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Accurate Harmonic/Anharmonic Vibrational Frequencies for Open-Shell Systems: Performances of the B3LYP/N07D Model for Semirigid Free Radicals Benchmarked by CCSD(T) Computations

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Abstract: Impressive growth of computer facilities and effective implementation of very accurate quantum mechanical methods allow, nowadays, the determination of structures and vibrational characteristics for small- to medium-sized molecules to a very high accuracy. Since the situation is much less clear for open-shell species, we decided to build a suitable database of harmonic and anharmonic frequencies for small-sized free radicals containing atoms of the first two rows of the periodic table. The level of theory employed is the CCSD(T) model in conjunction with triple- and quadruple-ζ basis sets, whose accuracy has been checked with respect to the available experimental data and/or converged quantum mechanical computations. Next, in view of studies of larger open-shell systems, we have validated the B3LYP/N07D model with reference to the above database: our results confirm previous suggestions about the remarkable reliability and reduced computational cost of this computational method. A number of test computations show that basis set extension has negligible effects and other density functionals (including last generation ones) deliver significantly worse results. Increased accuracy can be obtained, instead, by using CCSD(T) harmonic frequencies and B3LYP/N07D anharmonic corrections.

1. Introduction

Computational chemistry experiments have already been proven to provide highly accurate results for small molecules,[1−5] clearly demonstrating their potentiality as key tools for the prediction and understanding of spectroscopic properties of all kinds of molecular systems. At present, thanks to the progress in hardware and software, the a priori prediction of accurate low-lying vibrational levels of semirigid polyatomic molecules is becoming a viable task. It is now widely recognized that the computation of semidiagonal quartic force fields at the CCSD(T) (Coupled Clusters with Single, Double, and perturbative inclusion of Triple excitations)[6] level in conjunction with sufficiently large basis sets (at least of triple-ζ quality) followed by an effective second-order perturbative treatment usually provides results with an accuracy on the order of $10-15$ cm^{-1} for fundamental transitions.[7−19] Although perturbative vibrational treatment remains highly cost-effective for quite large systems, the unfavorable scaling of the CCSD(T) model with the number of active electrons limits the determination of quartic force fields to molecules containing at most five to six atoms. Additionally, a simple reduction of computational cost by combining correlated quantum mechanical (QM) methods with a small basis set should not be recommended, due to the quite unpredictable accuracy of the results. Thus,

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extension of computational studies to larger systems requires cheaper yet reliable electronic structure approaches.

Recently, several authors have reported anharmonic force fields for small- and medium-sized semirigid molecules computed by methods rooted in density functional theory (DFT).[20−25] Among the functionals tested, the hybrid ones provide satisfactory results when coupled to basis sets of at least double-ζ plus polarization quality supplemented by diffuse sp functions. An even more effective approach in terms of good accuracy, obtained at a computationally reduced cost, is based on the additivity of DFT anharmonic corrections to CCSD(T) harmonic force fields. This is well-known to further improve the agreement with experimental data.[26−30] The situation is much more involved for open-shell systems since experimental data are scarce and often of questionable reliability. Recently, we decided to start a comprehensive research project to extend the spectroscopic accuracy for studies of open-shell systems. To this purpose, some of the results available in the literature in this framework (HCO, HOC, HSiO, HOSi, HCS, HSC, HCCO, H_2CN, F_2CN, and F_2BO radicals) will be used here to build a representative set of reference force fields. Furthermore, a number of additional radicals have been purposely investigated for the present work (FCO, FSiO, FCS, FSC, NH_2, PH_2, $HOCl^+$, H_2BO, Cl_2CN, NH_3^+, PH_3^+, H_2CO^+, HCNN, and HNCN) in order to enlarge the benchmark set dimensions.

The present work has a 3-fold aim: (*i*) harmonic frequency results obtained by means of the B3LYP/N07D computational model, recently proposed for spectroscopic studies of free radicals, are validated by the comparison with corresponding computations at the CCSD(T) level; (*ii*) anharmonic corrections to vibrational frequencies computed from CCSD(T) quartic force fields are employed to confirm good performance of the B3LYP/N07D model in evaluating anharmonic contributions; (*iii*) the performances of last generation density functionals and basis set convergence are tested for both harmonic and anharmonic frequencies on a reduced set of radicals. Although, in order to facilitate comparison with CCSD(T) results, we have limited our benchmark set to the tri- and tetratomic radicals, we consider it significant, as molecules containing first- as well as second-row elements are included.

The manuscript is organized as follows. In the next section, all the computational details concerning the CCSD(T) and DFT calculations as well as the methodology employed are described. Then, the results are presented and discussed in the frame of the aims presented above.

2. Methodology and Computational Details

2.1. Coupled-Cluster Computations. The coupled-cluster (CC) computations have been performed at the CC level of theory with single and double excitations augmented by a quasi-perturbative account for triple substitutions [CCSD(T)].[6] The adequacy of the coupled-cluster model to treat the systems under consideration has been checked by means of the T_1[31,32] and D_1 (ROCCSD)[33] diagnostics, which provide values lower than 0.025 and 0.045, respectively, for all radicals considered. All CCSD(T) computations have been

carried out in conjunction with the correlation-consistent polarized (aug)-cc-pVnZ, with $n =$ T and Q, basis sets,[34,35] in the frozen core (fc) approximation. The CFOUR program package[36] has been employed, and the unrestricted Hartree−Fock (UHF) wave function has been used as a reference in the CCSD(T) computations.

