# ACCURACY ASSESSMENT OF THE ROHF-CCSD(T) CALCULATIONS OF DIPOLE MOMENTS OF SMALL RADICALS

Miroslav URBAN[a1], Pavel NEOGRADY[a2], Juraj RAAB[a3] and Geerd H. F. DIERCKSEN[b]

[a] *Department of Physical Chemistry, Faculty of Sciences, Comenius University, Mlynska dolina, SK-842 15 Bratislava, Slovak Republic; e-mail: [1] urban@fns.uniba.sk, [2] palo@fns.uniba.sk, [3] raab@fns.uniba.sk*

[b] *Max-Planck-Institute for Astrophysics, Karl-Schwarzschild-Strasse 1, POB 1523, 857 40 Garching, Germany; e-mail: ghd@mpa-garching.mpg.de*

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*This paper is dedicated to Professor Rudolf Zahradnik on the occasion of his 70th birthday. One of us (M. U.) would never continued in his scientific work in theoretical chemistry without his help, advice and almost inexhaustible enthusiasm.*

Dipole moments of a series of radicals, OH, NO, NS, SF, SO, PO, ClO, CN, LiO, $NO_2$, and $ClO_2$ were calculated by the Coupled Cluster CCSD(T) method with the single determinant restricted open shell Hartree–Fock (ROHF) reference. For all molecules theoretical dipole moments were carefully compared to experimental values. The size and the quality of the basis set were systematically improved. Spin adaptation in the ROHF-CCSD(T) method, largest single and double excitation amplitudes and the $T_1$ diagnostics were considered as indicators in the quality assessment of calculated dipole moments. For most molecules the accuracy within 0.01–0.03 D was readily obtained. For ClO and CN the spin adaptation was necessary – its contribution was as large as 0.03–0.045 D. Large deviation from experiment is observed for OH in its $A^2\Sigma^+$ excited state (0.135 D) and especially for LiO in its $^2\Pi$ ground state (0.22 D). No indication of the failure of theoretical calculations was found which leads to the conclusion that, even if there is still a space for the improvement of theoretical calculations, experimental values should be reconsidered.

**Key words**: Radicals; Dipole moments; CCSD(T); ROHF; Spin-adaptation; *Ab initio* calculations.

Electric properties, like multipole moments, polarizabilities and other belong among most important atomic and molecular characteristics. Their importance can hardly be overestimated in general, but special role play electric properties in intermolecular interactions, as is clearly demonstrated in a comprehensive work by Buckingham[1], Zahradnik and Hobza[2] and others. Yet availability of accurate experimental electric properties is far from being satisfactory. Important supplementary source of data certainly provides *ab initio* calculations. With properly selected sophisticated methods are theoreticians not only able to obtain more accurate data than can experimentalists in some difficult cases but also can predict molecular electric properties not accessible by experiment at all.

If *ab initio* data have to be generally accepted by chemical and physical community, their accuracy and reliability must be checked carefully. This seems to be quite obvious but in fact it is not so trivial, especially when one has in mind predictions of electric properties. To be more specific, in Coupled Cluster (CC) calculations[3–7] with a single determinant reference, there were suggested diagnostic methods applicable to the CCSD(T) version[8] of the CC method, which was selected in the present paper. CCSD(T) means that single and double excitation amplitudes within the CCSD method are solved iteratively and triples are calculated perturbatively[9] using converged $t_1$ and $t_2$ amplitudes. Most important are the $T_1$ diagnostics[7,10,11], examination of the convergence pattern in terms of the wave function, energy or other property perturbation series[12–15], and the detection of largest $t_1$ and $t_2$ (single and double, respectively) excitation amplitudes[13,15], see also Bartlett's review[5]. Quite easy is, *e.g.*, the inspection of a single fifth order term which extends the CCSD + T(CCSD) value[9] to CCSD(T), applied in some studies[12–15]. This is, however, suitable for closed shell systems or with the UHF reference, but not applicable with a ROHF reference for open shells. Alternatively, one can compare CCSD(T) result of a property calculation with approximate or full iterative CCSDT (refs[13–15]) result. These diagnostics can be considered as "internal" in a sense that they use no comparison with other data, either theoretical, and/or experimental to reveal possible failure of the method. The inspection of largest $t_1$ and $t_2$ amplitudes can, *e.g.*, detect the multireference character of the problem under investigation to which a single reference CC method, at least at the most often used level, *i.e.* CCSD(T), cannot be safely applied. Another possibility is to compare CCSD(T) data with those obtained from alternative theoretical methods, specifically multireference methods. An example is an examination of electric properties of BeO and $C_2$ (ref.[15]). CCSD(T) is very often used because it is applicable in a very straightforward way provided that a good single reference determinant can be safely selected. Multireference methods appear to be more generally applicable[16] but can provide accurate results only with large enough and properly selected active space which is in many cases a problem. Thus in a sense both classes of methods are complementary.

