $^3B_2$ (R; n → 4s) | | 97.6 | 5.72[a] | exFCI/AVDZ | dAVQZ | 5.76 |
| $^1A_2$ [F] (V; n → π*) | | 87.2 | 1.95 | exFCI/AVTZ | dAVQZ | 1.94 |
| water $^1B_1$ (R; n → 3s) | 0.054 | 93.4 | 7.62 | exFCI/AVQZ | dAV5Z | 7.70 |
| $^1A_2$ (R; n → 3p) | | 93.6 | 9.41 | | | 9.47 |
| $^1A_1$ (R; n → 3s) | 0.100 | 93.6 | 9.99 | | | 9.97 |
| $^3B_1$ (R; n → 3s) | | 98.1 | 7.25 | | | 7.33 |
| $^3A_2$ (R; n → 3p) | | 98.0 | 9.24 | | | 9.30 |
| $^3A_1$ (R; n → 3s) | | 98.2 | 9.54 | | | 9.59 |

[a]exCI/*aug*-cc-pVDZ data corrected with the difference between CCSDT/*aug*-cc-pVTZ and CCSDT/*aug*-cc-pVDZ values. [b]CCSDT/*aug*-cc-pVTZ value. [c]exCI/*aug*-cc-pVDZ data corrected with the difference between CC3/*aug*-cc-pVTZ and CC3/*aug*-cc-pVDZ values. [d]CCSDTQ/*aug*-cc-

**Table 6. continued**

pVDZ data corrected with the difference between CCSDT/*aug*-cc-pVTZ and CCSDT/*aug*-cc-pVDZ values. $^e$For each state, we provide the oscillator strength and percentage of single excitations obtained at the CC3(FC)/*aug*-cc-pVTZ level. Unless otherwise stated, the TBE(FC)/*aug*-cc-pVTZ have been obtained directly from exFCI. For the basis-set-corrected TBE, we provide the method used to determine the starting value and the basis set used at the CC3(full) level to correct it. CC3(full)/*aug*-cc-pVTZ geometries and abbreviated forms of Dunning's basis set are systematically used. R, V and F stand for Rydberg, valence and fluorescence, respectively.

excitation of (n, n) → ($\pi^*,\pi^*$) nature.[156] Indeed, CC3 returns a 2.5% single excitation character only for this second transition, to be compared to more than 80% (and generally more than 90%) in all other states treated in this work (*vide infra*). For example, the notoriously difficult $A_g$ dark state of butadiene has a 72.8% single character.[30] For the A″ state of nitrosomethane, CC3, CCSDT and exFCI yield similar results, and the corresponding transition energies are slightly larger than previous CASPT2 estimates.[156] In contrast, the CC approaches are expectedly far from the spot for the (n, n) → ($\pi^*,\pi^*$) transition: they yield values significantly blue-shifted and large discrepancies between the CC3 and CCSDT values are found. For this particular state, it is not surprising that the exFCI result is indeed closer to the CASPT2 value,[156] as modeling double excitations with single-reference CC models is not a natural choice.

Finally for the shortest model cyanine, a molecule known to be difficult to treat with TD-DFT,[170] all the theoretical results given in Table 5 closely match each other for both the singlet and triplet manifolds. For the former, the reported CASPT2 (with IPEA) value of 7.14 eV also fits these estimates.[128]

**3.6. Theoretical Best Estimates.** We now turn to the definition of theoretical best estimates. We decided to provide two sets for these estimates, one obtained in the frozen-core approximation with the *aug*-cc-pVTZ atomic basis set, and one including further corrections for basis set and "all electron" (full) effects. This choice allows further benchmarks to either consider a reasonably compact basis set, therefore allowing to test many levels of theory, or to rely on values closer to the basis set limit. For the former set, we systematically selected exFCI/*aug*-cc-pVTZ values except when explicitly stated. For the latter set, both the "all electron" correlation and the basis set corrections (see Supporting Information for complete data) were systematically obtained at the CC3 level of theory and used d-*aug*-cc-pV5Z for the nine smallest molecules, but slightly more compact basis sets for the larger compounds. At least for Rydberg states, the use of d-*aug*-cc-pVQZ apparently delivers results closer to basis set convergence than *aug*-cc-pV5Z, and the former basis set was used when technically possible. The interested readers may find in Supporting Information the values obtained with and without applying the frozen-core approximation for several basis sets. Clearly, the largest amount of the total correction originates from basis set effects. In other words, "full" and frozen-core transition energies are typically within 0.01−0.02 eV of each other for a given basis set. The results are listed in Table 6 and provide a total of 110 transition energies. This set of states is rather diverse with 61 singlet and 45 triplet states, 60 valence and 45 Rydberg states, 21 n → $\pi^*$ and 38 $\pi$ → $\pi^*$ states, with an energetic span from 0.70 to 13.27 eV. Among these 110 excitation energies, only 13 are characterized by a single-excitation character smaller than 90% according to CC3. As expected,[30] the dominant single-excitation character is particularly pronounced for triplet excited states. Therefore, this set is adequate for evaluating single-reference methods, though a few challenging cases are incorporated. Conse-

