# Theoretical 0−0 Energies with Chemical Accuracy

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ⓢ *Supporting Information*

ABSTRACT: Ab initio calculation of electronic excitation energies with chemical accuracy (ca. 1 kcal·mol^{-1} or 0.043 eV with respect to experiment) is a long-standing challenge in electronic structure theory. Indeed, the most advanced theories can, in practice, only be used to estimate vertical transition energies that cannot be measured experimentally, whereas the calculation of 0−0 energies requires excited-state structures and vibrations for both the ground and excited states, which drastically restrains the number of applicable methods. In this Letter, we present a composite computational protocol able to deliver chemically accurate theoretical 0−0 energies, with a mean absolute deviation of 0.018 eV for

a set of 35 singlet valence states. Such accuracy, achievable for the valence states of small- and medium-sized molecules only, allows pinpointing questionable experimental assignments with very high confidence and constitutes a step toward quantitative prediction of excited-state properties.
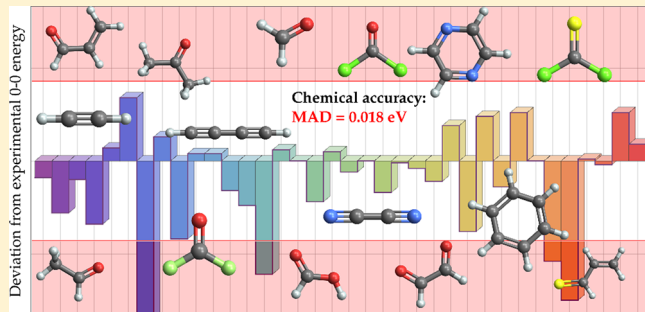
Advanced theoretical approaches and protocols able to accurately model electronic excited states (ESs) remain in the limelight as they are often required to interpret experiments. However, comparing experimental and theoretical results is far from straightforward. Indeed, the most directly accessible theoretical ES data, the vertical transition energy, has no clear experimental equivalent. Consequently, accurate vertical transition energies can be obtained by theoretical approaches only, with the notable exception of tiny compounds (e.g., diatomics) for which one can deduce experimental vertical transition energies from fully resolved vibronic spectra.[1] Several groups have designed comprehensive databases of accurate ab initio vertical energies[2−5] that can be used as reference to benchmark other theoretical methods. Unfortunately, they do not allow refined analyses of the experimental measurements. In contrast, experiment can deliver very accurate 0−0 energies (E^{0-0}) with uncertainties often smaller than 1×10^{-4} eV when a clear vibronic progression is found. However, from a theoretical point of view, computing 0−0 energies is no cakewalk. Indeed, for a given state, the 0−0 energy corresponds to the difference between the ES and ground-state energies at their respective geometrical minimum, the so-called adiabatic energy E^{adia}, corrected by the difference of zero-point vibrational energy (ZPVE) between the two states (ΔE^{ZPVE}). This means that computing 0−0 energies requires access to a suitable method for transition energies as well as for ES geometries and their corresponding vibrational corrections. This greatly limits the number of theoretical methods that one can use. Indeed, up to now, the vast majority of 0−0 energy calculations have been performed with time-dependent density functional theory

(TD-DFT) or wave function approaches (partly) incorporating contributions from the double excitations, i.e., the configuration interaction singles with a perturbative double correction [CIS(D)],[6] the second-order algebraic diagrammatic construction [ADC(2)],[7] and the coupled-cluster-based CC2 method.[8]

The first statistically significant comparison between experimental and TD-DFT 0−0 energies was performed in 2002 by Furche and Ahlrichs for 34 transitions in small molecules (mostly di- and triatomics).[9] They reported a mean absolute error (MAE) of 0.21 eV with TD-B3LYP. Two years later, Grimme and Izgorodina proposed a database of 32 gas-phase 0−0 energies and obtained MAEs of 0.19 and 0.27 eV with CIS(D) and TD-B3LYP, respectively.[10] Using a scaled-opposite-spin version of the former method, namely, SOS-CIS(D), Rhee and Head-Gordon could decrease the MAE to 0.13 eV for a very similar set of compounds.[11] In 2008, Hättig's group reported a MAE of 0.14 eV for Grimme and Izgorodina's set by computing CC2 E^{adia} on TD-B3LYP geometries.[12] For a subset of compounds, CC2 geometry optimizations were performed, and it was found that the results did not strongly changed for $\pi \rightarrow \pi^*$ transitions but significantly deteriorated for n $\rightarrow \pi^*$ transitions, compared to the hybrid CC2/TD-B3LYP protocol. This highlights the importance of the geometries in 0−0 calculations. More recently, the same group defined a new benchmark set of 66 gas-phase 0−0 energies, largely dominated by $\pi \rightarrow \pi^*$

