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Vibrational frequency scaling factors for correlation consistent basis sets and the methods CC2 and MP2 and their spin-scaled SCS and SOS variants

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We present scaling factors for vibrational frequencies calculated within the harmonic approximation and the correlated wave-function methods coupled cluster singles and doubles model (CC2) and Møller-Plesset perturbation theory (MP2) with and without a spin-component scaling (SCS or spin-opposite scaling (SOS)). Frequency scaling factors and the remaining deviations from the reference data are evaluated for several non-augmented basis sets of the cc-pVXZ family of generally contracted correlation-consistent basis sets as well as for the segmented contracted TZVPP basis. We find that the SCS and SOS variants of CC2 and MP2 lead to a slightly better accuracy for the scaled vibrational frequencies. The determined frequency scaling factors can also be used for vibrational frequencies calculated for excited states through response theory with CC2 and the algebraic diagrammatic construction through second order and their spin-component scaled variants. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4901725]

I. INTRODUCTION

The prediction of vibrational frequencies is one of the most important fields of applications for quantum chemical calculations. Many important advances have been made during the last decades to increase the accuracy and reduce the computational costs of vibrational frequency calculations. But still, for molecules with more than a dozen atoms it is very costly (in terms of computational resources) to use highly accurate correlated wavefunctions, such as coupled cluster singles and doubles with approximated triples (CCSD(T)), or to go beyond the harmonic approximation. Most vibrational frequency calculations for molecules with 10–200 atoms are today done with density functional theory (DFT) methods or, for electronically excited states, with time-dependent density functional theory. For slightly smaller molecules with up to 80 atoms second-order Møller-Plesset perturbation theory (MP2), the approximate coupled cluster singles and doubles model CC2, or other closely related second-order methods can be used in combination with the harmonic approximation.[1] Besides the latter approximation and the approximate treatment of electron correlation also the incompleteness of the one-electron basis set can limit the accuracy of such calculations. As early as 1981 it was, however, found that a large fraction of the errors in calculated vibrational frequencies consists of systematic shifts. Pople *et al.*[2] showed for Hartree-Fock calculations in the 3-21G basis set that calculated frequencies are about 12% higher than the experimental values and proposed to scale the frequencies computed with this method and basis set for better comparison with experiment with a scaling factor of 0.89. Hereby, the first method and basis set specific scaling factor for vibrational frequencies was introduced.

During the following decades a large variety of studies on scaling factors has been published. These scaling factors were fitted to test sets of experimental fundamental vibrational frequencies. Of great importance have been the studies by Radom and Scott[3] who optimized scaling factors for both semi-empirical and *ab initio* methods in combination with the split valence basis sets developed by Pople and co-workers,[2] which were standard during that time. In these studies, the F1 test set of 1066 experimental frequencies and 122 molecules involving first- and second-row elements has been introduced.[4] In follow-up studies, scaling factors for a large amount of method-basis set combinations have been optimized not only for vibrational spectra but also for zero point vibrational energies[5] and also their basis set dependence has been investigated.[5,6] Other studies dealt with the general accuracy of scaling factors.[7] Radom and co-workers also reported[3,5] scaling factors for the correlated wavefunction methods MP2, quadratic configuration interaction with singles and doubles (QCISD) with approximated triples (QCISD(T)), coupled cluster singles and doubles (CCSD), and CCSD(T), but as mentioned above, apart from MP2 these methods are still rarely used for vibrational frequency calculations because of their high computational demands. A study which focused on MP2 and some related methods for a small test was presented by Benoit and Domin in 2011 who reported scaling factors for MP2 and several MP2 related methods[8] which use the concept of spin-scaling introduced by Grimme[9] and Head-Gordon.[10] The accuracy of vibrational frequencies calculated with spin-component scaling (SCS)-MP2 has also been examined by Gerenkamp and Grimme who found that SCS-MP2 offers a significant improvement for the frequencies compared to MP2.[11]