Once the required geometry optimizations have been performed at the level of theory considered; anharmonic force field calculations have been carried out only for the main isotopic species of each radical under study. The harmonic part of the force field has been obtained using analytic second derivatives of the energy,[37] and the corresponding anharmonic force field has been determined in a normal coordinate representation via numerical differentiation of the analytically evaluated force constants as described in refs 11 and 38. Subsequently, the force field has been used to compute spectroscopic parameters, such as anharmonic frequencies, by means of the vibrational second-order vibrational perturbation theory (VPT2),[39] as implemented in the CFOUR package.[36]

2.2. Density Functional Theory Computations. Density functional theory computations have been performed with the B3LYP/N07D model, defined by a combination of the well-known B3LYP[40] density functional with the recently developed polarized double-ζ N07D basis set,[41−43] properly tailored for studying free radicals. This basis set has been constructed by adding a reduced number of polarization and diffuse functions to the 6-31G set (see refs 41 and 42 for details), leading to an optimum compromise between reliability and computer time.

All structures have been optimized using tight convergence criteria followed by computations of anharmonic frequencies by means of the VPT2 approach,[39,44] as implemented in the Gaussian package.[45] Semidiagonal quartic force fields have been evaluated by the numerical differentiation (with the standard 0.025 Å step) of analytical second derivatives. As VPT2 computations are sensitive to the proper treatment of Fermi resonances, it is crucial to automatically neglect nearly singular contributions (deperturbed computations). This is performed by effectively removing interactions in the second-order treatment, which are more properly treated in the first order. For this purpose, the VPT2 implementation[44] makes use of the criteria proposed by Martin and Boese,[23] implemented in an automated scheme that has already been shown to provide accurate results for at least fundamental bands.[46]

In addition to computations with the B3LYP functional, known to provide reliable predictions of vibrational properties,[20,21] it seemed important to check also the performance of other density functionals, in view of the recent developments aiming at improvement of long-range effects, i.e., the proper description of dispersion interaction or of the properties of excited electronic states. Concerning spectroscopic studies, an unsatisfactory description of vibrational frequencies computed by the M05(6)-2X[47,48] or LC-ωPBE[49] functionals has been found in the study of adenine,[50] in contrast to the accurate results obtained for functionals originating from the B3LYP one, such as B3LYP-D(M)[51,52] or CAM-B3LYP.[53] In this context, we decided to extend our benchmark to a broader range of recently introduced density

functionals, namely, M06,[48] the wB97 family,[54,55] and HSE06,[56] to check their performance in evaluating vibrational properties of open-shell systems. For the sake of completeness, the parameter-free PBE0 functional[57] has also been taken into consideration, and the basis set effect has been accounted for by comparison with the aug-cc-pVTZ[35] results.

All DFT computations have been performed employing the Gaussian suite of programs for quantum chemistry.[45]

2.3. Computations with Hybrid CCSD(T)/DFT Approach. As already mentioned in the Introduction, the hybrid CCSD(T)/DFT approach has also been applied to evaluate anharmonic frequencies. Such a methodology takes into account that CCSD(T) computations can be prohibitively expensive, even for medium-sized systems, whenever extended samplings of potential energy surfaces (PES) are required, whereas the main discrepancies between anharmonic frequencies computed at the CCSD(T) and B3LYP levels are related to the inaccuracies within the harmonic part.[26−28] In this respect, the hybrid CCSD(T)/DFT scheme[26−30] stands as a viable route to extend predictions of accurate anharmonic frequencies to relatively large systems.

In the present case, two possible approaches have been implemented. In the most simple one (DPT2), the harmonic frequencies computed at the CCSD(T) level are *a posteriori* corrected by anharmonic contributions ($\Delta\nu$) derived from VPT2 computations performed at the DFT level: $\nu_{CCSD(T)/DFT} = \omega_{CCSD(T)} + \Delta\nu_{DFT}$. Such an approximation has already been validated for several closed and open shell systems (see for instance refs 26−29). The second option is based on the introduction of the harmonic frequencies evaluated at the CCSD(T) level into the VPT2 computations along with the 3rd and 4th force constants obtained at the DFT level. Such an approach is available in the Gaussian package through the InDerAU and InFreq options and might significantly improve the quality of the results in difficult cases, i.e., when large discrepancies between harmonic frequencies computed at the DFT and CCSD(T) levels or Fermi resonances take place.

3. Results and Discussion

3.1. Equilibrium Structure. Evaluation of harmonic as well as anharmonic frequencies implies accurate prediction of molecular structures, which need to be computed at the corresponding level of theory. Therefore, in view of the connection between molecular structure and vibrational frequencies, we start our discussion by assessing the accuracy of the geometry parameters obtained at the computational levels subsequently applied to frequency evaluation. The results are organized as follows. In Table 1, optimized geometries for those radicals for which a systematic basis-set investigation at the CCSD(T) level is available are reported, while in Table 2 the structures computed at the CCSD(T) and B3LYP levels are compared to the available experimental data. For all the other radicals, molecular structures obtained at the CCSD(T) and B3LYP levels are collected in the Supporting Information.

