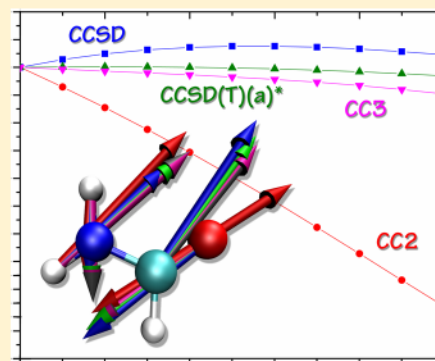


Accuracy of Coupled Cluster Excited State Potential Energy Surfaces

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ABSTRACT: The validation of the quality of the description of excited electronic states is of special importance in quantum chemistry as the general reliability of *ab initio* methods shows a much larger variation for these states than for the ground state. In this study, we investigate the quality of excited state energy gradients and potential energy surfaces on selected systems, as provided by the single reference coupled cluster variants CC2, CCSD, CCSD(T)(a)*, and CC3. Gradients and surface plots that follow the Franck–Condon forces are compared to the respective CCSDT reference values, thereby establishing a useful strategy for judging each variant's accuracy. The results reveal serious flaws of lower order methods - in particular, CC2 - in several situations where they otherwise give accurate vertical excitation energies, as well as excellent accuracy and consistency of the recently proposed CCSD(T)(a)* method.



1. INTRODUCTION

Characterization of excited electronic states by quantum chemical methods is of considerable interest and is generally more difficult than the ground state. Since experimental interpretations are also not straightforward for excited states, support by theoretical calculations is particularly important for spectroscopy. As the interests of spectroscopists are also turning toward larger and larger molecules, efficient methods for theoretical characterization are warranted.

However, many cost-effective computational approaches are unreliable or perform inconsistently for excited states and often require the user to have a high level of experience and advanced knowledge about the system being treated. Therefore, for accurate black-box excited state calculations, equation of motion (EOM)^{1–3} or Linear Response (LR)^{4–8} versions of coupled cluster (CC) theory^{9–11} are of interest. CC methods also offer the advantage of a hierarchical structure: truncation of the expansion can be done according to excitation level (singles, doubles, triples),¹⁰ but perturbational arguments can also be used^{7,8,12–16} to obtain cost-effective variants. Nowadays, a number of excited state CC approaches are available, several of which have become popular in application studies.

Many of these variants have been extensively benchmarked in the past years. Several studies by our group^{17,18} and others^{19–27} have addressed the quantification of errors for each method for vertical excitation energies and transition moments, sometimes revealing surprising behavior of popular techniques. The CC2-LR method,⁷ for example, was found to perform very badly for Rydberg-type excited states, while being exceptionally accurate for the valence type ones.¹⁸ A deeper investigation of CC2 done recently²⁸ found that the latter should be regarded as a result of fortuitous error cancellation, which does not occur for the Rydberg states. This also raised concern if one

may expect that the accuracy found for the vertical excitation energies of valence states also extends to the associated surfaces and energy derivatives.

The accuracy of excited state gradients and the quality of excited state potential energy surfaces (PESs) provided by a certain method is of high importance for judging the methods' overall reliability from the application perspective. In this study, we aim to do this by evaluating excited state gradients for several excited states of representative systems with single-reference coupled cluster methods and comparing them to accurate reference values. In addition, we also perform excited state PES scans via mass-weighted geometry steps in the direction of the forces acting at the Franck–Condon point, in order to characterize the accuracy of the PES itself.

In the following section, we review calculations made by several methods in detail, followed by the presentation of results for representative test systems. The paper concludes with a discussion of these findings.

2. METHODS

2.1. Coupled Cluster Methods for Excited States.

There are two general ways to extend coupled cluster (CC) theory for excited states: Linear Response (LR) theory^{4–8} and the Equation of Motion (EOM)^{1–3} extension of CC theory. These two families of methods have been reviewed in e.g. refs 29 and 30. The two strategies result in methods that are equivalent if the energy and, obviously, its derivatives are of interest.^{29,31} The differences between the two formalisms only impact molecular properties other than excitation energies (e.g., transition moments), but, as was confirmed in a recent

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benchmark study of our group,^{17,31} the magnitude of these differences is minor for typical systems. In the case of LR theory, CC2-LR⁷ has been derived as an approximation to CCSD-LR, while CC3-LR,⁸ as well as the CCSDR(T) and CCSDR(3)¹⁵ variants, approximates CCSDT-LR. In the case of EOM, the corresponding methods are EOM-CCSD(2)¹² and Partitioned EOM-MBPT(2)¹⁶ to approximate EOM-CCSD, as well as EOM-CCSD*,³² EOM-CCSDT-1,¹³ EOM-CCSDT-3,¹⁴ EOM-CCSD($\bar{T}$),¹⁴ EOM-CCSD(T),¹³ and EOM-CCSD(T)(a)*³³ to approximate EOM-CCSDT.³⁴ In the following sections, where we only focus on excitation energies and their gradients, the LR and EOM designations will be omitted for simplicity.

The very recent EOM-CCSD(T)(a)* method of Matthews and Stanton³³ incorporates the effect of triple excitations in a noniterative manner, via individual corrections to both the ground and the excited state energies. This approach scales as the seventh power of the system size and was found to provide a performance similar to the already available CCSDR(T) and CCSDR(3) methods for excitation energies. However, Matthews and Stanton found it to be promisingly accurate for excited states geometries and frequencies of various states of NO₃, NH₃, and C₂H₂, as well as for the potential energy surface of the S₁ state of acetylene.³³ In the latter case, CCSD(T)(a)* essentially reproduced the EOM-CCSDT potential surface as well as that obtained by the fully iterative EOM-CC3 and EOM-CCSDT-3 methods, while remaining a relatively inexpensive noniterative correction to EOM-CCSD. This finding encourages us to include this method in our tests and investigate if this is a general behavior of this method, which would make it a useful tool for calculating accurate excited state surfaces.