Most common way of the accuracy evaluation is the comparison of results with experiment. This is precisely what is the subject of the present work. It is a part of a more general project oriented towards construction of an expert system which can help a user to select the proper method corresponding to the specification of the accuracy required and availability of computer resources. It can also help in the assessment of the accuracy of obtained results. Present effort is oriented towards the "case based" expert system which relies on accumulated experience from a series of calculations[17].

While the accuracy of CCSD(T) calculations was carefully and systematically investigated in relation to properties like spectroscopic constants, dissociation energies, equilibrium distances[5–7], less is known about the accuracy of CC calculations of electric properties[6]. Quite extensive investigation of electric properties has been undertaken by Maroulis[18]. He has introduced a measure of similarity of different methods applicable to calculation of various properties like multipole moments and higher polarizabilities. A systematic work on one-electron properties was undertaken by a Scandinavian group[19,20], by Oliphant and Barttlet[21] and by Paldus and Li[22]. A series of benchmark calculations was published by, *e.g.*, Woon and Dunning[23a] and Scuseria and coworkers[23b].

Open shell molecules are certainly much less frequently investigated than closed shell systems. This means that we can extend our experience with the CCSD(T) approach applied to calculations of electric properties. However, this in not the most important issue of our research. Our ROHF-CCSD(T) calculations are performed with spin adapted $t_1$ and $t_2$ amplitudes of the singly and doubly excitation operators in CCSD (ref.[24]) which are subsequently used in the perturbative estimates[25] of triples, as defined in our series of papers[24,25]. Thus, we have an opportunity to investigate the effect of spin adaptation on calculated dipole moment which is a property expected to be more sensitive to the quality of the wave function than the energy itself. Second, we will analyze largest $t_1$ and $t_2$ CCSD excitation amplitudes and will use this information in the discussion of the similarity of molecules and in the assessment of the reliability of dipole moments when the agreement with experiment is not entirely satisfactory. Previous analyses on BeO and $C_2$ were based on comparisons with other theoretical methods for presumably "difficult" cases[15], for which, however, reliable experimental data were missing. This time we selected molecules for which experimental dipole moments are available and serve as a measure of the performance of ROHF-CCSD(T). Our aim was to obtain accuracy of about 0.03 D, which is, in fact, better than experimental accuracy for some molecules and quite satisfactory in predictions of dipole moments when experimental values are not available at all. Naturally, in many other cases experimental values are much more accurate (to within 0.001 D or better). Theoretical results with this accuracy would require specific investigations, at least further improvements of the basis sets effects and more detailed consideration of electron correlation, relativistic effects and vibration averaging for each molecule which was not the aim of the present work.