Table 1. Theoretical Estimates of E^{adia}, ΔE^{ZPVE}, and E^{0-0} for All Compounds along with Experimental Values and the Corresponding Theoretical Errors[a]

molecule	state E^{0-0}	exp. E^{0-0}	theory E^{adia}	ΔE^{ZPVE}	E^{0-0}	error
acetaldehyde	$^1A''$ (n → π*)	3.691	3.752	−0.070	3.683	−0.009
acetone	$^1A_2$ (n → π*)	3.773	3.808	−0.063	3.745	−0.028
acetylene	$^1\Sigma_u^-$ (π → π*)	5.232	5.298	−0.077	5.221	−0.010
	$^1\Pi_u$ (π → π*)	6.710	6.811	−0.136	6.675	−0.034
acrolein	$^1A''$ (n → π*)	3.206	3.302	−0.089	3.213	+0.007
benzene	$^1B_{2u}$ (π → π*)	4.722	4.919	−0.162	4.757	+0.034
carbonylfluoride	$^1A_2$ (n → π*)	4.867	4.749	−0.061	4.688	−0.179
cyanoacetylene	$^1\Sigma^-$ (π → π*)	4.772	4.903	−0.118	4.784	+0.013
	$^1\Delta$ (π → π*)	5.483	5.559	−0.119	5.440	−0.042
cyanoformaldehyde	$^1A''$ (n → π*)	3.259	3.326	−0.063	3.263	+0.004
cyanogen	$^1\Sigma_u^-$ (π → π*)	5.629	5.719	−0.086	5.633	+0.004
	$^1\Delta_u$ (π → π*)	5.96	6.022	−0.078	5.944	−0.016
diacetylene	$^1\Sigma_u^-$ (π → π*)	4.329	4.429	−0.125	4.304	−0.024
	$^1\Delta_u$ (π → π*)	5.064	5.149	−0.146	5.003	−0.061
difluorodiazirine	$^1B_1$ (n → π*)	3.518	3.596	−0.072	3.524	+0.006
formaldehyde	$^1A_2$ (n → π*)	3.495	3.580	−0.085	3.495	+0.000
formic acid	$^1A''$ (n → π*)	4.639	4.714	−0.096	4.619	−0.020
formylchloride	$^1A''$ (n → π*)	4.062	4.135	−0.069	4.067	+0.005
formylfluoride	$^1A''$ (n → π*)	4.648	4.706	−0.063	4.643	−0.006
glyoxal	^1A_u (n → π*)	2.724	2.785	−0.060	2.725	+0.000
isocyanogen	$^1\Sigma^-$ (π → π*)	5.272	5.333	−0.077	5.256	−0.017
nitrosomethane	$^1A''$ (n → π*)	1.786	1.811	−0.026	1.786	−0.001
nitrosylcyanide	$^1A''$ (n → π*)	1.406	1.398	+0.004	1.402	−0.004
propynal	$^1A''$ (n → π*)	3.244	3.325	−0.092	3.233	−0.011
phosgene	$^1A_2$ (n → π*)	4.058	4.166	−0.089	4.077	+0.019
pyrazine	$^1B_{3u}$ (n → π*)	3.828	4.007	−0.216	3.790	−0.038
selenoformaldehyde	$^1A_2$ (n → π*)	1.691	1.776	−0.062	1.714	+0.024
tetrazine	$^1B_{3u}$ (n → π*)	2.248	2.321	−0.087	2.234	−0.014
thioacrolein	$^1A''$ (n → π*)	1.875	1.951	−0.050	1.901	+0.026
thiocarbonylbromide	$^1A_2$ (n → π*)	2.231	2.264	−0.033	2.231	+0.000
thiocarbonylchlorofluoride	$^1A''$ (n → π*)	2.685	2.663	−0.032	2.631	−0.054
thiocarbonylfluoride	$^1A_2$ (n → π*)	2.911	2.870	−0.034	2.836	−0.075
thioformaldehyde	$^1A_2$ (n → π*)	2.033	2.100	−0.066	2.034	+0.001
thioformylchloride	$^1A''$ (n → π*)	2.330	2.382	−0.054	2.328	−0.002
thiophosgene	$^1A_2$ (n → π*)	2.320	2.375	−0.030	2.346	+0.026
trifluoronitrosomethane	$^1A''$ (n → π*)	1.727	1.753	−0.013	1.736	+0.009