2.2. Excited State Gradients. Geometrical first derivatives of the excited state electronic energy at the ground state equilibrium geometry (also referred to as the Franck–Condon gradient) can be obtained analytically or numerically. For the former approach, implementations are available at CC2,⁷ CCSD,^{35,36} and CCSDT^{37,38} levels in the CFOUR³⁹ program package, while for the CCSD(T)(a)* and CC3 methods numerical gradients are used here. These latter calculations tend to be very expensive if the molecule has many internal degrees of freedom, and several excited states are investigated.

Franck–Condon gradients carry the first-order information about the excited state potential energy surfaces around the ground state equilibrium geometry. Gradient vectors can be visualized using arrow plots, i.e. with arrows placed on the atoms whose length and direction indicate that of the gradient's atomic component. If, however, the system possesses a nontrivial point group symmetry, the direction of the gradients can partially or even completely be determined by symmetry. In this case, the comparison of two gradients calculated with different methods visually by an arrow plot is generally not informative. Comparability also suffers if the system is large, and several methods provide similar Franck–Condon gradients - which is normally the situation if none of the approaches turns out to be exceptionally different from the others.

Comparing the length and direction of gradient vectors seems to be more favorable by numerical measures. As for the latter, the angle of two vectors *a* and *b* is defined as

$$\gamma = \cos^{-1} \left(\frac{\mathbf{a} \cdot \mathbf{b}}{\|\mathbf{a}\| \cdot \|\mathbf{b}\|} \right) \quad (1)$$

which, together with the gradient norms, provides a convenient measure of similarity that is useful here.

2.3. Surface Plots Following Franck–Condon Forces. Franck–Condon gradients differing in length or direction correspond to forces driving the system to different displacements or regions of the potential energy surface. As the system is likely to follow a similar path immediately after being excited to the state of interest, altering the geometry in a stepwise manner in the direction of these forces with steps proportional to the gradient would explore an important region of the PES. The definition of such a function is

$$E_n^i = E^i[\mathbf{R}_0 - n \cdot \mathbf{S} \cdot (\bar{\nabla} E^i)_{\mathbf{R}_0}] - E^0[\mathbf{R}_0] \quad (2)$$

where $E^i[\mathbf{R}]$ is the total electronic energy of state *i* at geometry *R*, $\bar{\nabla} E^i$ refers to the mass-weighted gradient of this state, and $\mathbf{R}_0$ is the ground state equilibrium geometry. Normally, with the right value of the step size *S* (in this study, a choice of $0.6 m_u^{1/2} E_h^{-1} a_0^2$ was found to work well) such an exploration proceeds toward a minimum on the excited state surface. If the surfaces are harmonic in the gradient direction, the locations of the minima on these curves are determined by the force constants. Excited state surfaces cannot, however, generally assumed to be harmonic, thus the exact locations of the minima and their agreement is of little importance. The actual parallelity of these curves, however, can indeed illustrate the differences between methods, highlighting their impact on the quality of the PES (and, potentially, on applications like excited state spectroscopy or molecular dynamics) without requiring any further input but the Franck–Condon gradient. Note that, by using steps proportional to the gradient length, direct comparison of these curves between different states and systems will not be useful due to the very different nature and regions of the PESs being explored.

Surface plots defined by eq 2 were obtained for all investigated states of the benchmark systems mentioned below. The comparison of these plots for lower level methods can be done by investigating their “divergence” from a reference curve (in the examples below, with the exception of guanine, the CCSDT result)

$$\bar{E}_n^i = E_n^i - E_n^{i,ref} - (E_0^i - E_0^{i,ref}) \quad (3)$$

where the second term shifts the curve to 0 for *n* = 0.

2.4. Test Systems. Keeping the focus on small and medium sized systems containing π -bonds and nitrogen heteroatoms, a series of molecules was chosen as a benchmark set: methanimine (formaldimine), formamide, cytosine, and guanine. To study Franck–Condon gradients, the low lying valence excited states of these systems were selected, the gradients of which were calculated at the CC2, CCSD, CCSD(T)(a)*, CC3, and, with the exception of guanine, CCSDT levels. The calculations were performed using the cc-pVDZ basis set of Dunning et al.,⁴⁰ except in the case of the first π - π^* state of methanimine where the ANO0 basis set^{41,42} has been used. The reference structures were optimized at the CCSD/cc-pVDZ level. The core electrons were excluded from the correlation treatment in all cases. All calculations have been performed using the CFOUR³⁹ program package.

3. RESULTS

3.1. Methanimine. The methanimine (formaldimine) molecule can be regarded as one of the smallest neutral systems that contain both a π -bond and a nitrogen lone pair,

thereby being a simple model for interactions present in important medium sized heterocycles. The three investigated valence excited states are of the $n-\pi^*$, $\pi-\pi^*$, and $\sigma-\pi^*$ type, respectively. In the cc-pVDZ basis set, the $\pi-\pi^*$ state shows a significant n-Rydberg contribution around the Franck–Condon region, which is known to be a source of unreliability for CC2.^{18,28} To eliminate this known phenomenon from the analysis, the ANO0 basis set has been applied to calculate this state, where this contamination is not present. The Franck–Condon gradients of all three states are shown in the arrow plots of Figure 1, while the vertical excitation energies and the numerical measures of the gradients according to eq 1 are summarized in Table 1.

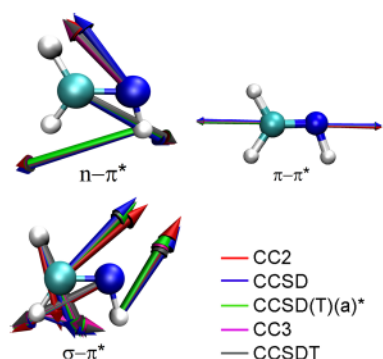


Figure 1. Mass-weighted excited state gradient vectors of methanimine (only components larger than $0.02 m_u^{-1/2} E_h a_0^{-1}$ are shown).