quently, we think that the TBE listed in Table 6 contribute to fulfill the need of more accurate reference excited state energies, as pointed out by Thiel one decade ago.[30] However, the focus on small compounds and the lack of charge-transfer states constitute significant biases in the present set of transition energies.

**3.7. Benchmarks.** We have used the TBE(FC)/*aug*-cc-pVTZ benchmark values to assess the performances of 12 wave function approaches, namely, ADC(2), ADC(3), CIS(D), CIS(D$_\infty$), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSDT-3, CC3, CCSDT, and CCSDTQ. The complete list of results can be found in Table S6 in the Supporting Information. As expected, only the approaches including iterative triples, that is, ADC(3), CCSDT-3, CC3, and CCSDT are able to predict the presence of the doubly excited (n, n) → ($\pi^*,\pi^*$) transition in nitrosomethane (see Tables 5 and S6), but they all yield large quantitative errors. Indeed, the TBE value of 4.72 eV is strongly underestimated by ADC(3) (3.00 eV) and significantly overshot by the three CC models with estimates of 6.02 eV, 5.76, and 5.29 eV with CCSDT-3, CC3, and CCSDT, respectively. This 0.26 eV difference between the CCSDT-3 and CC3 values is also the largest discrepancy between these two models in the tested set. Obviously, from a general perspective, one should not use the standard single-reference wave function methods to describe double excitations. Therefore, the (n, n) → ($\pi^*,\pi^*$) transition of nitrosomethane was removed from our statistical analysis. Likewise, for the three lowest $^1A'$ excited states of formamide, strong state mixing — involving two or three states — are found at all levels of theory, making unambiguous assignments impossible. Consequently, they are also excluded from our statistics.

In Table 7, we report, for the entire set of compounds, the mean signed error (MSE), mean absolute error (MAE) root-mean-square deviation (RMS), as well as the positive [Max(+)] and negative [Max(−)] maximum deviations. A graphical representation of the errors obtained with all methods can be found in Figure 1. Note that only singlet states could be computed with the programs used for CCSDR(3) and CCSDT-3. As shown in Figure 1, CCSDTQ is on the spot with tiny MSE and MAE, which is consistent with the analysis carried out for individual molecules. With this method, the negative and positive maximum deviations are as small as −0.05 eV (singlet n → 4s Rydberg transition of thioformaldehyde) and +0.06 eV ($^1\Sigma_u^+$ Rydberg transition of dinitrogen), respectively. The three other CC models with iterative triples (CCSDT-3, CC3, and CCSDT) also deliver extremely accurate transition energies with MAE of 0.03 eV only. In agreement with the analysis of Watson and co-workers, we do not find any significant (statistical) differences between CCSDT-3 and CC3,[57] and although the former theory is formally closer to CCSDT, it does not seem more advantageous nor disadvantageous than CC3 in practice. The very good performance of CC3 is also consistent with the analysis of Thiel and co-workers, who reported a strong agreement with CASPT2,[32] as well as with the conclusion of Szalay's group

**Table 7. Mean Signed Error (MSE), Mean Absolute Error (MAE), Root-Mean Square Deviation (RMS), Positive [Max(+)] and Negative [Max(−)] Maximal Deviations with Respect to TBE(FC)/aug-cc-pVTZ for the Transition Energies Listed in Table S6[a]**