## METHODS

ROHF-CCSD(T) approach with spin adapted $t_1$and $t_2$ amplitudes was described in our previous work[25]. To calculate electric dipole moment we employed the finite field approach using the field strength ±0.001 a.u. In many cases applying additional field strength checked the accuracy of the dipole moment. In most calculations the 1s (and 2s, 2p electrons) of the first (second) row atoms remained uncorrelated (for the Li atom all electrons were correlated). We mention that even if the reference ROHF wave function is a proper wave function of the spin operators $S^2$ and $S_z$, the resulting CCSD wave function is not and must be spin-adapted. Our spin adaptation is in principle the same as that introduced by Hampel, Werner and Knowles[26]. Our procedure is considered as approximate in the sense that products of $t_1$ and $t_2$ amplitudes remain non-adapted. This provides energies almost identical with the full adaptation scheme as implemented by Szalay[27] following general ideas by Li and Paldus[28]. In the present work we applied in most cases only the adaptation of $t_2$ amplitudes arising from excitations from doubly occupied to virtual orbitals (DDVV). It is not only computationally simpler than our "full" spin adaptation scheme but also applicable to any high spin state without the need of different formulae for any specific case. In all doublet states in our series of molecules, however, our "full" and "DDVV" spin adaptations gave virtually the same result. Reference ROHF orbitals were calculated by the MOLCAS 3 or MOLCAS 4 suite of programs[29,30]. ROHF-CCSD(T) calculations were performed by the program written by one of us (P. N.) which is a part of MOLCAS 4. The $T_1$ diagnostic was evaluated by the formula (compare refs[7,10,11,15])

$$T_1 = \left([\Sigma|t_{i,\alpha}^{a,\alpha}|^2]^{1/2} + [\Sigma|t_{i,\beta}^{a,\beta}|^2]^{1/2}\right)/2\,N^{1/2}\ ,$$

where in the nominators are Euclidean norms for the single excitation amplitudes with spins $\alpha$ and $\beta$, respectively, and $N$ is the number of correlated electrons.

All molecules were calculated at experimental equilibrium geometry to which all theoretical dipole moments are referred. Vibration averaging for diatomic molecules was performed by the solution of the rotational-vibration Schrödinger equation using the MOLCAS 3 program VIBROT with potential energy and dipole moment curves calculated with only one basis set, namely [5432/6532/432] contractions of Widmark *et al.*[31] Atomic Natural Orbitals (ANO) basis sets for first row/second row/hydrogen atoms. Usually 18–20 energy and dipole moment values were calculated and used subsequently for calculation of the vibrationally averaged dipole moments $\mu_0$ and $\mu_1$ for vibration quantum numbers $v = 0$ and $v = 1$, *i.e.* $\langle 0|\mu|0\rangle$ and $\langle 1|\mu|1\rangle$. These $\mu_0$ and (occasionally also) $\mu_1$ dipole moments are quantities available from experiment to which theoretical values have to be compared. Since our CCSD(T) calculations directly provide $\mu_e$ for all basis sets for the same experimental bond lengths, the vibrationally averaged dipole moments from a single basis set dipole moment curve were used for correction of results with other basis sets as well. In this way we corrected $\mu_e$ for final large basis sets. Thus, as it follows from the power expansion of the dipole moment in terms of $(v + 1/2)^n$, we calculated the quantity $\Delta^{\text{theor}} = \langle 1|\mu|1\rangle - \langle 0|\mu|0\rangle$ and obtained theoretical $\langle 0|\mu|0\rangle = \mu_e + 1/2\ \Delta^{\text{theor}}$.

Differently constructed, generally available basis sets were used in the present study. Sadlej's[32] polarized basis sets (POL) are specifically designated for calculations of electric properties. These are relatively small but flexible basis sets applicable to quite large molecules. The examination of their performance in comparison to more extended basis sets seems to be quite interesting. ANO basis sets are not specifically optimized for electric properties, but due to their construction (contraction coefficients follow from the averaging procedure in which also negative ion of the respective atom was used) they contain sufficiently diffuse functions needed for successful calculation of the dipole moment. Contractions used were in the range [4321] up to [6543] (and, in some cases [7743] ) for first row atoms and [5421] up to [7643] for second row atoms. Due to the fact that ANO basis sets are generally contracted these basis sets are suitable for the examination of the core correlation effects. Finally, we used augmented correlation consistent polarized valence basis sets[33] aug-cc-pVXZ, with X = T, Q and in some cases also X = 5, *i.e.* polarized valence triple zeta up to quintuple zeta basis sets. Basis sets specifically designated for core correlation effects (aug-cc-pCVTZ) are available for the first row atoms and were used in some cases. We have avoided double zeta basis sets since they are considered as unsatisfactory in calculations of reasonably accurate dipole moments as well as multiply augmented basis sets, which are not generally available for many atoms and, moreover are prohibitively extended for large molecules. The number of contracted gaussians in basis sets used in this work is summarized in Table I.