The excitation energies are in good agreement with our previous statistical findings,^{17,18} all triples methods are within a few 10^{-2} eV from each other, while from the doubles methods the CC2 vertical excitation energies are closer to CCSDT than those provided by CCSD. The latter exhibits its general tendency of overestimating excitation energies.¹⁷ The arrow plots of the Franck–Condon gradients show a high level of

agreement among the different methods, as is confirmed by the numerical measures of Table 1 as well. The nonparallelity with respect to CCSDT is up to 6 degrees, the latter shown by CC2 for the $\sigma-\pi^*$ state. This is also accompanied by an inaccuracy of the CC2 gradient magnitude for this state. For the lowest lying $n-\pi^*$ state, CCSD turns out to be the least accurate, deviating from all other methods with a nonparallelity of more than 4 degrees and a gradient 7% smaller than that of CCSDT. These values, however, still reflect a qualitatively acceptable description of this state.

The surface plots described in eqs 2 and 3 are shown in the left and right panels of Figure 2, respectively. The overall similarity of the curves among the benchmarked methods is also apparent here, and the triples methods are barely distinguishable from each other. For the $n-\pi^*$ state, CCSD does not seem to show the deviation that might be suggested by the gradient measures discussed above. However, one has to keep in mind that a significant difference in the driving gradient causes the system to explore different regions of the PES, thus the points on the surface plot may represent very different geometries. This is likely the case here where, in fact, none of the plots diverge more than 0.05 eV from CCSDT for any of the points. For the $\pi-\pi^*$ state, on the other hand, CCSD shows a quite large deviation from the other methods. Considering the fact that, for this state, all gradients are basically parallel (as shown in Table 1), this divergence must be attributed to the smaller length of the CCSD gradient. Although the difference compared to CCSDT is no more than five percent for the gradient length, the corresponding curves clearly deviate: the minimum on the CCSD plot is located at point $n = 5$ instead of point $n = 6$ seen for the other methods. For the $\sigma-\pi^*$ state, the CC2 curves show a pronounced deviation: here the CC2 gradient vector is substantially longer than those obtained with any other method, causing the energy curve to decrease more rapidly in the initial steps. The difference in energy between the Franck–Condon point and the minimum is, however, much larger: 1.19 eV for CC2 while about 1.0 eV for CCSD and the triples methods. This likely

Table 1. Vertical Excitation Energies (in electron volts) and the Length (in atomic units) and Angle (degrees) of Excited State Gradient Vectors of Methanimine

			angles/degrees				
	excitation energy	gradient length	CC2	CCSD	CCSD(T)(a)*	CC3	CCSDT
State 1 ($n-\pi^*$)							
CC2	5.65	0.1626	0.00	3.33	1.61	1.67	1.56
CCSD	5.54	0.1576		0.00	4.45	4.52	4.37
CCSD(T)(a)*	5.48	0.1681			0.00	0.09	0.56
CC3	5.49	0.1686				0.00	0.53
CCSDT	5.47	0.1692					0.00
State 2 ($\pi-\pi^*$)							
CC2	9.74	0.2927	0.00	0.99	1.06	1.06	0.91
CCSD	9.71	0.2843		0.00	1.07	1.09	0.99
CCSD(T)(a)*	9.51	0.3025			0.00	0.14	0.41
CC3	9.49	0.3031				0.00	0.31
CCSDT	9.52	0.2983					0.00
State 3 ($\sigma-\pi^*$)							
CC2	9.92	0.2606	0.00	4.74	4.65	5.26	6.12
CCSD	9.79	0.2423		0.00	2.01	2.53	3.18
CCSD(T)(a)*	9.69	0.2456			0.00	0.77	1.81
CC3	9.68	0.2429				0.00	1.07
CCSDT	9.65	0.2387					0.00