Before proceeding in this discussion, general notes on the accuracy of CCSD(T) and B3LYP optimized geometries are deserved. Concerning coupled-cluster determinations, according to ref 58, the accuracy of molecular structures of closed-shell systems optimized at the CCSD(T) level in conjunction with the (aug)-cc-pVQZ basis sets is expected to be on the order of 0.002−0.004 Å for distances and 0.1−0.3° for angles. This accuracy range is not straightforwardly applicable to open-shell molecules as for them the situation is more involved from a theoretical as well as experimental point of view. The accuracy of CCSD(T)/(aug)-cc-pVQZ optimized geometries can be derived from the comparison to computed geometries for which extrapolation to the complete basis set limit (CBS) and core correlation (CV) effects are accounted for. This comparison is summarized for selected radicals in Table 1. On the basis of the results available in the literature[5,15,26,27,59,60] and those of Table 1, we can conclude that the overall accuracy is analogous to that of closed-shell systems. Going a little more into detail, we note that quadruple-ζ bases tend to provide geometrical parameters quite close to the CBS limit, in particular when only first-row elements are involved. The discrepancies are in general in the ranges 0.001−0.01 Å for distances and 0.01−0.1° for angles, where the larger values refer to the parameters involving second-row atoms. CV corrections range from 0.001 to 0.005 Å for bonds and from 0.01 to 0.1° for angles. Once again, larger values are observed when second-row elements are involved.

Concerning the accuracy of DFT structures, in benchmark studies performed to validate and develop the B3LYP/N07D computational model, it has been pointed out that the overall performance of the N07D basis set is comparable to that of the aug-cc-pVDZ one,[41] but with increased computational efficiency. Additionally, recent B3LYP/N07D studies performed on vinyl,[61] propyl, and phenyl radicals[62] showed agreements within 0.01 Å for C−C and C−H bond lengths, and 2° for angles with respect to highly accurate computational studies at the CCSD(T)[63,64] and multireference[64] levels in conjunction with extended basis sets. Further hints on the accuracy of geometric structures computed at the B3LYP/N07D level of theory can be obtained from the analysis of the data reported in Tables 1 and 2. Comparison with CCSD(T)/VQZ results shows that in most cases DFT slightly overestimates bond lengths by about 0.005−0.02 Å, while larger discrepancies, 0.026 and 0.034 Å, have been found for two difficult cases: the C−S and Si−O bonds, respectively. In contrast, C−N and B−O bond lengths are slightly (less than 0.01 Å) underestimated by DFT, whereas all angles agree within 1.5°. In view of the good accuracy of the CCSD(T)/VQZ structures, similar conclusions can be drawn from the comparison of B3LYP/N07D structures with most elaborated computational methodologies. In summary, B3LYP/N07D optimized geometries differ by about 0.01 Å and 1° from their CCSD(T) counterparts. Thus, B3LYP/N07D structures can be considered sufficiently accurate for studies not requiring extreme accuracy, and this is particularly encouraging for large systems for which expensive coupled cluster calculations are still unfeasible.

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Table 1. Basis-Set Effects on Equilibrium Geometrical Parameters Computed at the CCSD(T) Level[a]

molec./param.	B3LYP/N07D	CCSD(T)/VQZ	CCSD(T)/V5Z	CCSD(T)/V6Z	CCSD(T)/CBS	CCSD(T)/CBS+CV
HCS[b]						
R(CH)	1.0942	1.0877	1.0872	1.0872	1.0872	1.0854
R(CS)	1.5783	1.5660	1.5622	1.5610	1.5594	1.5554
∠HCS	131.61	131.99	132.21	132.24	132.28	132.49
HSC[b]						
R(SH)	1.3850	1.3671	1.3662	1.3662	1.3662	1.3639
R(CS)	1.6773	1.6517	1.6457	1.6442	1.6421	1.6370
∠HSC	103.72	102.89	103.01	103.04	103.08	103.06
NH$_2$[c]						
R(NH)	1.0312	1.0250	1.0248	1.0247	1.0246	1.0233
∠HNH	103.55	102.72	102.95	103.01	103.08	103.21
PH$_2$[c]						
R(PH)	1.4358	1.4186	1.4183	1.4183	1.4183	1.4155
∠HPH	91.7	91.87	91.88	91.88	91.88	91.81
H$_2$CN[d]						
R(CH)	1.1016	1.0947	1.0946	1.0946	1.0946	1.0933
R(CN)	1.2479	1.2493	1.2486	1.2482	1.2479	1.2451
∠HCN	121.78	121.16	121.11	121.10	121.09	121.10
H$_2$BO						
R(BH)	1.2132	1.2046	1.2046	1.2046	1.2046	1.2025
R(BO)	1.2861	1.2927	1.2915	1.2911	1.2909	1.2868
∠HBO	120.33	118.99	119.00	119.00	119.00	119.08
F$_2$CN[e]		(aug)				+(diff)
R(CF)	1.3177	1.3079 (1.3087)	1.3076	1.3074	1.3074	1.3056
R(CN)	1.2572	1.2565 (1.2570)	1.2560	1.2558	1.2557	1.2532
∠FCN	124.55	124.51 (124.52)	124.52	124.52	124.52	124.5
F$_2$BO[e]		(aug)				+(diff)
R(BF)	1.3311	1.3133 (1.3142)	1.3129	1.3128	1.3125	1.3102
R(BO)	1.3602	1.3640 (1.3648)	1.3636	1.3634	1.3632	1.3602
∠FBO	119.4	119.30 (119.29)	119.29	119.29	119.29	119.28
Cl$_2$CN						
R(CCl)	1.7508	1.7354	1.7242	1.7236	1.7232	1.7195
R(CN)	1.2458	1.2493	1.2491	1.2489	1.2488	1.2474
∠ClCN	122.04	122.00	121.88	121.88	121.88	121.88
NH$_3^+$[c]						
R(NH)	1.0281	1.0212	1.0210	1.0210	1.0210	1.0201
∠HNH	120.0	120.0	120.0	120.0	120.0	120.0
PH$_3^+$[c]						
R(PH)	1.4124	1.3974	1.3972	1.3972	1.3972	1.3946
∠HPH	113.15	113.21	113.21	113.21	113.21	113.24

[a] DFT results are given for comparison. [b] Ref 15. [c] Ref 70. [d] Ref 5. [e] Ref 27.