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Almost all of these studies focused either on DFT or on single-reference wavefunction methods that are, apart from CCSD, only suitable for the electronic ground state. The main topic of this work is the determination of scaling factors for the CC2 model which has been introduced by Christiansen *et al.* in 1995[12] and is mainly used for calculations on excited states in the framework of coupled cluster response theory. Technically, closely related to CC2 is the algebraic diagrammatic construction through second order (ADC(2)) method,[13] which uses similar as MP2 the wavefunction amplitudes from first-order Møller-Plesset theory to describe the ground state. These two are nowadays the most commonly used correlated wavefunction methods for calculating 0-0 excitation energies and characterizing the structure of excited states. The computation of 0-0 excitation energies requires vibrational frequencies for the ground and the excited state. Optimized frequency scaling factors for CC2 and MP2 will thus also be useful for applications on excited states with these methods. Even though the errors in vibrational frequencies of excited states might behave somewhat different and are usually larger than for the ground state, one would use the same scaling factors, since in particular in larger molecules electronic excitations mostly effect only few molecular orbitals while most bonds remain unchanged compared to the ground state. Using scaling factors that have been optimized for the ground state to scale excited state frequencies has another advantage: Since there is no fitting to excited state frequencies, there is also no influence of large method specific errors for certain classes of excited states, e.g., charge transfer and Rydberg states or states with significant double excitation character. This would make the scaling factors strongly dependent on the character of the excited states in the test set.

The scaling factors optimized in this work are intended to scale calculated harmonic frequencies to experimental fundamental frequencies. Especially in combination with the resolution of the identity (RI) approximation for the two-electron repulsion integrals (ERIs) this approach shows a high performance for the calculation of excitation energies[14] and ground- and excited-state structures and vibrational frequencies.[1,15,16] Similar as for MP2, also for CC2 the molecular structure and thereby adiabatic excitation energies are significantly improved by spin-component scaling.[17] Therefore, we included the SCS- and the SOS-variants of the MP2 and CC2 models in our study. Of particular interest is the comparison between CC2 and MP2, since the two methods are closely related. Both treat electron correlation correct through second-order in the fluctuation potential. The main difference between MP2 and CC2 is that CC2 includes the singles excitations and their coupling to double excitations iteratively. The comparison between the two methods thus also illustrates the influence of single excitations on vibrational frequencies.

II. COMPUTATIONAL DETAILS

A. Test set

We use the F1″ test set which was developed by Merrick, Moran, and Radom[5] for the optimization of scaling factors for single reference wavefunction methods. It is a subset of the full F1 test set[4] where some molecules (NO_2, O_3, ClCCCl, ClCCH, and HCCCCH) which are problematic for single reference wavefunction methods have been removed. The F1″ test set consists of 1033 frequencies in molecules containing the elements H, B, C, N, O, F, Al, Si, N, P, S, and Cl. It has also been used by Merrick *et al.*[5] to fit scaling factors for the MP2 model. All our scaling factors were determined using this test set apart from the ones for CC2, SCS-CC2, and SOS-CC2 in the cc-pVQZ basis. For CC2 the CH_3COCH_3 molecule had to be removed from the test set due to optimization problems with the nearly free rotating methyl groups. The same occurred for the CH_3CCCH_3 molecule in the SCS-CC2 and SOS-CC2 models. Therefore, these test sets do not contain 1033 but 1009 vibrational frequencies. A list of the molecules which are contained in the test set as well as the experimental frequencies can be found in the supplementary material of Ref. 5.

B. Calculations

All structures have been optimized at the same level of theory on which also the Hessians and harmonic vibrational frequencies have been calculated. The latter were calculated with isotopically averaged atomic masses. We optimized scaling factors for the correlation consistent basis sets cc-pVDZ, cc-pVTZ, and cc-pVQZ developed by Dunning and Woon[18,19] and for the segmented contracted TZVPP basis set by Weigend *et al.*[20] For the evaluation of the two-electron repulsion integrals in the correlation part, the corresponding optimized auxiliary basis sets[20,21] have been used. With these it is assured that the errors introduced by the RI approximation in the molecular structures and frequencies are completely negligible.[15,22] All calculations have been done with the TURBOMOLE suite of programs,[23] in particular the direct SCF program dscf and the RI-MP2 and RI-CC2 program ricc2 with its analytic gradient[15] and Hessian[1] implementations. The vibrational frequencies of the open-shell molecules in the test set have been calculated using a numerical approach. For all non-hydrogen atoms, we correlated in accordance with the design principles[18–20] of the cc-pVXZ and TZVPP basis sets only the valence electrons and froze the occupation of the core orbitals ($1s^2$ for B–F and $1s^2 2s^2 2p^6$ for Al–Cl).