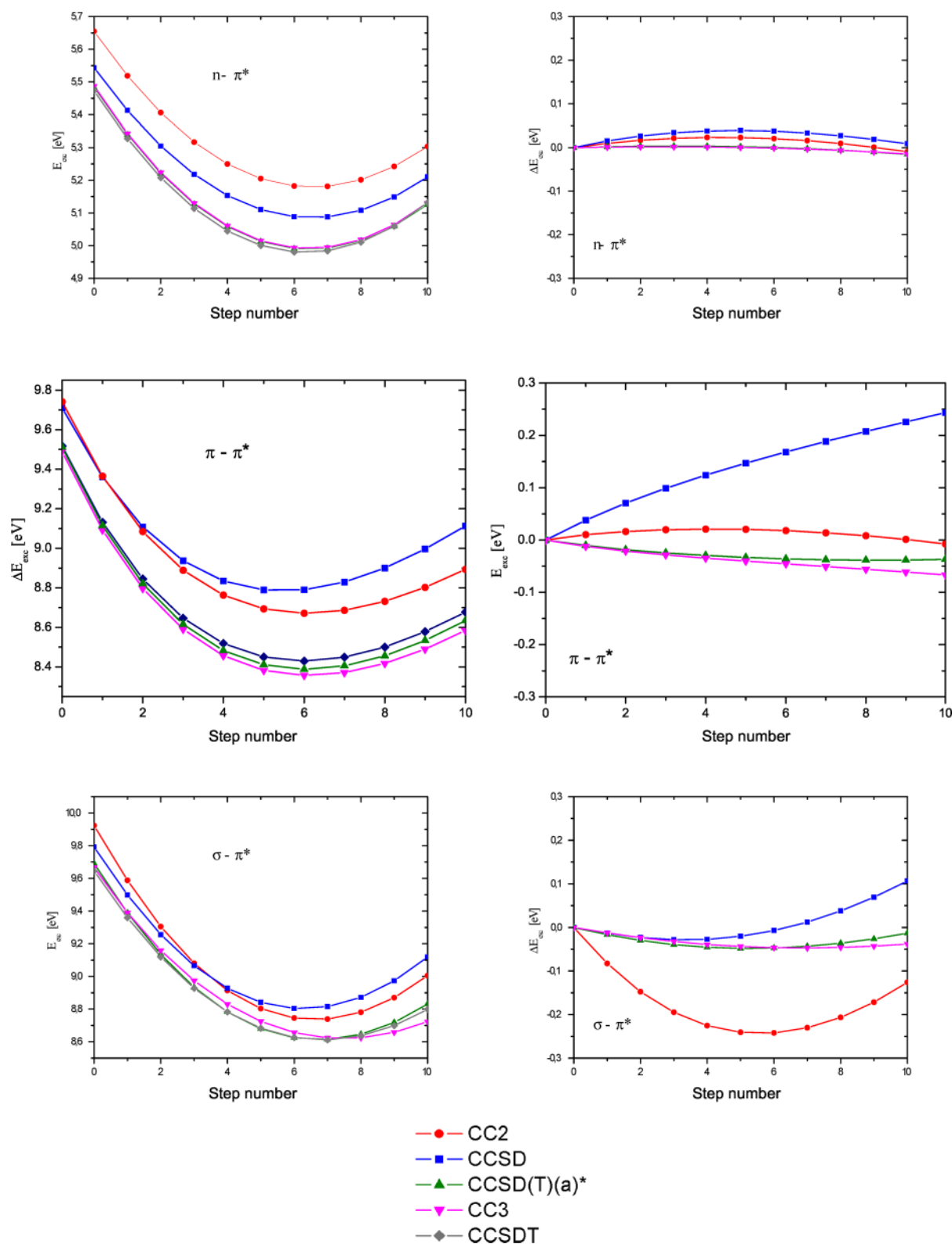


Figure 2. Potential energy curves following the gradient of low lying excited states of methanimine relative to the ground state equilibrium energy (left panels) and their divergence from the respective CCSDT curve (right panels).

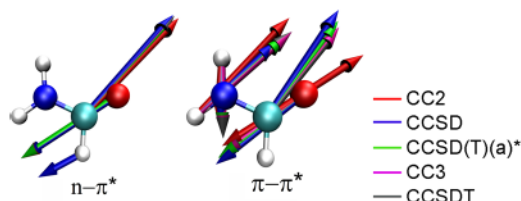
would be exhibited in a simulated spectrum by correspondingly long (CC2) and short (CCSD) vibrational progressions, relative to CCSDT.

3.2. Formamide. The two lowest lying valence excited states of formamide were investigated, one of $n-\pi^*$ and the other of $\pi-\pi^*$ type. The results are presented in Table 2 and

Figures 3 and 4. The latter state is known to be a challenge for the CCSD method due partially to valence-Rydberg mixing in this state. The vertical excitation energy is indeed very inaccurate, almost 0.3 eV above the CCSDT value. Surprisingly, however, the CCSD gradient does not seem to be comparably bad. Its length is, in fact, in very good

Table 2. Vertical Excitation Energies (in electron volts) and the Length (in atomic units) and Angle (degrees) of Excited State Gradient Vectors of Formamide

			angles/degrees				
	excitation energy	gradient length	CC2	CCSD	CCSD(T)(a)*	CC3	CCSDT
State 1 ($n-\pi^*$)							
CC2	6.00	0.3063	0.00	3.46	2.57	2.46	2.52
CCSD	5.87	0.2683		0.00	1.59	1.63	1.58
CCSD(T)(a)*	5.87	0.2858			0.00	0.11	0.70
CC3	5.87	0.2851				0.00	0.00
CCSDT	5.84	0.2850					0.00
State 2 ($\pi-\pi^*$)							
CC2	7.72	0.2427	0.00	21.31	18.59	19.36	16.00
CCSD	7.92	0.2019		0.00	4.98	13.70	6.80
CCSD(T)(a)*	7.74	0.2166			0.00	15.76	3.07
CC3	7.65	0.2105				0.00	0.84
CCSDT	7.64	0.2066					0.00

Figure 3. Mass-weighted excited state gradient vectors of formamide (only components larger than $0.02 m_u^{-1/2} E_h a_0^{-1}$ are shown).

agreement with that of the higher level methods, and the plots show a surface highly parallel with the CCSDT one. This indicates that despite the questionable Franck–Condon excitation energy, the potential energy surface of this $\pi-\pi^*$ state should itself be well described by CCSD. CC2 results, however, show completely opposite characteristics for this state: the vertical excitation energy is much better than the CCSD one, but the gradient is grossly wrong both in size and direction, some 16° askew from the respective CCSDT vector.

On the surface plots, both CC2 surfaces diverge from the CCSDT ones. The CCSD(T)(a)* method, on the other hand, performs very well for both states. In the case of the $n-\pi^*$ state, both the gradient and the surface plot are practically indistinguishable from CC3, and the $\pi-\pi^*$ surface shows excellent parallelity with the CCSDT one, clearly outperforming CC3 in this case.

3.3. Cytosine. Results for the two lowest $\pi-\pi^*$ and one $n-\pi^*$ excited states of cytosine are presented in Table 3 and Figures 5 and 6. As reported already in previous studies,^{17,18,43} CCSD systematically overestimates all excitation energies, while CC2 happens to be very accurate for this quantity, overestimating the $\pi-\pi^*$ and underestimating the $n-\pi^*$ excitation energies, respectively, by just ca. 0.1 eV.

The $\pi-\pi^*$ surfaces seem to be generally well described by all methods. CCSD(T)(a)* results are largely indistinguishable from CCSDT, and even CCSD provides surfaces much more parallel than might be suggested by the accuracy of the vertical excitation energy or the magnitude of the gradient vector: the divergence remains under 0.2 and 0.1 eV for the first and the second state, respectively. Although the points, as mentioned earlier, may represent different structures due to the variation of gradient directions and lengths, this high level of parallelity among all the curves suggests that the CCSD surfaces are still of good quality after all. The CC2 results are, at least in the

case of the first state, less convincing: despite the good accuracy of the gradient, the surface plot shows a remarkable divergence from CCSDT.

For the first $n-\pi^*$ state, results are much more interesting, as already suggested by the very intricate nature of the arrow plot in Figure 5. CCSD(T)(a)* seems to perform more similarly to CCSD than to CC3: the surface plots provided by the two methods show equally good agreement with CCSDT, while that from CC3 diverges significantly from the reference. The similarity is not reflected by the gradient vectors, where CCSD(T)(a)* seems to be the most accurate approximate method, and CCSD is clearly problematic. CC3 also shows a significant 11° angle with the CCSDT gradient, much larger than in the previous examples. This, along with the apparent revelations of the surface plots, clearly indicates a problem with CC3 for this state.