[a]All values are in eV. See Tables S-1 and S-2 in the SI for additional details.

transitions (63 out of 66). They obtained MAEs of 0.07 and 0.19 eV with CC2 and TD-B3LYP, respectively, the CC2 value being almost unchanged when ΔE^{ZPVE} was determined with TD-DFT.[13] In 2011, Send et al. collected a set of 119 gas-phase 0−0 values for molecules of various sizes and reported a MAE of 0.22 eV with TD-B3LYP, an average error that could only be slightly decreased when using ADC(2) or CC2.[14] There are also significant benchmarks comparing experimental and theoretical 0−0 energies for large molecules in the condensed phase.[15−20] Typically, the MAE obtained with TD-DFT ranges between 0.2 and 0.3 eV, depending on the selected exchange−correlation functional. The smallest deviations are obtained with optimally tuned hybrids.[18] Estimates of E^{adia} at the ADC(2) or CC2 level decreases the MAE to ca. 0.15 eV.[16,19−21] In short, as stated by Send et al., "None of the investigated methods reaches "chemical accuracy" of 0.05 eV."[14] The purpose of the present Letter aims at paving the way toward that goal for a significant set of compounds. To

this end, we were inspired by an early work of Kallay and Gauss,[22] who obtained E^{0-0} = 5.230 eV for the trans isomer of acetylene, in near perfect agreement with experiment (5.232 eV).[23] To achieve such a feat, these authors relied on extrapolation techniques in addition to very large basis sets and high-order coupled cluster expansions (up to CCSDTQ). Obviously, such an approach can also be applied to diatomics[24,25] but rapidly becomes beyond reach for medium-sized systems.

To take up the challenge of chemically accurate 0−0 energies, one needs high-quality geometries. This is particularly challenging for ESs as experimental data are often missing, preventing fair comparisons and hence the selection of a "cheap-yet-efficient" method. In a recent benchmark,[26] we have shown that CC2 and CCSD yield, respectively, too long and too short multiple bond lengths in the ES and that the inclusion of contributions from the triples, at least perturbatively, is mandatory when highly-accurate ES
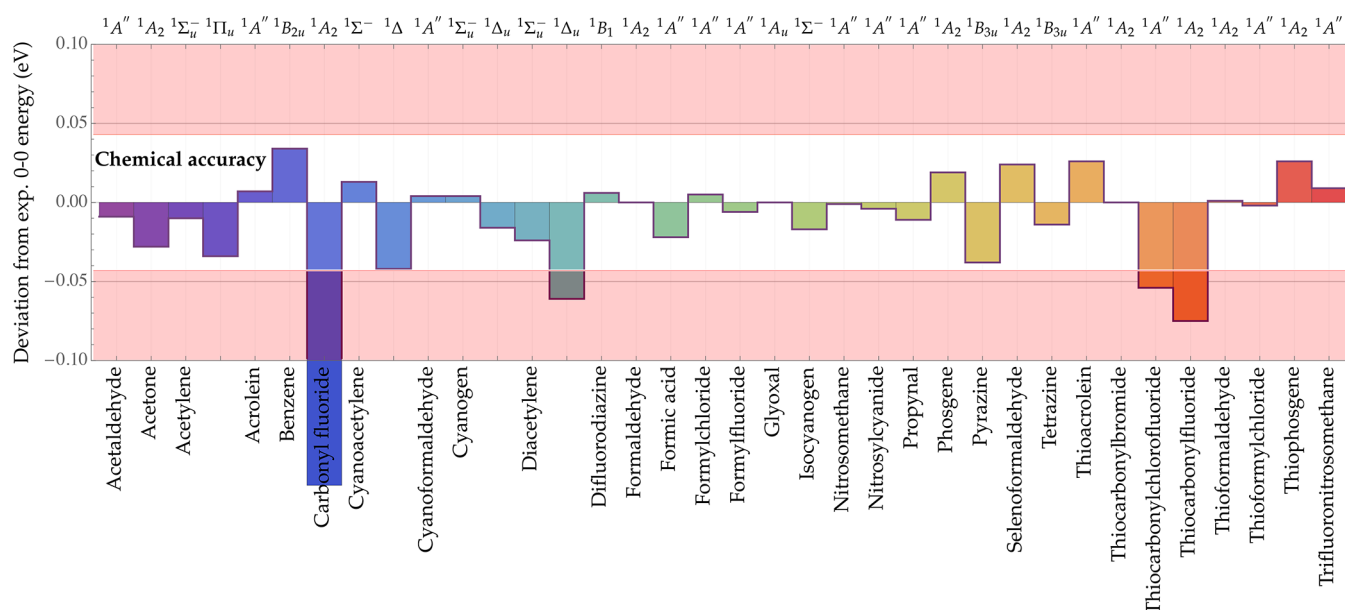
Figure 1. Deviation (in eV) from the experimental 0−0 energy of the theoretical 0−0 energy determined with the present computational protocol. See Table 1 for raw data.