| method | no. of states | MSE | MAE | RMS | Max(+) | Max(−) |
|---|---|---|---|---|---|---|
| CIS(D) | 106 | 0.10 | 0.25 | 0.32 | −0.63 | 1.06 |
| CIS(D$_\infty$) | 106 | −0.01 | 0.21 | 0.28 | −0.76 | 0.57 |
| CC2 | 106 | 0.03 | 0.22 | 0.28 | −0.71 | 0.63 |
| STEOM-CCSD | 102 | 0.01 | 0.10 | 0.14 | −0.56 | 0.40 |
| CCSD | 106 | 0.05 | 0.08 | 0.11 | −0.17 | 0.40 |
| CCSDR(3) | 59 | 0.01 | 0.04 | 0.05 | −0.07 | 0.25 |
| CCSDT-3 | 58 | 0.01 | 0.03 | 0.05 | −0.07 | 0.24 |
| CC3 | 106 | −0.01 | 0.03 | 0.04 | −0.09 | 0.19 |
| CCSDT | 104 | −0.01 | 0.03 | 0.03 | −0.10 | 0.11 |
| CCSDTQ | 73 | 0.00 | 0.01 | 0.02 | −0.05 | 0.06 |
| ADC(2) | 106 | −0.01 | 0.21 | 0.28 | −0.76 | 0.57 |
| ADC(3) | 106 | −0.15 | 0.23 | 0.28 | −0.79 | 0.39 |

[a]All values are in eV and have been obtained with the aug-cc-pVTZ basis set.

who found it very close to CCSDT.[59] Nevertheless, CCSDT is not, on average, significantly more accurate than CC3 nor CCSDT-3. In other words, CCSDT is probably not a sufficiently accurate benchmark to estimate the accuracy of CCSDT-3 nor CC3. The perturbative inclusion of triples via CCSDR(3) stands as a good compromise between computational cost and accuracy with a MAE of 0.04 eV, a conclusion also drawn in the benchmark study performed by Sauer and co-workers.[51] These very small average deviations are related to the fact that the majority of our set is constituted of large single-excitation character transitions (see % $T_1$ in Table 6). Reasonably, we predict that they would slightly deteriorate for larger compounds.

For the second-order CC series, as expected, the errors increase when one uses more approximate models. Indeed, the MAE are 0.08, 0.10, and 0.22 eV with CCSD, STEOM-CCSD, and CC2, respectively. The magnitude of the CC2 average deviation is consistent with previous estimates obtained for Thiel's set (0.29 eV for singlets and 0.18 eV for triplets),[30] for fluorescence energies (0.21 eV for 12 small compounds),[174] as well as for larger compounds (0.15 eV for 0−0 energies of conjugated dyes).[11] Likewise, the fact that CCSD tends to overestimate the transition energies (positive MSE) was also reported previously in several works.[26,30,57−59,159,174] It can be seen that Nooijen's STEOM approach, which was much less benchmarked previously, delivers an accuracy comparable to CCSD, with a smaller MSE but a large dispersion. More surprisingly, we found a MAE smaller with CCSD than with CC2, which contrasts with the results reported for Thiel's set,[51] but is consistent with Kannar, Tajti and Szalay conclusion.[59] We attribute this effect to the small size of the compounds treated herein. Indeed, analyzing the TZVP values of ref 30., it appears clearly that CC2 more regularly outperforms CCSD for larger compounds.

As expected, the results for CIS(D$_\infty$) and ADC(2), two closely related theories,[6,144] are nearly equivalent, with only 4 (out of 106) cases for which a difference of 0.01 eV could be evidenced (Table S6). In addition, Table 7 evidences that ADC(2) provides an accuracy similar to CC2 for a smaller computational cost, whereas CIS(D) is slightly less accurate.

Both outcomes perfectly fit previous benchmarks.[10,11,48,144,174] Conversely, we found that ADC(3) results are rather poor with average deviations larger than the ones obtained with ADC(2) and a clear tendency to provide red-shifted transition energies with a MSE of −0.15 eV. This observation is in sharp contrast with a previous investigation which concluded that ADC(3) and CC3 have very similar performances,[48] though the ADC(3) excitation energies were also found to be, on average, smaller by 0.20 eV compared to their CC3 counterparts. At this stage, it is difficult to know if the large MAE of ADC(3) reported in Table 7 originates solely from the small size of the compounds treated herein. However, the fact that the CCSD MSE is relatively small compared to previous benchmarks hints that the choice of compact compounds has a non-negligible effect on the statistics.