This, however, still looks pleasing in light of the rather catastrophic performance of CC2 for this state: the massive divergence of the surface plots exaggerates the already large error of the gradient. One should note that there is absolutely no indication of this unreliability of CC2 at the level of the vertical excitation energy; in fact, it is no more than 0.13 eV away from the CCSDT value.

3.4. Guanine. Three $\pi-\pi^*$ and two $n-\pi^*$ excited states of guanine were investigated, with the results presented in Table 4 and Figures 7 and 8. As CCSDT calculations for this system are computationally demanding, and CCSD(T)(a)* showed excellent accuracy and consistency in the previous examples, we use these results as a reference for the other methods. The orientation of the gradients for all $\pi-\pi^*$ states agree fairly well with the respective CCSD(T)(a)* results. Unlike cytosine, this also holds for the first $n-\pi^*$ state, with all gradients showing a very high level of parallelity. There is some variation in the gradient lengths, though. For the first two $\pi-\pi^*$ states as well as the first $n-\pi^*$ one, CC2 and CCSD show roughly the same deviation from CCSD(T)* but with opposite sign: the CC2 gradients are larger, and CCSD ones are smaller. For the third $\pi-\pi^*$ state, CCSD gives a significantly smaller gradient, while CC2 happens to agree very well with CC3. CC3 exhibits nearly perfect agreement with CCSD(T)(a)* for all four states.

The results for the second $n-\pi^*$ state show larger variations among the methods, however. CC2, despite providing an excellent vertical excitation energy, seriously overestimates the size of the corresponding gradient, with remarkable non-parallelity: the angle with the CCSD(T)(a)* gradient is as

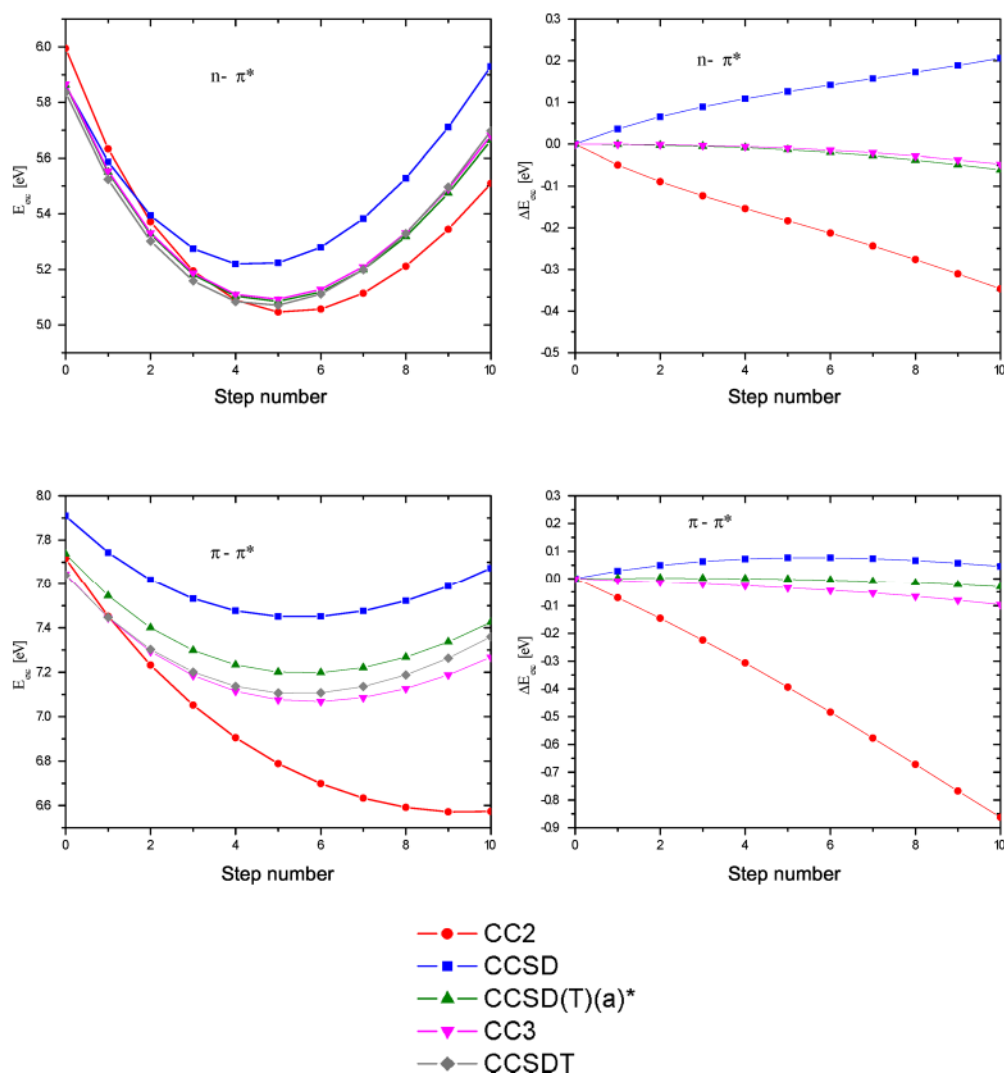


Figure 4. Potential energy curves following the gradient of low lying excited states of formamide relative to the ground state equilibrium energy (left panels) and their divergence from the respective CCSDT curve (right panels).

large as 39 degrees; and, for that matter, CCSD also does quite badly compared to the examples seen before. The gradient vector is - just like in case of the other states - shorter than the CCSD(T)(a)* one. Even CC3 shows a remarkable disagreement with CCSD(T)(a)* for this state. The differences are, however, still small compared to both CC2 and CCSD, and with the absence of a higher level reference value, it is not clear if either CC3 or CCSD(T)(a)* should be regarded as a certainly more accurate result.

The surface plots for the $\pi-\pi^*$ states generally reflect the agreement between the methods seen for the gradients. The CC3 surfaces exhibit excellent parallelity with CCSD(T)(a)* until to the minimum point, and even beyond that their divergence remains moderate. This even holds for the third state where the vertical excitation energy is underestimated by 0.15 eV. The CC2 and CCSD surfaces are fairly accurate as well, both predicting essentially the same minima for all states. This suggests that, despite the variation of the vertical excitation energies, all methods may provide a reasonable description of these states.