Table 2. Comparison between the Original and Improved Protocols for a Selection of Compounds[a]

molecule	state	original protocol[b]			improved protocol[c]			exp.
		E^{adia}	ΔE^{ZPVE}	E^{0-0}	E^{adia}	ΔE^{ZPVE}	E^{0-0}	
acetylene	$^1\Sigma_u^-$ $(\pi \to \pi^*)$	5.298	−0.077	5.221	5.339	−0.111	5.228	5.232
	$^1\Pi_u$ $(\pi \to \pi^*)$	6.811	−0.136	6.675	6.810	−0.174	6.656	6.710
carbonylfluoride	$^1A_2$ $(n \to \pi^*)$	4.749	−0.061	4.688	4.776	−0.060	4.716	4.867
cyanoacetylene	$^1\Delta$ $(\pi \to \pi^*)$	5.559	−0.119	5.440	5.560	−0.105	5.455	5.483
cyanogen	$^1\Sigma_u^-$ $(\pi \to \pi^*)$	5.719	−0.086	5.633	5.712	−0.073	5.638	5.629
	$^1\Delta_u$ $(\pi \to \pi^*)$	6.022	−0.078	5.944	6.012	−0.064	5.948	5.96
diacetylene	$^1\Delta_u$ $(\pi \to \pi^*)$	5.149	−0.146	5.003	5.159	−0.149	5.010	5.064
formaldehyde	$^1A_2$ $(n \to \pi^*)$	3.580	−0.085	3.495	3.602	−0.093	3.509	3.495
nitrosomethane	$^1A''$ $(n \to \pi^*)$	1.811	−0.026	1.786	1.808	−0.014	1.794	1.786
selenoformaldehyde	$^1A_2$ $(n \to \pi^*)$	1.776	−0.062	1.714	1.790	−0.059	1.731	1.691
thioformaldehyde	$^1A_2$ $(n \to \pi^*)$	2.100	−0.066	2.034	2.112	−0.070	2.042	2.033

[a]All values are in eV. See the text for details. [b]CC3/aug-cc-pVTZ energies, CCSDR(3)/def2-TZVPP geometries, and B3LYP/6-31+G(d) ZPVE. [c]CC3/d-aug-cc-pVQZ energies, CC3/aug-cc-pVTZ geometries, and CCSD/def2-TZVPP ZPVE.

structures are desired. It was also previously shown that computing CC3 fluorescence energies on CC2 or CCSD geometries yields a MAE larger than 0.1 eV compared to the "full" CC3 values,[27] an error incompatible with our goals. We therefore select here the CCSDR(3)/def2-TZVPP approach to optimize both the ground-state and ES geometries. Using these structures, E^{adia} is determined with the de facto standard method for single-reference ES calculations, i.e., CC3/aug-cc-pVTZ. This choice is justified by two recent benchmarks demonstrating that CC3 yields vertical transition energies closer to CCSDT[4] and full CI ones[5] than other coupled cluster methods including approximate triples. Given that ΔE^{ZPVE} is known to be relatively insensitive to the selected method,[13,17,26] it is computed at the TD-B3LYP/6-31+G(d) level of theory. The selection of B3LYP is justified by recent work showing that this functional yields ES geometries in good agreement with the CC3 ones, at least for small compounds.[28]