As far as the comparison with experiment is concerned, the results of Table 2 allow us to point out that equilibrium structures obtained at the CCSD(T) level usually well agree with the experimental ones when the latter are accurately determined. On the other hand, in most cases, the accuracy and reliability of experimental determinations for open-shell species are quite limited; for such cases, best estimates (CBS+CV) such as those reported in Table 1 represent better reference geometries. We furthermore note that the B3LYP/ N07D level of theory is able to provide a good semiquantitative description of equilibrium structures, with geometrical parameters usually overestimated by about 0.01−0.02 Å for bond lengths. In view of this, we do not expect any particular effect of molecular structures on vibrational frequencies. We only note that larger discrepancies have been observed for FSC, HSiO, and FSiO, for which at the DFT level the F−S and F−Si distances are overestimated by about 0.1 Å, the Si−O bond length is longer by more than 0.03 Å, and the ∠HSiO and ∠FSiO angles are underestimated by ∼4 and ∼2°, respectively. For these molecules, we actually noticed for some vibrational modes discrepancies in harmonic frequencies larger than the average (i.e., on the order of 100 cm^{-1}), but a clear correspondence between anomalies in the

molecular structure and large deviations for vibrational frequencies cannot be drawn.

3.2. Vibrational Frequencies. We start the analysis of vibrational frequencies by discussing the accuracy of harmonic frequencies computed by different methods as well as that of the corresponding anharmonic contributions. This is then followed by the validation of the computational approaches considered in this work against available experimental data.

Concerning harmonic frequencies computed at the CCSD(T) level, it is well-known from the literature that for closed-shell systems they have an overall accuracy of 15−20 cm^{-1} when basis sets of at least triple-ζ quality are used (see for example refs 19 and 65). For radicals, the situation is not so well assessed, but some recent investigations seem to confirm that an analogous accuracy can be reached (see for instance refs 5, 26, and 27). Hints on the quality of CCSD(T) anharmonic frequencies can be derived from Table 3, where they are compared with the available experimental data. From this comparison, it is apparent that, on average, anharmonic frequencies computed at the CCSD(T)/cc-pVQZ level for the harmonic part and employing either a triple-ζ or a quadruple-ζ basis

Table 2. Equilibrium Geometric Parameters Computed at the CCSD(T) and DFT Levels of Theory for Selected Tri- and Tetra-Atomic Free Radicals

	B3LYP/N07D	CCSD(T)/VnZ	exptl
HCO		$n = Q$	$r_e{}^a$
R(CH)	1.1274	1.1162	1.1191(50)
R(CO)	1.1804	1.1759	1.1754(15)
∠HCO	124.36	124.57	124.43(25)
HSiO		$n = Q$	$r_e{}^b$
R(SiH)	1.5393	1.5209	1.4971(fix)
R(SiO)	1.5672	1.5331	1.5286(2)
∠HSiO	115.84	119.63	116.8(1)
HCS		$n = Q$	$r_0{}^c$
R(CH)	1.0942	1.0877	1.079(3)
R(CS)	1.5783	1.5660	1.56228(3)
∠HCS	131.61	131.99	132.8(3)
HSC		$n = Q$	$r_e{}^d$
R(SH)	1.3850	1.3671	1.379(3)
R(CS)	1.6773	1.6517	1.6343(5)
∠HSC	103.72	102.89	104.2(2)
NH$_2$		$n = Q$	$r_e{}^e$
R(NH)	1.0312	1.0250	1.0254 (12)
∠HNH	103.55	102.72	102.85 (14)
H$_2$CN		$n = Q$	$r_0{}^f$
R(CH)	1.1016	1.0947	1.11(postulated)
R(CN)	1.2479	1.2493	1.247
∠HCN	121.78	121.16	121.65
F$_2$CN		$n = Q$ (aug)	$r_0{}^g$
R(CF)	1.3177	1.3087	1.31(postulated)
R(CN)	1.2572	1.2570	1.265
∠FCN	124.55	124.52	123.25
F$_2$BO		$n = Q$ (aug)	$r_0{}^i$
R(BF)	1.3311	1.3142	1.30(5)
R(BO)	1.3602	1.3648	1.40(5)
∠FBO	119.4	119.29	126(5)
NH$_3^+$		$n = Q$	$r_e{}^k$
R(NH)	1.0281	1.0212	1.014
∠HNH	120.0	120.0	120.0

^{a} Ref 71. ^{b} Ref 72. ^{c} Ref 73. ^{d} Ref 74. ^{e} Ref 75. ^{f} Ref 76. ^{g} Ref 77. ^{i} Ref 78. ^{k} Ref 79.

for the anharmonic contributions are able to reproduce experimental data within $10-20$ cm^{-1}. Some larger deviations, i.e., more than 40 cm^{-1}, are observed only for C$-$H stretching modes: ν_1 of HCO and H$_2$CO$^+$ and ν_5 of H$_2$CN. Interestingly, in the two former cases the B3LYP/N07D computations led to significantly better agreement with respect to the experiment. For the ν_5 vibration of H$_2$CN, the discrepancy should be attributed to difficulties in assignment of the experimental band, as already discussed in refs 5 and 66, rather than to possible anharmonic resonances, as supported by the good agreement between variational and perturbative computations.[66−68] However, it should be noted that, for molecular systems which are significantly plagued by resonances, improvements with respect to perturbative results are expected by performing fully variational frequency computations.