This is clearly not the situation for the $n-\pi^*$ states, though. The most vividly apparent feature seen on the respective panels of Figure 8 is the very bad performance of CC2, with

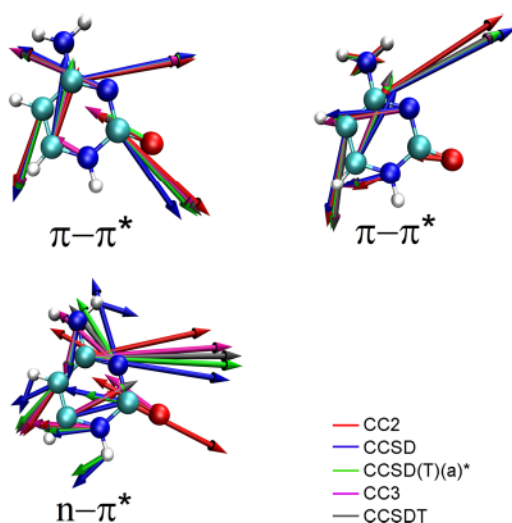
the surfaces diverging from the CCSD(T)(a)* ones by up to 0.5 eV. One should note that this poor performance occurs despite the very good accuracy of the vertical excitation energies. CCSD also diverges considerably for the first $n-\pi^*$ state but, at least, seems to show an accurate minimum point. For the second $n-\pi^*$ state, CCSD seems to be reliable, with the divergence remaining below 0.1 eV throughout the surface scan. The agreement of CC3 with CCSD(T)(a)* remains very good for the $n-\pi^*$ states as well, a noticeable divergence only shows up way beyond the minimum point on the first $n-\pi^*$ curve. This provides evidence for the contention that CCSD(T)(a)* provides a consistently reliable description of excited states, the quality of which are, more or less, in line with CC3.

4. DISCUSSION

Various ways to judge the quality of excited state gradients and potential energy surfaces were presented in the previous sections and illustrated by calculations with the CC2, CCSD, CCSD(T)(a)*, CC3, and CCSDT methods. All these ways of characterizing the accuracy and reliability of these techniques can thereby be regarded as a benchmark strategy to calibrate the performance of excited state methods.

Table 3. Vertical Excitation Energies (in electron volts) and the Length (in atomic units) and Angle (degrees) of Excited State Gradient Vectors of Cytosine

			angles/degrees				
	excitation energy	gradient length	CC2	CCSD	CCSD(T)(a)*	CC3	CCSDT
State 1 ($\pi-\pi^*$)							
CC2	4.96	0.2468	0.00	11.74	5.49	4.00	4.24
CCSD	5.11	0.2034		0.00	6.82	8.88	7.97
CCSD(T)(a)*	4.93	0.2268			0.00	2.32	1.01
CC3	4.86	0.2304				0.00	0.81
CCSDT	4.86	0.2267					0.00
State 2 ($\pi-\pi^*$)							
CC2	5.86	0.2172	0.00	9.92	6.12	6.67	7.14
CCSD	6.10	0.1961		0.00	6.67	7.92	7.57
CCSD(T)(a)*	5.86	0.2141			0.00	1.89	2.18
CC3	5.76	0.2129				0.00	1.31
CCSDT	5.75	0.2095					0.00
State 3 ($n-\pi^*$)							
CC2	5.15	0.2489	0.00	54.90	43.16	24.44	35.42
CCSD	5.53	0.1538		0.00	14.59	31.97	21.42
CCSD(T)(a)*	5.36	0.1635			0.00	19.16	8.20
CC3	5.25	0.1739				0.00	11.14
CCSDT	5.28	0.1628					0.00

Figure 5. Mass-weighted excited state gradient vectors of cytosine (only components larger than $0.02 m_u^{-1/2} E_h a_0^{-1}$ are shown).

Three dimensional arrow plots, although a nice way to depict gradients, do not seem to be very effective for comparisons between different methods. This can be mainly attributed to the fact that even minor rotations of the entire vector can cause large changes in the individual atomic contributions, thereby overemphasizing the perceived variation of gradients. For larger systems, the complexity of the gradient vector also poses difficulties, leading to very confusing figures in many cases.

The gradient angles and lengths, however, seem to be practical benchmarks if evaluated against a well chosen reference. The former can characterize the direction, and the latter the magnitude, of the Franck–Condon forces, obviously both being important in the whole picture. However, differences in the gradient lengths, as is shown by the surface plots, seem to be generally more sensitive measures of goodness than in their directions. Good examples of this are the CC2 gradient of the first $\sigma-\pi^*$ state of methanimine and