The scaling factors have been optimized as proposed in Ref. 5 by minimizing the sum of squared deviations

$$\Delta = \sum_i (\lambda \cdot \nu_{\text{theor,i}} - \nu_{\text{expt,i}})^2, \tag{1}$$

where $\nu_{\text{theor},\,i}$ are the calculated harmonic and $\nu_{\text{expt},\,i}$ the experimental fundamental frequencies (in units of cm^{-1}). Setting the derivative of Δ with respect to the scaling factor λ to zero results in the following expression for λ:

$$\lambda = \sum_i \frac{\nu_{\text{theor,i}} \cdot \nu_{\text{expt,i}}}{\nu^2_{\text{theor,i}}}. \tag{2}$$

Using the optimized λ, the residual for every frequency $\Delta_{\text{min},\,i}$ can be calculated according to

$$\Delta_{\text{min,i}} = (\lambda \cdot \nu_{\text{theor,i}} - \nu_{\text{expt,i}})^2, \tag{3}$$

TABLE I. Scaling factors for the different models. The values in parenthesis are the root-mean squared errors rms_{ov} (see text). MP2 values in the row marked with † are from Ref. 5 and repeated here for comparison. Results marked with ‡ were calculated with a modified test set which does not contain the CH_3COCH_3 molecule. Results marked with * were calculated with a modified test set which does not contain the CH_3CCCH_3 molecule.

	cc-pVDZ	cc-pVTZ	cc-pVQZ	TZVPP
CC2	0.9623 (65)	0.9617 (58)	0.9621‡ (56)	0.9615 (57)
SCS-CC2	0.9631 (57)	0.9614 (50)	0.9614* (49)	0.9601 (51)
SOS-CC2	0.9638 (55)	0.9614 (48)	0.9608* (48)	0.9607 (49)
MP2	0.9543 (49)	0.9542 (45)	0.9540 (44)	0.9536 (45)
MP2†	0.9538 (45)	0.9564 (41)		0.9528 (46)
SCS-MP2	0.9566 (47)	0.9553 (42)	0.9553 (43)	0.9542 (42)
SOS-MP2	0.9575 (45)	0.9550 (40)	0.9550 (40)	0.9541 (42)

which is used to determine the overall root-mean square errors (RMS)

$$\mathrm{rms}_{\mathrm{ov}} = \sqrt{\sum_i \frac{\Delta_{\mathrm{min},i}}{n}}, \tag{4}$$

where n is the number of vibrational modes in the test set.

III. RESULTS AND DISCUSSION

A summary of the scaling factors and the corresponding RMS errors of the scaled frequencies for CC2 and MP2 and their SCS and SOS variants is given in Table I. In general, we observe for both methods only a weak dependence of the results on the basis sets and the spin-component scaling. Slightly larger are the differences between CC2 and MP2 (*vide infra*).

A. MP2 model

For MP2, we observe that for the spin-scaled variants SCS-MP2 and SOS-MP2 the frequency scaling factors are slightly larger (i.e., closer to 1). Also the remaining RMS errors for SCS- and SOS-MP2 are slightly smaller than for the parent MP2 method. These findings are in line with earlier observations in the literature.[11] The results for the scaling factors and the RMS errors for the cc-pVQZ basis are very similar to those for the triple-ζ basis sets cc-pVTZ and TZVPP. Only the double-ζ basis cc-pVDZ leads to RMS errors which are about 10% larger.

Comparing the present results for MP2 with those obtained by Merrick *et al.*[5] we note that there are deviations between 0.0005 (cc-pVDZ) and 0.0022 (cc-pVTZ) in the scaling factors. The RMS errors we find are considerably higher than the ones found by Merrick and co-workers.[5] These differences are probably due to small differences in the structures and the treatment of the core orbitals. Although both studies used structures that were optimized at the same level of theory for which the vibrational frequencies were determined small differences in the structure can occur especially for molecules with more or less freely rotating methyl groups, such as but-2-yne.

B. CC2 model

The frequency scaling factors obtained for the CC2 model are even less dependent on the basis set than those obtained for MP2. Only the results for the RMS values increase significantly when the basis set quality is decreased to double-ζ. We observe that the RMS values are in all cases slightly larger than the ones found for MP2. This reflects that the iterative inclusion of single excitations makes the CC2 model more susceptible to strong correlation effects than MP2. The smallest RMS values are found for the cc-pVQZ basis while – in accordance with what one expects – the largest RMS error is obtained with the cc-pVDZ basis.