Let us analyze the ADC(3) errors more thoroughly. First, ADC(3) deviations are quite large for all subsets (*vide infra*). Second, we have found that, for the 46 transition energies for which ADC(2) yields an absolute error exceeding 0.15 eV compared to our TBE, the signs of the ADC(2) and ADC(3) errors systematically differ (see Figure 2); i.e., ADC(3) goes in the right "direction" but has the tendency to overcorrect ADC(2). This is clearly reminiscent of the well-known oscillating behavior of the Møller−Plesset perturbative series for ground state properties. Third, this overestimation of the corrections pertains for the states in which the ADC(2) absolute error is smaller than 0.15 eV. Indeed, in those 60 cases, there are only 10 transitions for which the ADC(3) values are more accurate than their second-order counterpart. As a consequence, taking the average between the ADC(2) and ADC(3) transition energies yield rather accurate estimates with a MAE as small as 0.10 eV for the full set, half of the MAE obtained with the parent methods.

We provide a more detailed analysis for several subsets of states in Table S7 in the Supporting Information. Globally, we found no significant difference between the singlet and triplet transitions, though all CC models (except STEOM-CCSD) provide slightly smaller deviations for the latter transitions, in line with their larger single-excitation character. With the computationally lighter methods, CIS(D), CIS(D$_\infty$), ADC(2), and CC2, the MAEs are significantly smaller for the valence transitions (0.20, 0.15, 0.15, and 0.18 eV, respectively) than for the Rydberg transitions (0.32, 0.29, 0.29, and 0.26 eV, respectively). We also found MSE of opposite sign for valence and Rydberg transitions with CC2, which fits the results of Kannar and co-workers.[59] Surprisingly, ADC(3) gives 0.28 and 0.17 eV MAE for valence and Rydberg, respectively. All CC methods including triples deliver similar deviations for both sets of states. All methods provide smaller (or equal) MAE for the n → $\pi^*$ than for the $\pi$ → $\pi^*$ transitions, which was already found for Thiel's set.[30] The differences are particularly significant with CIS(D), CC2, STEOM-CCSD, and ADC(3) with errors twice larger for $\pi$ → $\pi^*$ than n → $\pi^*$ states. Finally, when considering the few states with %$T_1$ smaller than 90%, we logically found larger statistical errors with, for example, MAE of, e.g., 0.03 eV for CCSDTQ, 0.04 eV for CC3, and 0.06 eV for CCSDT-3.