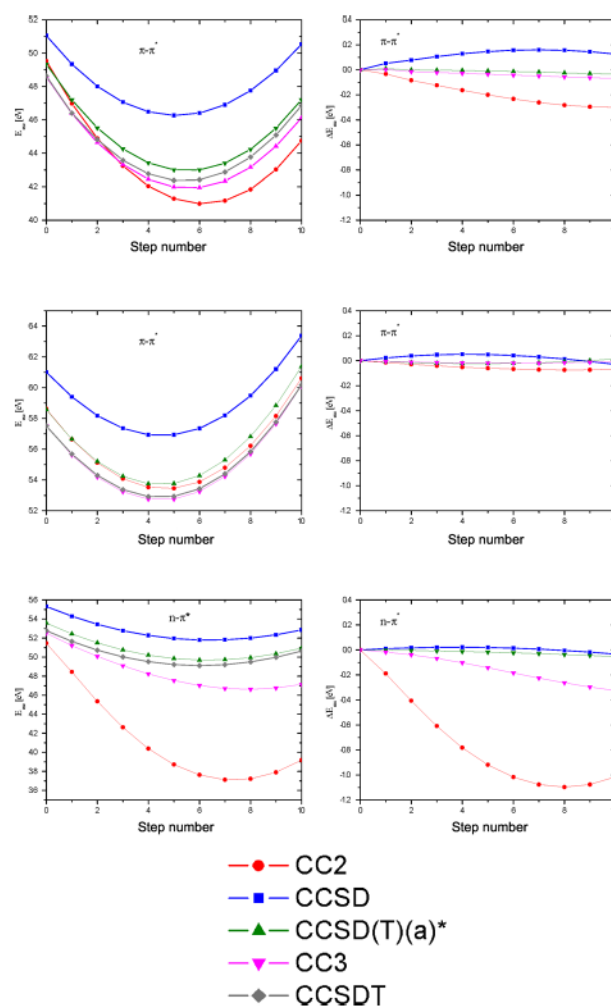
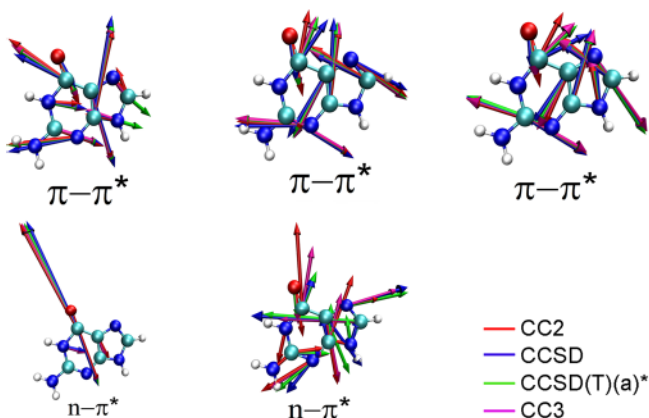


Figure 6. Potential energy curves following the gradient of low lying excited states of cytosine relative to the ground state equilibrium energy (left panels) and their divergence from the respective CCSDT curve (right panels).

Table 4. Vertical Excitation Energies (in electron volts) and the Length (in atomic units) and Angle (degrees) of Excited State Gradient Vectors of Guanine

			angles/degrees			
	excitation energy	gradient length	CC2	CCSD	CC3	CCSD(T)(a)*
State 1 ($\pi-\pi^*$)						
CC2	5.35	0.1982	0.00	11.44	5.14	6.39
CCSD	5.44	0.1697		0.00	8.43	6.60
CC3	5.24	0.1835			0.00	2.54
CCSD(T)(a)*	5.32	0.1843				0.00
State 2 ($\pi-\pi^*$)						
CC2	5.88	0.2077	0.00	9.35	5.27	4.94
CCSD	6.11	0.1798		0.00	7.30	6.55
CC3	5.81	0.1940			0.00	1.39
CCSD(T)(a)*	5.91	0.1957				0.00
State 3 ($\pi-\pi^*$)						
CC2	6.91	0.1843	0.00	11.90	5.88	6.57
CCSD	7.10	0.1498		0.00	6.96	6.04
CC3	6.72	0.1840			0.00	2.15
CCSD(T)(a)*	6.87	0.1788				0.00
State 4 ($n-\pi^*$)						
CC2	5.75	0.3173	0.00	9.11	3.60	5.21
CCSD	5.80	0.2626		0.00	6.54	4.94
CC3	5.69	0.2852			0.00	2.40
CCSD(T)(a)*	5.75	0.2835				0.00
State 5 ($n-\pi^*$)						
CC2	6.57	0.2339	0.00	47.84	25.18	38.52
CCSD	6.87	0.1705		0.00	24.34	11.90
CC3	6.61	0.1932			0.00	14.62
CCSD(T)(a)*	6.73	0.1823				0.00

Figure 7. Mass-weighted excited state gradient vectors of guanine (only components larger than $0.02 m_u^{-1/2} E_h a_0^{-1}$ are shown).

the CCSD result for the first $n-\pi^*$ state of guanine where, despite fairly accurate directions, the overall description is of bad quality due to the large differences in the gradient lengths.

The surface plots that follow Franck–Condon forces via equidistant mass-weighted steps proved effective in highlighting differences between methods and, especially, pointing out the occasional discrepancies in the description of certain surfaces by lower level methods. However, if the excited state possesses a minimum along these surface plots – as is the case for all systems investigated – the locations of these minima show only a minor variance among the methods, even in cases where there was a clear disagreement between the gradients. This is, however, not very surprising in light of the considerations mentioned in Section 2. The parallelity of

surfaces with the reference one seems to be, however, very informative about the description quality. Especially, plotting these results as divergences from the chosen reference (e.g., as differences from the reference surface, shifted to zero in the Franck–Condon point) seems very practical for comparisons. It should be kept in mind, however, that depending on the magnitude of Franck–Condon forces, these plots may explore regions quite far from the ground state equilibrium, potentially leaving the area where the single-reference description of the ground state can be considered reliable. In these regions, all results may be compromised to a certain extent, and any comparison between methods might become useless. Therefore, attention should be paid to the quality of the ground state wave function, and preferably no conclusions should be drawn from the furthest regions of these plots that lie way beyond the minimum point. The results in the first few, practically most important, points should be, however, reasonably modeled by these curves.

We note that one may regard the above analysis as a simplified and cost-effective alternative for a steepest-descent scan of the excited state PES between the Franck–Condon point and the actual excited state minimum – a very expensive procedure without analytic gradients being available for all methods.