Also the scaling factors itself are larger for CC2 than for MP2. This is in line with the observations made in Ref. 15: CC2 provides for harmonic vibrational frequencies a similar accuracy as MP2, although the two methods differ somewhat in the trends of the deviations from experimental values. The additional inclusion of single excitations in CC2 leads to slightly larger occupations of non- and anti-bonding orbitals and thereby to longer bonds and lower vibrational frequencies, which in turn leads to slightly larger scaling factors.

A comparison of the scaled and unscaled frequencies for the TZVPP basis set is given in Fig. 1. It illustrates well how the scaling moves the frequencies in most cases closer to the experimental values. Significant modifications in the opposite direction are seen for some experimental frequencies between 1000 cm^{-1} and 1500 cm^{-1} as well as between 2000 cm^{-1} and 2400 cm^{-1}. These are frequencies which are already underestimated by the unscaled calculated harmonic frequencies.

C. SCS- and SOS-MP2

The frequency scaling factors for the SCS-MP2 model are a little bit higher than the ones for regular MP2, but the corresponding RMS errors of the scaled frequencies are very similar. There is no difference between the scaling factors for the cc-pVTZ and the cc-pVQZ basis sets which indicates that at this level the basis errors are unimportant compared to the inherent errors of MP2. The TZVPP basis set gives similar results as the two larger Dunning basis sets, in particular for the RMS value. A comparison with the experimental values for both scaled and unscaled frequencies is shown in Fig. 2. The trends observed in this plot are very similar to those observed in Fig. 1. The findings for SOS-MP2 are very similar to those for the MP2 and SCS-MP2 models. Compared to SCS-MP2 the basis set dependence is slightly larger. Nevertheless, the RMS values compare well with those for SCS-MP2 and MP2. The plot in Fig. 3 shows a comparison between the scaled and unscaled frequencies on the one side with experimental frequencies on the other side. It demonstrates that the spin-opposite scaling (SOS) and the SCS lead to very similar results. The slightly smaller RMS values for SOS-MP2 are probably a consequence of a slightly better robustness of SOS-MP2 with respect to strong correlation effects.[17]

D. SCS- and SOS-CC2

As for the SCS-MP2 model we find a very weak basis set dependence of the scaling factors for SCS-CC2. Even the

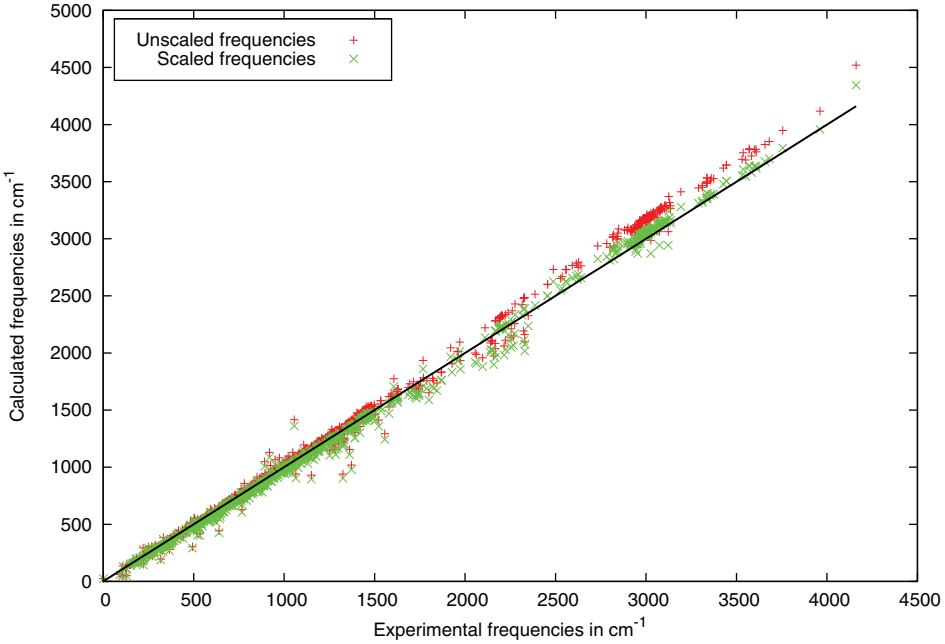


FIG. 1. Comparison of scaled and unscaled frequencies from CC2 using the TZVPP basis set. The solid black line is a linear function with slope 1.