TABLE I
Contractions and the size of selected Gaussian basis sets

| Basis set[a] | Size of the atomic basis set | | |
|---|---|---|---|
| | P, S, Cl | Li[b], C, N, O, F | H |
| POL | | | |
| [7s5p2d/5s3p2d/3s2p] | 32 | 24 | 9 |
| ANO | | | |
| [5s4p2d1f/4s3p2d1f/3s2p1d] | 34 | 30 | 14 |
| [6s5p3d2f/5s4p3d2f/4s3p2d] | 50 | 46 | 23 |
| [7s6p4d3f/6s5p4d3f/5s4p3d] | 66 | 62 | 32 |
| aug-cc-pVXZ | | | |
| X = T: [6s5p3d2f/5s4p3d2f/4s3p2d] | 50 | 46 | 23 |
| X = Q: [7s6p4d3f2g/6s5p4d3f2g/5s4p3d2f] | 84 | 80 | 46 |
| X = 5: [–/7s6p5d4f3g2h/6s5p4d3f2g] | – | 127 | 80 |

[a] Contraction for atoms [P, S, Cl/Li, C, N, O, F/H]; [b] aug-cc-pVXZ basis sets are not available for Li.

## RESULTS

Results are summarized in Tables II–VIII. The sign of the dipole moment cannot be usually determined from experimental measurements and is presented as a positive number. Our definition is a positive sign connected with the polarity $A^{(+)}B^{(-)}$. Largest excitation amplitudes and the $T_1$ diagnostic are collected in Table IX.

TABLE II
Dipole moment (debye) of the NO radical in its $X^2\Pi_r$ ground state and the NS radical in its $X^2\Pi_r$ ground state[a]

| Basis set[b] | NO[c] | | | NS[c] | | |
|---|---|---|---|---|---|---|
| | SCF | CCSD | CCSD(T) | SCF | CCSD | CCSD(T) |
| POL | 0.288 | –0.135 | –0.163 | –1.551 | –1.792 | –1.784 |
| A[5421/4321] | 0.273 | –0.136 | –0.176 | –1.588 | –1.828 | –1.823 |
| A[6532/5432] | 0.283 | –0.125 | –0.172 | –1.593 | –1.837 | –1.835 |
| A[6532/5432] – no adapt. | 0.283 | –0.125 | –0.171 | –1.593 | –1.824 | –1.820 |
| A[6532/5432] – all el. corr. | 0.283 | –0.125 | –0.172 | –1.593 | –1.851 | –1.849 |
| A[6543/5432] | – | – | – | –1.601 | –1.845 | –1.844 |
| A[7643/6543] | 0.288 | –0.120 | –0.167 | –1.597 | –1.846 | –1.846 |
| aug-cc-pVTZ | 0.288 | –0.123 | –0.168 | –1.570 | –1.827 | –1.825 |
| aug-cc-pCVTZ – all el. corr. | 0.289 | –0.118 | –0.166 | – | – | – |
| aug-cc-pVQZ | 0.287 | –0.115 | –0.162 | –1.585 | –1.831 | –1.830 |
| aug-cc-pVQZ – all el. corr. | – | – | – | –1.585 | –1.850 | –1.848 |
| Effect of the DDVV spin adapt. | | | –0.001 | | | –0.015 |
| Effect of the core corr. | | | 0.000 | | | –0.014 |
| Vibr. aver. corr. | | | 0.009 | | | 0.013 |
| aug-cc-pVQZ + core corr. + vibr. aver.[d] | | | –0.153 | | | –1.831 |
| Experimental value ($v = 0$) | | | 0.15782 ± 0.00002[e] | | | 1.81 ± 0.029[g] |
| | | | 0.1574 ± 0.0014[f] | | | 1.86 ± 0.03[h] |

[a] The polarity is $N^{(-)}O^{(+)}$ and $N^{(-)}S^{(+)}$ using the CC correlated results; [b] A[X/Y] means contractions of the ANO basis for X = S and Y = N, O; [c] calculated at experimental bond distance of NO, $r_e = 1.15077 . 10^{-10}$ m and NS, $r_e = 1.49402 . 10^{-10}$ (from ref.[34]); [d] included CCSD(T) core correlation and vibration correction calculated with the ANO[5432] and [6532/5432] basis sets for NO and NS, respectively; [e] ref.[35]; [f] ref.[36]; [g] Amano *et al.*[42a]; [h] Byfleet *et al.*[42b].