The good performance of the B3LYP model for the computation of harmonic frequencies of open-shell species has already been pointed out,[69] and data collected in Table 3 are in line with such findings. Indeed, the comparison between harmonic frequencies computed at the CCSD(T) and B3LYP levels shows that the latter are on average off by only 1.5% from the CCSD(T) reference, with a maximum error of about 4.5%. Nevertheless, such an overall good agreement leads in absolute terms to discrepancies in the

range of -30 to $+60$ cm^{-1}, which implies that the B3LYP/N70D level of theory might not be adequate for accurate spectroscopic studies. More interestingly, both methods predict very similar anharmonic corrections which agree within about 10 cm^{-1}. The only exceptions are FCO and H$_2$CO$^+$, but in both cases the largest discrepancies are related to the incorrect prediction of Fermi resonances at the DFT level. It should be stressed that, in the VPT2 implementation employed, vibrational modes which might be involved in Fermi or Darling-Denison resonances are excluded from the perturbative treatment[44] and are thus treated separately at the variational level. However, as such mode selection is performed on the basis of harmonic frequencies, any inaccuracy in the latter strongly influences the final results. In fact, as soon as accurate harmonic frequencies are included in the VPT2 treatment (and also used to predetermine resonances), significant improvements are achieved.

The first conclusion that can be drawn is that the good accuracy of anharmonic corrections computed by DFT validates the use of a hybrid scheme in which the harmonic part is computed with high accuracy by means of coupled cluster theory while anharmonic contributions are obtained by relatively inexpensive DFT computations. As mentioned before, the standard approach is to simply add DFT anharmonic contributions, $\Delta\nu$, to harmonic frequencies computed at the CCSD(T) level; however, sometimes the second approach, where harmonic CCSD(T) frequencies are directly used in perturbative vibrational analysis along with 3rd and 4th force constants computed at the DFT level, might be more suitable.[28] This is indeed the case for FCO and H$_2$CO$^+$, where application of corrected harmonic values leads to much better agreement (within 3 cm^{-1} for FCO and 15 cm^{-1} for H$_2$CO$^+$) between the hybrid scheme and full CCSD(T) results. It seems, therefore, that hybrid computations using CCSD(T) quadratic force fields and B3LYP/N07D cubic and semidiagonal quartic force constants closely approach the accuracy of complete CCSD(T) anharmonic computations at a much reduced computational cost. Anharmonic frequencies derived from full B3LYP/N07D force fields also agree fairly well with the experiment, but in most cases the improvements achieved by the hybrid CCSD(T)/cc-pVQZ//B3LYP/N07D scheme are significant: for example, for F$_2$CN, the mean absolute error (MAE) reduces from 18 cm^{-1} to 6 cm^{-1}. The hybrid scheme is thus advisable whenever possible.

In the following analysis, anharmonic DFT and hybrid frequencies will be compared with benchmark CCSD(T) values which have been shown to yield results in good agreement with the experiment. Tables 4 and 5 list such results for the triatomic and tetratomic radicals not considered in Table 3, respectively. From these tables, the conclusions drawn from Table 3 are confirmed: with only a few exceptions (some of them already discussed in the previous section), the anharmonic B3LYP/N07D frequencies agree with their CCSD(T) counterparts within $5-60$ cm^{-1}. All the discrepancies are then removed once the hybrid approach is considered; in fact, in almost all cases, the agreement is within $1-30$ cm^{-1}. For the

Table 3. Harmonic (ω) and Anharmonic (ν) Vibrational Frequencies (in cm^{-1}) Computed at Various Levels of Theory for Selected Tri- and Tetra-Atomic Free Radicals

	B3LYP/N07D		CCSD(T)[a]		CCSD(T)+DFT[b]	exptl[c]
	ω	ν	ω	ν	ν	
HCO			CBS/aCV	CBS+QZ		
ν_1	2677	2441	2717	2460	2481	2435
ν_2	1930	1906	1905	1878	1882	1868
ν_3	1099	1066	1120	1093	1087	1081
FCS			augVQZ	aVTZ		
ν_1	1306	1275	1338	1308	1306	1297
ν_2	934	919	933	919	918	918
ν_3	456	451	461	456	456	457
FCO			augVQZ	augVTZ		
ν_1	1915	1847	1900	1864	1862[d]	1862
ν_2	1022	977	1054	1025	1028[d]	1026
ν_3	621	610	634	624	624[d]	628[e]
NH$_2$			VQZ	VQZ		
ν_1	3346	3193	3377	3219	3223	3219
ν_2	1518	1475	1549	1504	1505	1497[f]
ν_3	3450	3281	3471	3297	3301	3301
PH$_2$			VQZ	VQZ		
ν_1	2353	2254	2401	2305	2302	2298
ν_2	1120	1096	1127	1101	1103	1102
ν_3	2364	2262	2409	2310	2306	
HOCl$^+$			VQZ	VQZ+augVTZ		
ν_1	3463	3276	3524	3338	3337	
ν_2	1257	1221	1288	1248	1251	
ν_3	888	875	915	901	902	830 $\pm$ 50
HCCO			VQZ	VQZ+VTZ		
ν_1	3348	3217	3352	3214	3221	3232[g]
ν_2	2085	2047	2097	2056	2058	2022[h]
ν_3	1258	1250	1246	1245	1239	
ν_4	546	553	567	576	574	
ν_5	497	447	505	467	455	494[i]
ν_6	488	517	500	524	529	
H$_2$CN			VQZ	VQZ		
ν_1	2985	2822	3000	2836	2837	2820[j]
ν_2	1720	1692	1706	1672	1677	1725[k]
ν_3	1384	1346	1383	1343	1346	1330
ν_4	988	968	989	967	969	950
ν_5	3044	2867	3069	2893	2893	3103[k]
ν_6	931	912	939	913	919	909
F$_2$CN			augVQZ	aVQZ+augVTZ		
ν_1	1790	1759	1811	1781	1781	1771
ν_2	957	941	974	957	958	955
ν_3	540	535	552	546	546	
ν_4	666	658	679	673	671	660
ν_5	1239	1206	1295	1262	1263	1257
ν_6	492	487	501	496	497	497
NH$_3^+$			VQZ	VQZ		
ν_1	3351	3206	3375	3231	3230	3232[l]
ν_2	873	914	865	910	906	917[m]
ν_3	3538	3365	3559	3388	3386	
ν_4	3538	3365	3559	3388	3386	3389[n]
ν_5	1532	1492	1551	1507	1510	1507[o]
ν_6	1532	1491	1551	1507	1510	
PH$_3^+$			VQZ	VQZ		
ν_1	2448	2361	2497	2400	2410	
ν_2	726	652	751	670	678	695[p]
ν_3	2525	2435	2568	2469	2477	
ν_4	2525	2436	2568	2469	2479	2462
ν_5	1040	1018	1054	1029	1032	1044
ν_6	1040	1017	1054	1029	1031	
H$_2$CO$^+$			VQZ	VQZ		
ν_1	2783	2603	2807	2625	2635[d]	2580
ν_2	1711	1742	1676	1636	1652[d]	1675
ν_3	1251	1207	1263	1210	1220[d]	1210[r]
ν_4	1062	1037	1068	1039	1044[d]	1036[s]
ν_5	2873	2675	2915	2711	2724[d]	2718[r]
ν_6	848	858	848	823	810[d]	823[s]