variations with the individual basis sets show a very similar behavior as the ones for SCS-MP2. Since for the CC2 and SCS-MP2 methods the differences between the scaling factors for the cc-pVTZ and cc-pVQZ basis are so small that we can assume that they are essentially converged with respect to the basis set. Also for CC2 the behavior of the scaling factor for the SOS variant is similar to those for the spin-component scaled counterpart SCS-CC2. As already observed for MP2, the SOS variant leads to the smallest RMS values for the scaled frequencies, probably because spin-opposite scaling dampens strong correlation effects slightly more than spin-component scaling.[17]

IV. DISCUSSION

In summary, we find that the influence of spin-component scaling on the frequency scaling factors for CC2 and MP2 is relatively small. The trends are similar to those found in previous studies for other properties. Hellweg *et al.*, for example, compared ground state bond lengths for the SOS, SCS, and unscaled variants[17] of MP2 and CC2 and another study by Winter *et al.* benchmarked the CC2 model and its spin-scaled variants for 0-0 excitation energies which depend on vertical excitation energies and the equilibrium structures in the ground and excited states.[24] Both these studies showed that most spin-component scaled results are in between the

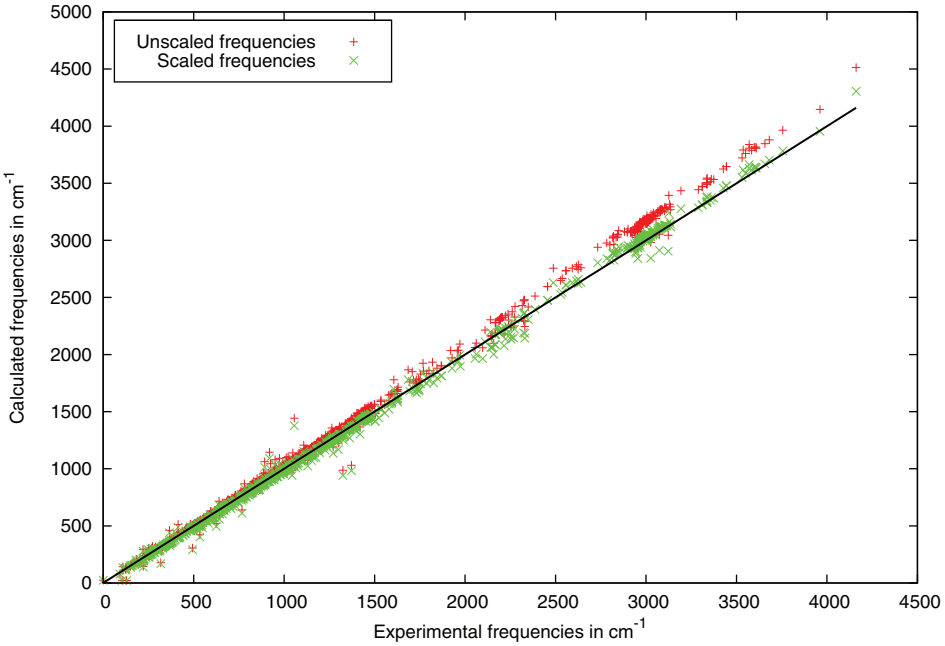


FIG. 2. Comparison of scaled and unscaled frequencies from SCS-MP2 using the TZVPP basis set. The solid black line is a linear function with slope 1.