### *NO and NS Radicals*

Excellent agreement of the theoretical dipole moment with experiment for NO, Table II, was obtained in a very straightforward way. Spin adaptation, inner shell correlation and vibration correction were all quite small. What can be stressed is tremendous effect of the electron correlation: the SCF value gives even wrong sign. Relatively important are triple excitations as measured from the difference CCSD(T)-CCSD. Since we did not include at this stage relativistic effects and since we are unable to calculate the spin–orbit interaction within our ROHF-CCSD(T) approach, we cannot resolve the states with quantum numbers *J* = 1/2 and *J* = 3/2. The two states cannot be distin-

TABLE III
Dipole moment (debye) of the PO radical in its $X^2\Pi_r$ ground state and the ClO radical in its $X^2\Pi_i$ ground state[a]

| Basis set[b] | PO[c] | | | ClO[c] | | |
|---|---|---|---|---|---|---|
| | SCF | CCSD | CCSD(T) | SCF | CCSD | CCSD(T) |
| POL | 2.546 | 1.996 | 1.872 | 0.739 | 1.217 | 1.256 |
| A[5421/4321] | 2.560 | 2.071 | 1.918 | 0.729 | 1.224 | 1.269 |
| A[6532/5432] | 2.567 | 2.077 | 1.918 | 0.727 | 1.208 | 1.251 |
| A[6532/5432] – full adapt. | – | – | – | 0.727 | 1.206 | 1.251 |
| A[6532/5432] – no adapt. | 2.567 | 2.072 | 1.914 | 0.727 | 1.239 | 1.283 |
| A[6532/5432] – all el. corr. | 2.567 | 2.093 | 1.932 | 0.727 | 1.214 | 1.258 |
| A[7643/6543] | 2.575 | 2.089 | 1.930 | 0.733 | 1.218 | 1.263 |
| aug-cc-pVTZ | 2.565 | 2.064 | 1.908 | 0.735 | 1.225 | 1.271 |
| aug-cc-pVQZ | 2.574 | 2.095 | 1.935 | 0.733 | 1.204 | 1.250 |
| aug-cc-pVQZ – no adapt. | – | – | – | 0.733 | 1.237 | 1.283 |
| aug-cc-pVQZ – all el. corr. | – | – | – | 0.733 | 1.213 | 1.259 |
| Effect of the DDVV spin adapt. | | | 0.004 | | | –0.032 |
| Effect of the inner shell corr. | | | 0.014 | | | 0.007 |
| A[6532/5432] vibr. aver. corr. | | | 0.010 | | | –0.011 |
| aug-cc-pVQZ + core corr. + vibr. aver.[d] | | | 1.959 | | | 1.246 |
| Experimental value ($v = 0$) | | | 1.88 ± 0.07[e] | | | 1.239 ± 0.010[f] |

[a] The polarity is $P^{(+)}O^{(-)}$ and $Cl^{(+)}O^{(-)}$; [b] A[X/Y] means contractions of the ANO basis for X = P, Cl and Y = O; [c] calculated at experimental bond distances of PO, $r_e = 1.4759 \cdot 10^{-10}$ m and ClO, $r_e = 1.56963 \cdot 10^{-10}$ m (from ref.[34]); [d] included CCSD(T) core correlation and vibration correction calculated with the ANO[6532/5432] basis set; [e] ref.[45]; [f] ref.[46].

guished experimentally either, but the difference $^2\Pi_{3/2}$ ($v$ = 1) – $^2\Pi_{3/2}$ ($v$ = 0) = 0.01735 D is available[36]. Dipole moments for $J$ = 1/2 are $^2\Pi_{1/2}$ ($v$ = 0) = 0.1574 ± 0.0014 and $^2\Pi_{1/2}$ ($v$ = 1) = 0.1416 ± 0.0004 D, *i.e.* the difference for $v$ = 1 and $v$ = 0 is –0.0158 ± 0.001 D. Our values with the ANO[5432] basis are μ ($v$ = 0) = –0.1535 and μ ($v$ = 1) = –0.1348 D. The difference between the two vibration states, 0.0187 D, agrees with experiment very well (note that experimental dipole moments are presented as positive numbers). Similar accuracy is obtained also for other radicals where reference data were available.