Our results are listed in Table 1 for 36 valence states of 32 compounds, encompassing 4−12 atoms. The interested reader will find additional details, geometries, and experimental

references in the Supporting Information (SI). This set of compounds incorporates compact molecules and singlet states only, two limitations imposed by our methodological choices. However, it contains a large number of n → π* transitions involving strong density reorganizations. As one can see in the rightmost column of Table 1, chemical accuracy (absolute error smaller than 1.0 kcal.mol^{-1} or 0.043 eV) is reached for the vast majority of the cases (32 out of 36), a success achieved for the first time for a statistically significant set of 0−0 energies. Noticeably, the largest discrepancy appears for carbonylfluoride (−0.179 eV). A Dixon Q-test reveals that this point is an outlier with a 99% confidence level. Given that more advanced levels of theory do not significantly change the theoretical value (vide infra), one can reasonably assume that the experimental 0−0 value has been incorrectly assigned. Indeed, for this particular molecule, the 0−0 peak was not directly observed but its position was deduced from the vibronic progression, the lowest actually observed band being identified as presenting two quanta in the out-of-plane vibrational mode (ν_4').[29] By assuming that four quanta were

in fact present in this lowest-energy band, we deduce an experimental 0−0 energy of 4.691 eV (37 833 cm^{-1}), in much better agreement with theory. Though the errors are smaller, it seems possible that the values reported for thiocarbonyl-fluoride and thiocarbonylchlorofluoride may also deserve some additional experimental analyses.[30] By removing the 99%-confident outlier only (carbonylfluoride), we obtain a mean signed error, MAE, standard deviation, and root-mean-square deviation of −0.008, 0.018, 0.018, and 0.026 eV, respectively, with 32 out of 35 cases with errors smaller than 1 kcal·mol^{-1}. Therefore, we can safely and trustfully conclude that chemical accuracy has indeed been reached for this set of compounds, as illustrated in Figure 1.

Having reached chemical accuracy for a large data set, it is worth (i) checking if the present protocol significantly relies on error compensation and how close we are from "methodo-logical convergence" and (ii) assessing the limits of the present scheme.

To answer the former question, we evaluated several modifications of the present protocol (labeled as original protocol in Table 2). First, we selected a subset of compounds and applied an improved protocol by computing (i) the geometries at the CC3/aug-cc-pVTZ level, (ii) ΔE^{ZPVE} with EOM-CCSD/def2-TZVPP, and (iii) E^{adia} with a much larger atomic basis set containing additional diffuse functions [CC3/d-aug-cc-pVQZ]. Our results are displayed in Table 2 and clearly show that the changes are insignificant when one goes from the original to the improved protocol. Indeed, the mean absolute deviation between the two sets of results is 0.009 eV with a maximal change of 0.028 eV. By comparing the theoretical estimates to experiment, one also obtains similar MAEs, 0.019 and 0.023 eV for the original and improved protocols, respectively (in both cases, carbonylfluoride has been excluded from the statistics). Second, we evaluated relativistic effects for selenoformaldehyde and thiocarbonyl-bromide, the compounds encompassing the heaviest atoms (see the SI for details). The sum of the scalar-relativistic and spin−orbit coupling corrections on E^{adia} are −0.053 and −0.006 eV for the former and latter compounds, respectively. Because of the n → π* nature of these transitions, it makes sense that the relativistic corrections are larger when the heaviest atom bears the lone pair. For selenoformaldehyde, relativity brings the nonrelativistic E^{0-0} estimate of 1.731 eV (see Table 2) to 1.678 eV, a value even closer to experiment. Obviously, the relativistic contributions are therefore non-negligible for that compound, and it is likely the case for all molecules encompassing fourth-row (or higher) atoms in their chromophoric center. Third, for three compounds, we evaluated the impact of anharmonic terms on ΔE^{ZPVE} at the TD-B3LYP/6-31+G(d) level. For carbonylfluoride, cyanogen ($^{1}\Sigma_{u}^{-}$ state), and formaldehyde, these anharmonic corrections were found to be negligible with respective corrections of 0.000, −0.004, and −0.004 eV compared to the harmonic result.