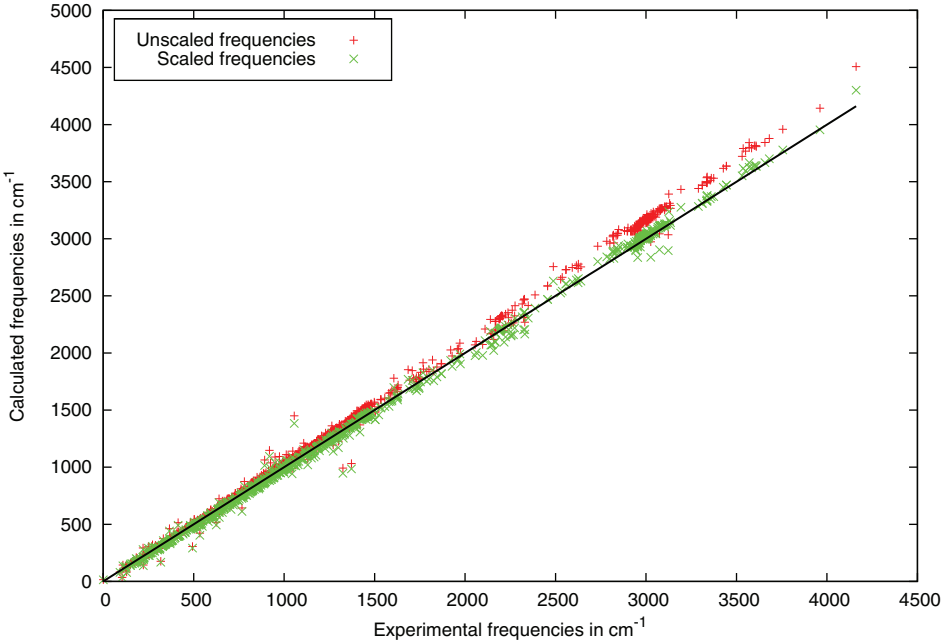


FIG. 3. Comparison of scaled and unscaled frequencies from SOS-MP2 using the TZVPP basis set. The solid black line is a linear function with slope 1.

unscaled and the scaled opposite spin results. For the frequency scaling factors, we observe such an ordering for MP2 with the cc-pVDZ basis and for CC2 with the cc-pVDZ and cc-pVQZ basis.

Concerning the remaining RMS errors of the scaled frequencies we can note that the errors for the CC2 methods are in general slightly larger than for MP2 and its variants. As mentioned above, this has its origin in the iterative treatment of the single excitations which makes CC2 more sensitive to strong correlation effects and causes a larger scattering of the results. For both methods, MP2 and CC2, we find that the SOS variant gives the smallest RMS errors and thus the most accurate results for the scaled vibrational frequencies

The exceptions from the expected order of the results of the spin-scaled variants for the frequency scaling factors can be explained by comparing calculated and experimental frequencies. An analysis of the calculated frequencies for the MP2 methods shows that especially for the cc-pVTZ and cc-pVQZ basis sets the number of frequencies with the order $\nu_{\text{MP2}} > \nu_{\text{SCS-MP2}} > \nu_{\text{SOS-MP2}}$ is about the same as the number of frequencies with the order $\nu_{\text{MP2}} < \nu_{\text{SCS-MP2}} < \nu_{\text{SOS-MP2}}$ while for the cc-pVDZ basis the order $\nu_{\text{MP2}} > \nu_{\text{SCS-MP2}} > \nu_{\text{SOS-MP2}}$ is clearly dominating.

The scaling factors for SCS-MP2 and SOS-MP2 in the cc-pVTZ and cc-pVQZ basis sets are very similar (deviations of 0.0003 in each case) and the deviation from the expected order is caused by averaging results for vibrational frequencies that decrease in the order $\nu_{\text{MP2}} > \nu_{\text{SCS-MP2}} > \nu_{\text{SOS-MP2}}$ and such that increase in the series $\nu_{\text{MP2}} < \nu_{\text{SCS-MP2}} < \nu_{\text{SOS-MP2}}$. A similar analysis applies to the CC2 results for the frequency scaling factors and explains the exceptions in the ordering.

For the cc-pVQZ basis set, Benoit and Domin have determined[8] the scaling factors of 0.9489, 0.9464, and 0.9465 for standard MP2, SCS-MP2, and SOS-MP2 models, respectively, which are considerably smaller than the results obtained in the present study and for (unscaled) MP2 by Merrick *et al.* (cmp. Ref. 5). The reason for the discrepancy is that Benoit and Domin[8] used a much smaller test set that consisted of only 18 diatomic molecules and five slightly larger molecules covering hydrogen and the second row elements and contained neither unsaturated hydrocarbons nor conjugated or aromatic systems.

Also Gerenkamp and Grimme[11] have assessed SCS-MP2 for the calculation of vibrational frequencies and found a considerable improvement of the results. They did, however, not evaluate any frequency scaling factors. Since they also used a different and smaller test, we cannot directly compare their results with those from the current study.

Anyway, the general picture obtained from results from the literature and from the present study is that for both, MP2 and CC2, spin-component scaling slightly improves the calculated vibrational frequencies. A part of the effect consists of a systematic scaling and is thus absorbed in the frequency scaling factors. Another part consists of a reduced scattering of the errors and leads to slightly smaller remaining RMS errors of the scaled frequencies. This effect is for the SOS variants larger than for the SCS variants. This opens an interesting perspective for applications of the low-scaling SOS variants of MP2 and CC2.