**3.8. On the Use of a Compact Basis Set.** In several of the molecules considered here, we have found that adding corrections for basis set effects determined at the CC3 level to exFCI/aug-cc-pVDZ results effectively provides accurate estimates of the exFCI values directly determined with larger bases. Nevertheless, the dreadful scalings of both exFCI and
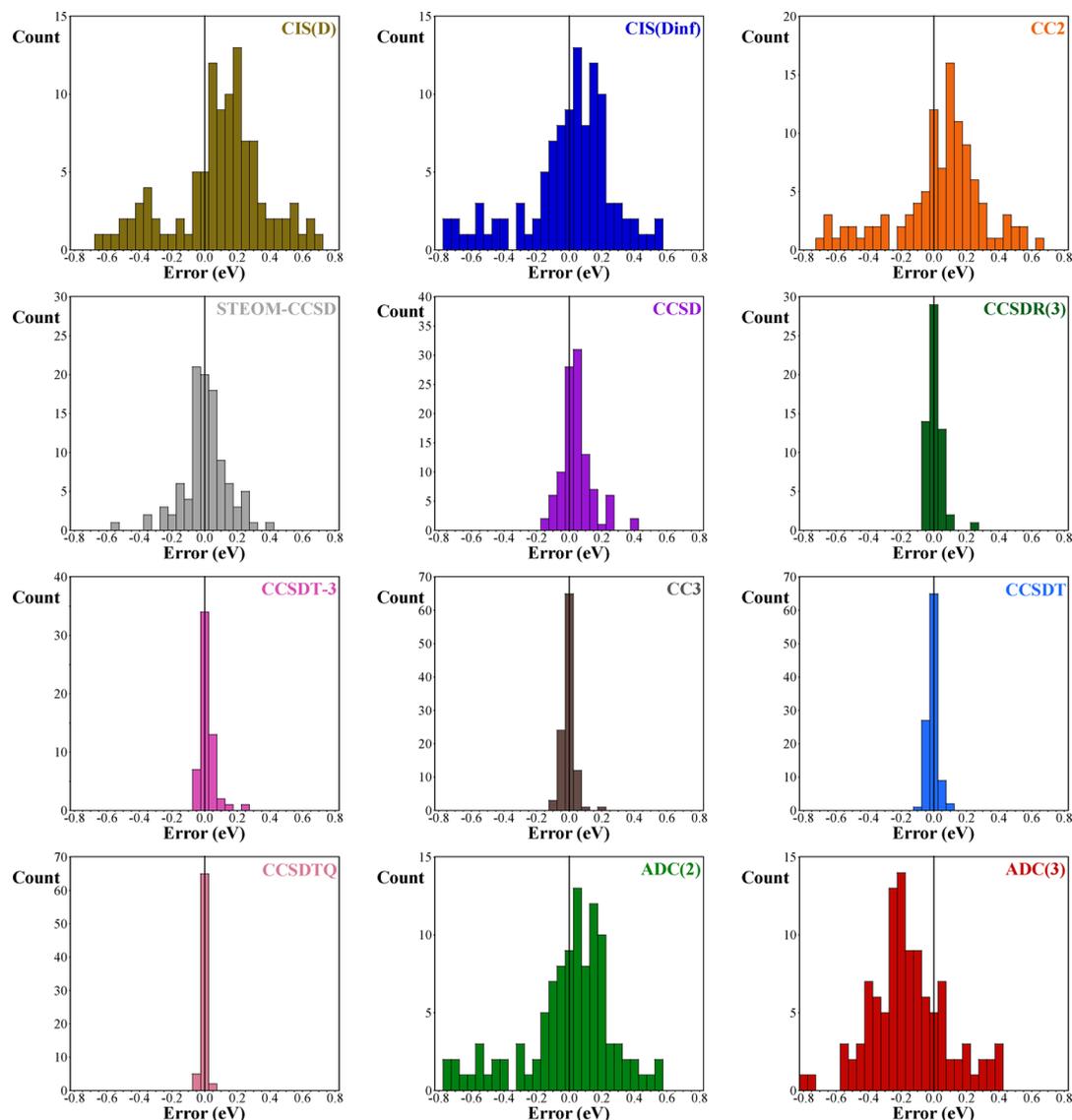
**Figure 1.** Histograms of the error patterns for several wave function methods compared to TBE(FC). Note the variation of scaling of the vertical axes.
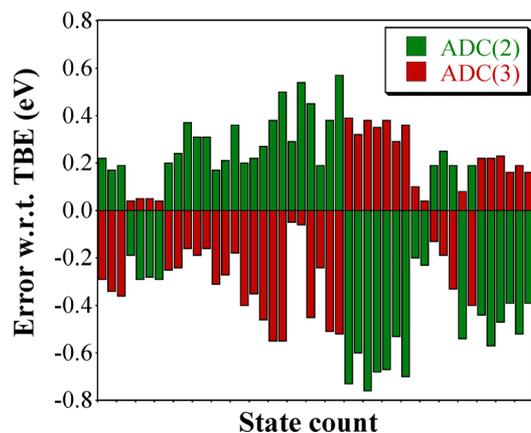


**Figure 2.** Comparison between the errors obtained with ADC(2) and ADC(3) [compared to TBE(FC)] for the 46 states for which ADC(2) yields an absolute deviation larger than 0.15 eV. All values are in eV.

CCSDTQ make the size of the atomic basis the central bottleneck. For this reason, we have tested the use of one of the most compact basis encompassing both diffuse and polarization functions, namely Pople's 6-31+G(d). We have performed CC3, CCSDT, and CCSDTQ calculations with this particular basis. The results are collected in the Supporting Information (Table S8). First, we compare the 6-31+G(d) results to those obtained with the same theoretical method in conjunction with the *aug*-cc-pVTZ basis set. As expected, large discrepancies are found with mean absolute deviation of 0.20, 0.19, and 0.25 eV, for CC3, CCSDT, and CCSDTQ, respectively.[175] Second, by adding the differences between the CC3/*aug*-cc-pVTZ and CC3/6-31+G(d) results to the CCSDT/6-31+G(d) and CCSDTQ/6-31+G(d) values, we obtained improved values. Such procedure yields very good estimates of the actual *aug*-cc-pVTZ results, as the MAE are down to 0.01 eV with no error larger than 0.04 eV for both CCSDT and CCSDTQ. This is a particularly remarkable result for Rydberg states that are extremely basis set dependent. For example, for the $^3A_2(n \rightarrow 3p)$ transition in water, the CCSDTQ/6-31+G(d) value of 10.34 eV is more than 1 eV

above its CCSDTQ/*aug*-cc-pVTZ counterpart (9.23 eV, see Table 1). Applying the CC3 basis set correction makes the final error as small as 0.03 eV. This composite methodology opens the way to calculations on larger systems without significant loss of accuracy.