[a] CCSD(T) data from HCO/HOC, ref 80; HCCO, ref 81; H$_2$CN/F$_2$CN, ref 5; NH$_3^+$/PH$_3^+$, ref 70; others, this work. [b] Anahrmonic corrections at the B3LYP/N07D level. [c] Experimental results from references: HCO,[82] FCS,[83] FCO,[84] NH$_2$,[85] PH$_2$,[86] HOCl$^+$,[87] H$_2$CN,[88] F$_2$CN,[77] PH$_3^+$,[89] H$_2$CO$^+$,[90,91] [d] Anahrmonic corrections computed with CCSD(T) harmonic frequency and 3rd and 4th force constants obtained at the B3LYP/N07D level. [e] Ref 92. [f] Ref 93. [g] Ref 94. [h] Ref 95. [i] Ref 96. [j] Ref 97. [k] Ref 98. [l] Refs 99, 100 and 101. [m] Ref 102. [n] Ref 79. [o] Refs 103, 104, 100, and 105. [p] Also, ref 106. [r] Also, refs 107 and 108.

molecules gathered in Tables 4 and 5, the simple DPT2 hybrid scheme usually provided satisfactory results, whereas, for more demanding cases like HOC, FSiO, and

Cl$_2$CN radicals, good accuracy has only been achieved with the InFreq approach. For the latter radical, in analogy to what was discussed above for FCO and H$_2$CO$^+$, the

Table 4. Anharmonic Frequencies (in cm^{-1}) for Triatomic Radicals Obtained with B3LYP/N07D, CCSD(T), and Hybrid Models

	B3LYP/N07D	CCSD(T)	CCSD(T)+DFT[a]
HOC		VQZ	
ν_1	2887	3144	3117[b]
ν_2	1337	1375	1374[b]
ν_3	1075	1108	1109[b]
HSiO		V5Z(PES)//VQZ	
ν_1	1774	1828//1829	1847//1842
ν_2	1068	1166// 1168	1162//1161
ν_3	558	622// 622	624//627
HOSi		V5Z(PES)//VQZ	
ν_1	3634	3667//3667	3671//3671
ν_2	797	869//869	860//859
ν_3	749	743//749	755//760
HCS		CBS(PES)//VQZ	
ν_1	2962	2993/2992	2979//2977
ν_2	1175	1188//1181	1187//1180
ν_3	807	794//802	791//798
HSC		CBS(PES)//VQZ	
ν_1	2196	2252//2256	2264//2266
ν_2	881	930//920	931//921
ν_3	745	773//768	785//779
FSC		aVTZ	
ν_1	1030	1046	1046
ν_2	518	626	622
ν_3	214	241	242
FSiO		aVTZ	
ν_1	1064	1206	1181[b]
ν_2	758	845	844[b]
ν_3	265	308	301[b]

[a] Anharmonic corrections at the B3LYP/N07D level. [b] Anharmonic corrections computed with the CCSD(T) harmonic frequency and 3rd and 4th force constants obtained at the B3LYP/N07D level.

difficulties are related to Fermi resonances. On the other hand, for HOC and FSiO, abnormally large discrepancies (over 100 cm^{-1}) between harmonic frequencies computed at the CCSD(T) and DFT levels are an issue.