V. SUMMARY AND CONCLUSIONS

We determined scaling factors for vibrational frequencies calculated within the harmonic approximations with CC2 and MP2 and their spin-component scaled SCS and SOS variants. Results for the scaling factors and the remaining RMS errors of the scaled vibrational frequencies have been obtained for the double-, triple-, and quadruple-ζ basis sets of the generally contracted correlation-consistent cc-pVXZ basis set hierarchy and for the segmented contracted triple-ζ basis set TZVPP. We found that the influence of spin-component

scaling for both MP2 and CC2 is small but significant and that the largest improvement in the scaled frequencies (i.e., the smallest RMS errors) are obtained with the SOS variants. The vibrational frequencies obtained with CC2 and its spin-component variants SCS-CC2 and SOS-CC2 have slightly larger RMS errors as with MP2, but are still in the same ballpark. Anyway, the results for CC2 and its variants are mainly important for application on excited states, where the frequency scaling factors determined in this study can be applied for the improvement of calculated 0-0 transition energies. Similarly, the scaling factors determined for MP2 and its SCS and SOS variants can be used for the algebraic diagrammatic construction through second order,[13] which uses the first-order MP1 wavefunction for the ground state. In this respect, it is in particular encouraging that with SOS-CC2 and SOS-MP2 the remaining RMS errors in the scaled vibrational frequencies are even slightly smaller than for the SCS variants. SOS-CC2 and SOS-ADC(2) can be implemented with computational costs that scale only as $\mathcal{O}(\mathcal{N}^4)$ with the system size $\mathcal{N}$ while for the unscaled parent methods CC2 and ADC(2) the costs scale as $\mathcal{O}(\mathcal{N}^5)$. For both methods, it has already been shown that the SOS variants give 0-0 excitation energies that are as accurate as for the unscaled and SCS variants.

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[1] D. H. Friese, C. Hättig, and J. Koßmann, J. Chem. Theory Comput. **9**, 1469 (2013).
[2] J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. Defrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, Int. J. Quantum Chem. **20**, 269 (1981).
[3] A. P. Scott and L. Radom, J. Phys. Chem. **100**, 16502 (1996).
[4] J. A. Pople, A. P. Scott, M. W. Wong, and L. Radom, Isr. J. Chem. **33**, 345 (1993).
[5] J. P. Merrick, D. Moran, and L. Radom, J. Phys. Chem. A **111**, 11683 (2007).
[6] M. P. Andersson and P. Uvdal, J. Phys. Chem. A **109**, 2937 (2005).
[7] K. K. Irikura, R. D. Johnson, and R. N. Kacker, J. Phys. Chem. A **109**, 8430 (2005).
[8] D. Domin and D. M. Benoit, ChemPhysChem **12**, 3383 (2011).
[9] S. Grimme, J. Chem. Phys. **118**, 9095 (2003).
[10] Y. Jung, R. C. Lochan, A. D. Dutoi, and M. Head-Gordon, J. Chem. Phys. **121**, 9793 (2004).
[11] M. Gerenkamp and S. Grimme, Chem. Phys. Lett. **392**, 229 (2004).
[12] O. Christiansen, H. Koch, and P. Jørgensen, Chem. Phys. Lett. **243**, 409 (1995).
[13] J. Schirmer, Phys. Rev. A **26**, 2395 (1981).
[14] C. Hättig and F. Weigend, J. Chem. Phys. **113**, 5154 (2000).
[15] C. Hättig, J. Chem. Phys. **118**, 7751 (2003).
[16] A. Köhn and C. Hättig, J. Chem. Phys. **119**, 5021 (2003).
[17] A. Hellweg, S. A. Grün, and C. Hättig, Phys. Chem. Chem. Phys. **10**, 4119 (2008).
[18] T. H. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[19] D. E. Woon and T. H. Dunning, J. Chem. Phys. **98**, 1358 (1993).
[20] F. Weigend, M. Häser, H. Patzelt, and R. Ahlrichs, Chem. Phys. Lett. **294**, 143 (1998).
[21] F. Weigend, A. Köhn, and C. Hättig, J. Chem. Phys. **116**, 3175 (2002).
[22] F. Weigend and M. Häser, Theor. Chem. Acc. **97**, 331 (1997).
[23] Turbomole v6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
[24] N. O. C. Winter, N. K. Graf, S. Leutwyler, and C. Hättig, Phys. Chem. Chem. Phys. **15**, 6623 (2013).