## 4. CONCLUSIONS AND OUTLOOK

We have defined a set of more than 100 vertical transition energies, as close as possible to the FCI limit. To this end, we have used both the coupled cluster route up to the highest computationally possible order and the selected configuration interaction route up to the largest technically affordable number of determinants, that is here about few millions. These calculations have been performed on 18 compounds encompassing one, two or three non-hydrogen atoms, using geometries optimized at the CC3 level and a series of diffuse Dunning's basis sets of increasing size. It was certainly gratifying to find extremely good agreements between the results obtained independently with these two distinct approaches with typical differences as small as 0.01 eV between CCSDTQ and exFCI transition energies. In fact, during the course of this joint work, the two groups involved in this study were able to detect misprints or incorrect assignments in each others calculations even when the differences were apparently negligible. For the two diatomic molecules considered in this work, $N_2$ and CO, the mean absolute deviation between our theoretical best estimates and the "experimental" vertical transition energies deduced from spectroscopic measurements using a numerical solution of the nuclear Schrödinger equation is as small as 0.04 eV, and it was possible to resolve previous inconsistencies between these "experimental" values. A significant share of the remaining error is likely related to the use of theoretically determined geometries. Although, it is not possible to provide a definitive error bar for the 110 TBE listed in this work, our estimate, based on the differences between the two routes as well as the extrapolations used in the sCI procedure, is ±0.03 eV.

In another part of this work, we have used the TBE(FC)/*aug*-cc-pVTZ values to benchmark a series of 12 popular wave function approaches. For the computationally most effective approaches, CIS(D), CIS($D_\infty$), ADC(2), and CC2, we found average deviations of ca. 0.21−0.25 eV with strong similarities between the ADC(2) and CC2 results. Both conclusions are backed up by previous works. Likewise, we obtained the expected trend that CCSD overestimates the transition energies, though with an amplitude that is quite small here, likely due to the small size of the compounds investigated. More interestingly, we could demonstrate that STEOM-CCSD is, on average, as accurate as CCSD, and we were also able to benchmark the methods including contributions from triples using reliable theoretical references. Interestingly, we found no significant differences between CCSDT-3, CC3, and CCSDT, which all yield a MAE of 0.03 eV. In other words, we could not demonstrate that CCSDT is statistically more accurate than its approximated (and computationally more effective) forms, nor highlight significant differences between CCSDT-3 and CC3. We have observed that the use of perturbative triples, as in CCSDR(3), allows to correct most of the CCSD error. This evidences that CCSDR(3) is a computationally appealing method as it gives average deviations only slightly larger than with iterative triples. In contrast, for the present set of molecules, ADC(3) was found significantly less accurate than CC3, and it was showed that ADC(3) overcorrects ADC(2).

Whether this surprising result is related to the size of the compounds or is a more general trend remains to be confirmed.

As stated several times throughout this work, the size of the considered molecules is certainly one of the main limitations of the present effort, as it introduces a significant bias, e.g., charge-transfer over several Å are totally absent of the set. Obviously, the respective $O(N^{10})$ and $O(e^N)$ formal scalings of CCSDTQ and FCI do not offer an easy pathway to circumvent this limit. Nevertheless, it appears that performing exFCI calculations with a relatively compact basis, e.g., *aug*-cc-pVDZ or even 6-31+G(d), and correcting the basis set effects with a more affordable approach, e.g., CC3, might be a valuable and efficient approach to reach accurate vertical excitations energies for larger molecules, at least for the electronic transitions presenting a dominant single excitation character. Indeed, we have shown here that such basis set extrapolation approach is trustworthy. We are currently hiking along that path.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.8b00406.

> Basis set and frozen-core effects, geometries used, full list of transition energies for the benchmark section, additional statistical analysis, 6-31+G(d) results, and additional information for selected CI calculations (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Authors
*(P.-F.L.) E-mail: loos@irsamc.ups-tlse.fr.
*(D.J.) E-mail: Denis.Jacquemin@univ-nantes.fr.
### ORCID Ⓘ
Pierre-François Loos: 0000-0003-0598-7425
Denis Jacquemin: 0000-0002-4217-0708
### Notes
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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