The last part of our work is devoted to the analysis of the performance of several recently developed density functionals for computation of vibrational frequencies within both the DFT/N07D and hybrid models. For this purpose, Table 6 compares mean absolute errors (MAEs), with respect to CCSD(T) computations, over all normal modes of H_2CN, N_2H^+, and FCS radicals, for which a good agreement with both the experiment and the benchmark CCSD(T) studies has been obtained at the B3LYP/N07D level. First of all, we discuss the overall accuracy of harmonic frequencies obtained by means of the functionals under study. It has to be noted that an accuracy only slightly lower than that of B3LYP, with discrepancies on the order of $15-25$ cm^{-1} with respect to CCSD(T) results, has been achieved by most functionals, except LC-ωPBE and wB97(X), which show MAEs in range $40-50$ cm^{-1}. Such findings are also valid for anharmonic frequencies, for which most functionals show MAEs lower than 30 cm^{-1}. However, larger discrepancies are observed for higher frequencies, as depicted in panel a of Figure 1. Additionally, in two cases, namely, for LC-ωPBE and M06-2X, the MAE exceeded 60 cm^{-1}: in the former case, the error originates from the inaccurate harmonic frequency values, but in the latter case the problems are directly related to anharmonic corrections. All functionals have been also tested for their performance within hybrid

Table 5. Anharmonic Frequencies (in cm^{-1}) for Tetratomic Radicals Obtained with B3LYP/N07D, CCSD(T), and Hybrid Models

	B3LYP/N07D	CCSD(T)	CCSD(T)+DFT[a]
HCNN		VQZ+VTZ	
ν_1	3013	3020	3015
ν_2	1828	1746	1742
ν_3	1233	1176	1176
ν_4	830	861	871
ν_5	533	530	534
ν_6	485	519	518
HNCN		VQZ+VTZ	
ν_1	3304	3313	3308
ν_2	1881	1781	1773
ν_3	1188	1131	1137
ν_4	1019	1037	1030
ν_5	491	472	473
ν_6	470	461	465
H_2BO		VQZ+VTZ	
ν_1	2312	2327	2331
ν_2	1384	1355	1354
ν_3	949	975	988
ν_4	881	912	900
ν_5	2323	2364	2368
ν_6	545	547	564
F_2BO		aVQZ+VTZ	
ν_1	1372	1427	1425
ν_2	842	873	873
ν_3	442	462	460
ν_4	648	662	659
ν_5	1330	1427	1423
ν_6	362	389	387
Cl_2CN		VQZ+VTZ	
ν_1	1710	1577	1575[b]
ν_2	564	589	583[b]
ν_3	363	364	364[b]
ν_4	495	492	490[b]
ν_5	776	828	837[b]
ν_6	281	283	283[b]

[a] Anharmonic corrections at the B3LYP/N07D level. [b] Anharmonic corrections computed with CCSD(T) harmonic frequency and 3rd and 4th force constants obtained at the B3LYP/N07D level.

Table 6. Performances of Modern Density Functionals in the DFT/N07D Models[a]

MAE [cm^{-1}]	DFT/N07D		$CCSD(T)_{harm} + DFT_{anh}$	
	Harm	Anh	DPT2	InFreq
B3LYP	15.0	14.5	2.4	4.1
B3LYP-D	19.9	18.7	4.0	4.3
CAM-B3LYP	20.0	24.3	4.4	3.0
PBE0	19.6	22.3	4.9	3.6
LC-ωPBE	50.9	61.1	11.5	6.5
M06	25.2	23.2	13.9	15.3
M06-2X	25.5	74.9	54.0	52.4
wB97	39.0	31.4	18.6	23.5
wB97X	33.7	27.1	12.4	15.7
wB97XD	21.9	26.5	17.3	20.0
HSE06	17.6	20.9	6.0	4.7

[a] Mean absolute error (MAE) with respect to CCSD(T) computations over all normal modes of H_2CN, NH_2^+, and FCS.

models, and the results obtained applying both hybrid approaches (the simple DPT2 correction and the InFreq) are listed in Table 6. Additional insights can also be drawn from panel b of Figure 1, which shows differences with respect to CCSD(T) results as a function of the frequency for all normal modes of the selected radicals. It is immediately apparent that among the tested functionals those originated
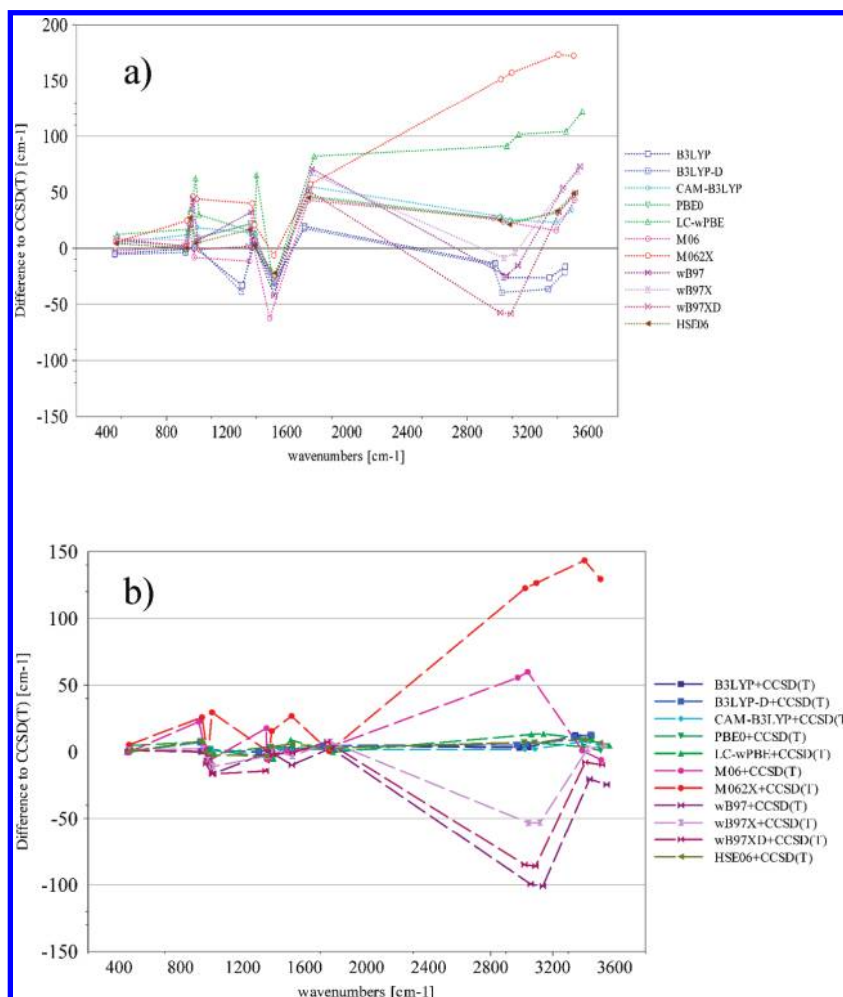
Figure 1. Performance of different density functionals in prediction of vibrational frequencies beyond harmonic approximation. (a) Perturbative computations performed fully at the DFT level. (b) Hybrid CCSD(T)+DFT scheme. Relative discrepancies from the values computed at the CCSD(T) level are shown for each normal mode of H_2CN, NH_2^+, and FCS, which are listed according to their wavenumbers.