The fact that excited state surfaces definitely need benchmarking via such strategies is underscored by our results that show that excited state gradients illustrate much larger discrepancies for lower level methods than vertical excitation energies do. Another important property revealed by these results is the correlation between the type of excited states and the overall reliability of their description via CC methods: while generally accurate gradients and surfaces are found for

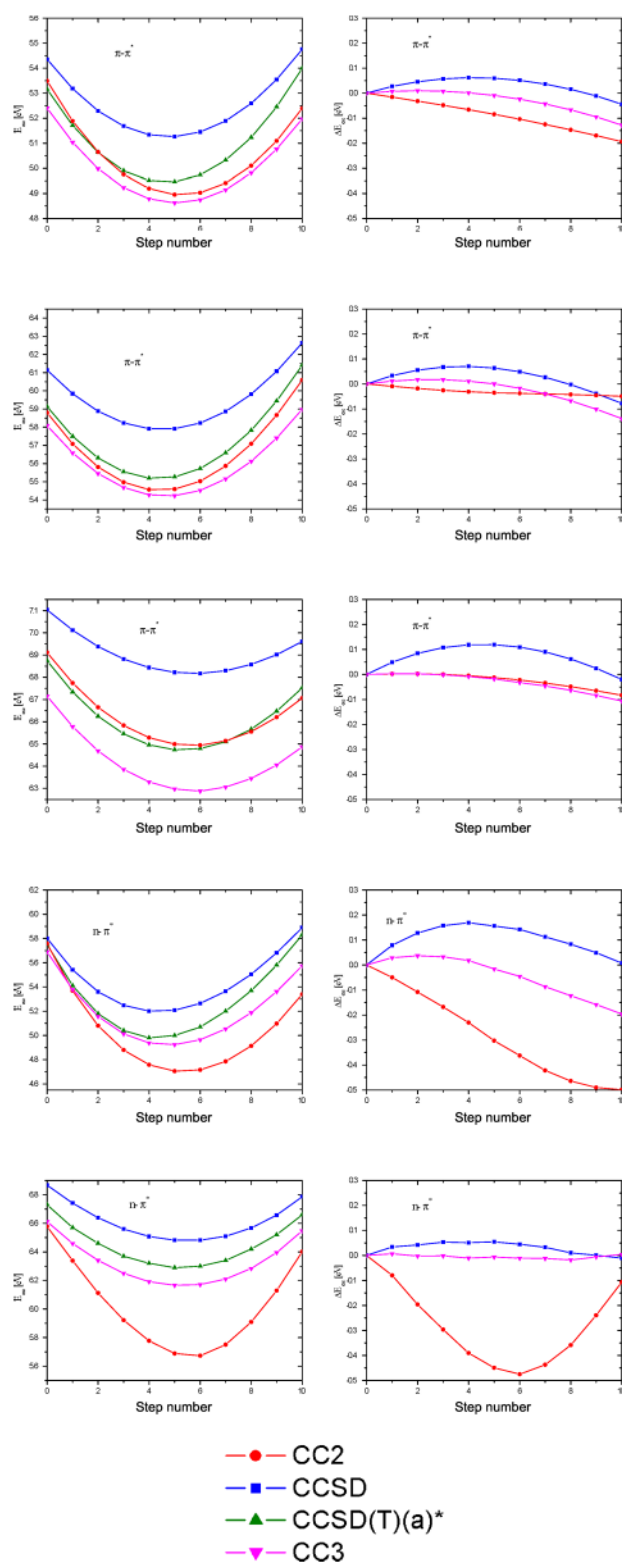


Figure 8. Potential energy curves following the gradient of low lying excited states of guanine relative to the ground state equilibrium energy (left panels) and their divergence from the respective CCSD(T)(a)* curve (right panels).

$\pi-\pi^*$ states, the results for $n-\pi^*$ type states tend to show a significantly larger level of inconsistency among the methods. For the $\pi-\pi^*$ states, the doubles methods CCSD and CC2 both seem to perform acceptably, and the CCSD surfaces barely diverge from the reference by more than a few 0.1 eV.

CC2 is somewhat less consistent, but the only worrisome result we find is that for the first $\pi-\pi^*$ state of formamide, where the Franck–Condon gradient is considerably overestimated. For $n-\pi^*$ states, on the other hand, our results clearly raise questions about the general reliability of doubles methods. CC2, in particular, can suffer from enormous errors, as is seen in excited state gradients and potential energy surfaces in many cases. Considering that CC2 is also known for its poor description of Rydberg type states,¹⁸ these findings raise serious questions about the intrinsic consistency of CC2 theory. The fact that the $\pi-\pi^*$ surfaces were apparently more accurate than $n-\pi^*$ ones should, however, probably not be regarded as an incentive for blindly trusting doubles methods for $\pi-\pi^*$ states, either: the consequence of the planar symmetry of our test molecules is that the two types of contributions were not allowed to mix in the excited state wave functions, which will not apply for larger systems with no point group symmetry.

5. CONCLUSIONS

The calculations performed in this study reveal several important facts about the reliability of coupled cluster excited state methods. Although the selected systems and states do not form a sufficient set for a rigorous statistical analysis - performing such analysis on a wider set (e.g., the Mülheim set¹⁹) is beyond the scope of this work -, they belong to those that received wide interest in recent excited state studies, and thus, important conclusions can be drawn from the above results.

The CCSD(T)(a)* technique was found to be very accurate and consistent throughout the study, basically providing the accuracy of the iterative CC3 method for a significantly lower cost. The very low divergence of the CCSD(T)(a)* surface plots from the higher level references - even in regions far from the Franck–Condon point - is a very pleasing finding for potential black-box applications of this method in the future and provides motivation for the development of analytic gradients for this approach. None of our results revealed any inherent flaw of this method; in fact, the surfaces show it to be a considerably more powerful method than what is suggested by the accuracy of excitation energies. This is in agreement with the findings of ref 33. In this sense, one may regard CCSD(T)(a)* as a cost-effective way to include the effect of triple excitations in excited electronic state surfaces.

Generally, the possibly most important conclusion of our study is that the quality of the excited state gradients and potential energy surfaces is definitely not related to that of the vertical excitation energy. CC2, in particular, was found to perform surprisingly badly for many states where it otherwise gives a very good excitation energy. This supports the conclusion of our previous studies,^{18,28} where the remarkable accuracy of CC2 valence excitation energies was shown to be a consequence of certain error cancellation phenomena. This apparently breaks down not only for Rydberg states but also for the derivatives of the excited state energy and, thus, potential energy surfaces. This definitely raises concerns about the reliability of many excited state molecular dynamics studies performed with CC2 or similar methods (including the popular ADC(2) technique⁴⁴), where the early nuclear motions are driven by forces acting in the Franck–Condon region.

We believe that the investigation techniques presented in this paper provide a robust and easily applicable way to

prevalidate these approaches for similar applications and thereby increase the reliability of their results.

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Notes

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