To tackle the second question, that is, to probe the limits of our protocol, we modeled both nonvalence and triplet states. For the former family of states, we chose the two lowest ESs of silylidene, a rigid molecule, and methylamine, a more flexible compound. For silylidene, our estimates of 1.877 and 3.591 eV for transitions to 3p states are consistent with the experimental measurements at 1.876 and 3.634 eV, respectively (see Table S2 in the SI), though the error very slightly exceeds the 1 kcal·mol^{-1} limit for the second state. In contrast, for methylamine,

the theoretical E^{0-0} values of 5.301 and 6.465 eV, obtained with the same protocol as that in Table 1, considerably overestimate the experimental values of 5.179 and 6.219 eV (see Table S1 in the SI). This unsatisfying result is likely due to the well-known basis set sensitivity of high-lying Rydberg states. One could potentially reach chemical accuracy by employing diffuse-rich atomic basis sets for both the geometry optimization and the computation of the excitation energies. For instance, optimizing the geometries at the CCSDR(3)/aug-cc-pVTZ level allows one to obtain a theoretical E^{0-0} value of 5.165 eV for the lowest state of methylamine, in much better agreement with experiment. For triplet states, CCSDR(3) geometry optimizations are not technically feasible, and we used CC3/aug-cc-pVTZ geometries for the T_1 state of formaldehyde, thioformaldehyde, and selenoformaldehyde (see the SI for details). This led to E^{0-0} values of 3.092, 1.760, and 1.501 eV for the oxygen, sulfur, and selenium species, respectively, again within 1 kcal·mol^{-1} of the experimental values of 3.124, 1.799, and 1.509 eV.[31,32] As triplet transition energies are generally characterized by a strong single excitation character,[2] it is not surprising that a coupled-cluster-based protocol is adequate for such transitions.

Before concluding, we would like to discuss whether or not it is possible to design a computationally lighter protocol while still achieving chemical accuracy. To do so, we first computed frozen-core (FC) CC3 E^{adia} using the same geometries as in Table 1. The results collected in Table S-6 show that applying the FC scheme significantly increases the MAE (0.045 eV) compared to the "full" CC3 results (0.018 eV for the same set). This indicates that the small impact of the FC approximation found on vertical excitations (typically 0.01 eV)[5,33,34] is enhanced when considering different geometries. Second, we computed E^{adia} at the CCSDR(3), CCSD, and CC2 levels on the same geometries (see results in Tables S-7−S-9), and we found MAEs of 0.046, 0.207, and 0.078 eV, respectively. These orders of magnitude and accuracy rankings are rather typical of ES calculations for these methods with, in particular, larger errors with CCSD than with CC2.[2,27,35] Therefore, none of these computationally more effective approaches is able to achieve chemical accuracy for the present set of compounds.

In conclusion, we have determined the 0−0 energies for a set of 36 singlet valence states of organic molecules and showed that chemical accuracy can be achieved at the cost of using coupled cluster approaches including contributions from the triples for both the ground-state and ES energies and geometries. Indeed, the proposed protocol delivers an error smaller than 1 kcal·mol^{-1} in the vast majority of the cases presented here and a MAE of 0.018 eV or 0.415 kcal·mol^{-1}. By comparing CC3 and full CI vertical energies for many transitions, a very similar MAE (0.02 eV) was recently reported by us for valence states,[5] hinting that this error bar is indeed indicative of the accuracy of CC3 for single-reference valence states of small organic molecules. Thanks to the high accuracy that we have reached in the present study, we have been able to pinpoint a "questionable" experimental assignment. This would have been out of reach with lower-level methods as the deviation would have fallen within the typical theoretical error bar of TD-DFT and second-order methods. Of course, the present effort is a first (yet significant) step toward chemically accurate ab initio predictions of ES properties. Several challenges are still standing, especially to design tractable approaches for larger systems. In that respect, analytic gradients would be a valuable asset, and the same

holds for the inclusion of environmental effects at a similarly high level of accuracy.

COMPUTATIONAL DETAILS

The geometries were determined following the protocol described in ref 26. We first optimized the structures at the (EOM-)CCSD/def2-TZVPP level using the analytic gradients implemented in Gaussian 16[36] and confirmed their minimal nature by determining the Hessian at the same level of theory. Next, these optimized structures were used as starting points for the CCSDR(3) minimizations that have been performed numerically using Dalton.[37] The CC3 calculations were performed with the same program, whereas the B3LYP calculations were achieved with Gaussian 16.[36] During all calculations presented herein, all electrons were correlated, i.e., we did not apply the FC approximation. Dalton's default thresholds and procedures were used for all CC calculations.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.8b02058.

Details about ground and excited states and experimental references, CCSDR(3) Cartesian coordinates for all compounds, and details of the relativistic and triplet calculations (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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