from B3LYP and PBE0, together with the recently introduced HSE06, yield accurate anharmonic frequencies, with MAEs as low as $3-7$ cm^{-1}. It should be noted that, in the case of the LC-ωPBE model, such good agreement can be achieved only by the InFreq approach, due to large errors in harmonic frequencies. In contrast, recently developed functionals belonging to the M06 and wB97 families yield significantly less accurate results, with MAEs in the range $12-55$ cm^{-1}, and with discrepancies up to 150 cm^{-1}, thus far off the accuracy required for spectroscopic studies. It is also noteworthy that the performance of M06 functionals is significantly worsened by the addition of Hartree−Fock exchange (2X). A further check of the above conclusions has been performed by comparing frequencies obtained using DFT/N07D models with much more expensive DFT/aug-cc-pVTZ computations. The results are listed in Table 7 for the H_2CN radical showing that indeed the large errors in anharmonic corrections obtained at the M06/N07D and wB97/N07D levels are not removed by the larger basis set.

4. Conclusions

The present paper has been devoted to the validation of the DFT/N07D and hybrid CCSD(T)/DFT models for studying

Table 7. Harmonic Frequencies and Anharmonic Contributions Computed by Several Modern Density Functionals with N07D and aug-cc-pVTZ Basis Sets[a]

MAE [cm^{-1}]	harmonic frequencies		anharmonic contribution	
	N07D	aVTZ	N07D	aVTZ
B3LYP	10.4	20.4	2.9	3.5
B3LYP-D	16.5	26.6	6.7	7.4
CAM-B3LYP	19.7	15.8	5.6	6.3
PBE0	14.7	16.5	6.6	7.2
LC-ωPBE	43.8	29.9	12.3	12.7
M06	24.0	36.4	26.0	20.6
M06-2X	20.7	12.7	55.5	66.2
wB97	35.9	28.9	31.4	23.0
wB97X	31.1	22.7	21.4	16.5
wB97XD	17.8	11.0	30.5	24.7
HSE06	13.5	16.0	6.7	6.2

[a] Mean absolute errors (MAE) with respect to benchmark results from CCSD(T) computations for the H_2CN radical.

vibrational properties of free radicals. In this respect, we have chosen several small radicals containing first- and second-row elements for which it was possible to compare methodologies rooted in the density functional theory with computations at the CCSD(T) level. At the same time, comparison with several experimental results allowed ex-

ploration of the ability of the DFT/N07D and CCSD(T)/DFT models to critically analyze results from spectroscopic studies. It has been shown that the accuracy of the CCSD(T) model is nearly the same for closed- and open-shell systems: this finding is by itself significant since the reliability of experimental data is usually strongly reduced when going from closed-shell to open-shell systems, essentially because of the short lifetime of the latter ones. On the other hand, the B3LYP/N07D model is fairly robust for geometries and harmonic and anharmonic frequencies and becomes nearly quantitative when used only for anharmonic contributions to be added to harmonic force fields obtained at more sophisticated levels. Furthermore, extension of the N07D basis set has only marginal effects, and the use of other functionals (including the most recent ones) does not improve the results. As a matter of fact, some of the most successful last generation functionals (M06-2X and wB97X) provide quite disappointing results: this suggests that vibrational frequencies should be added to the databases used for the optimization of parameters in this kind of functionals. In conclusion, we think that the B3LYP/N07D model can represent a very effective tool coupling a remarkable reliability in the computation of geometric and vibrational properties of organic and inorganic free radicals with a very favorable scaling with the number of electrons. Furthermore, empirical dispersion terms (leading to B3LYP-D) can be added without worsening the performances of the model whenever dispersion interactions come into play. The relatively low computational cost of the B3LYP/N07D computational model allows taking into proper account the vibrational effects beyond the harmonic approximation even for quite large systems of biological and/or technological interest.

Supporting Information Available: Geometry parameters computed at the B3LYP/N07D and CCSD(T)/VnZ levels for HOC, HOSi, FCS, FSC, FCO, FSiO, HOCl$^+$, HCCO and H$_2$CO$^+$ radicals. Harmonic and anharmonic frequencies computed by DFT/N07D, DFT/aug-cc-pVTZ, and hybrid models for the H$_2$CN radical, as well as harmonic and anharmonic frequencies computed by DFT/N07D and hybrid models for NH$_2$ and FCS radicals. This information is available free of charge via the Internet at http:// pubs.acs.org/.

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