Recent calculations[38] employing aug-cc-pVTZ basis with uncontracted innermost s- and p-type functions in conjunction with ROHF-CCSD(T) and variants of Configuration Interaction (CI) led to results very similar to those in Table II when

TABLE IV
Dipole moment (debye) of the SO radical in its $^3\Sigma^-$ ground state and the SF radical in its $^2\Pi$ ground state[a]

| Basis set[b] | SO[c] | | | SF[c] | | |
|---|---|---|---|---|---|---|
| | SCF | CCSD | CCSD(T) | SCF | CCSD | CCSD(T) |
| POL | 2.183 | 1.623 | 1.525 | 1.168 | 0.879 | 0.825 |
| A[5421/4321] | 2.217 | 1.650 | 1.528 | 1.107 | 0.883 | 0.811 |
| A[6532/5432] | 2.224 | 1.651 | 1.525 | 1.109 | 0.880 | 0.805 |
| A[6532/5432] – no adapt. | 2.224 | 1.646 | 1.529 | 1.109 | 0.876 | 0.801 |
| A[6532/5432] – all el. corr. | 2.224 | 1.663 | 1.534 | 1.109 | 0.889 | 0.813 |
| A[7643/6543] | 2.238 | 1.666 | 1.539 | 1.111 | 0.881 | 0.806 |
| A[7643/6543] – no adapt. | – | – | – | 1.111 | 0.877 | 0.801 |
| aug-cc-pVTZ | 2.223 | 1.653 | 1.531 | 1.120 | 0.878 | 0.805 |
| aug-cc-pVQZ | 2.235 | 1.663 | 1.535 | 1.114 | 0.881 | 0.805 |
| aug-cc-pVQZ – all el. corr. | 2.235 | 1.679 | 1.548 | – | – | – |
| Effect of the DDVV spin adapt. | | | –0.004 | | | 0.004 |
| Effect of the core corr. | | | 0.009 | | | 0.008 |
| Vibr. aver. corr. | | | 0.003 | | | 0.007 |
| aug-cc-pVQZ + core corr. + vibr. aver.[d] | | | 1.547 | | | 0.820 |
| Experimental value ($v$ = 0) | | | 1.55 ± 0.02[e] | | | 0.79 ± 0.04[f] |

[a] The polarity is $S^{(+)}F^{(-)}$ and $S^{(+)}O^{(-)}$; [b] A[X/Y] means contractions of the ANO basis for X = S and Y = F, O; [c] calculated at experimental bond distances of SO, $r_e$ = 1.48109 . $10^{-10}$ m and SF, $r_e$ = 1.600575 (from ref.[34]); [d] included CCSD(T) core correlation and vibration correction calculated with the ANO[6532/5432] basis set; [e] ref.[48]; [f] ref.[51].

ROHF-CCSD(T) method was used ($\mu_e$ = –0.164 D). CI with Complete Active Space (CAS) reference overshoot experiment by ≈0.04 D which was reduced to ≈0.02 D when approximate quadruple excitations (CAS-CISD+Q) were considered. There are several Density Functional Theory (DFT) calculations[21,39,40] which lead to very diverse results both underestimating and (mostly) overestimating the experimental value depending on the basis set and the actual functional. With the augmented TZP basis set the DFT dipole moments were found in the range 0.180–0.235 D.

The isovalence radical NS has not been so extensively studied[42–44] by experimental or theoretical techniques as NO. The polarity of both species is the same, $N^{(-)}A^{(+)}$, but the dipole moment of NS is much higher than that of NO. Huber and Herzberg[34] report two experimental values[42], 1.81 and 1.86 ± 0.03 Debye. Our value lies just in between.

TABLE V
Dipole moment (debye) of the CN radical in its $^2\Sigma^+$ ground state[a]

| Basis set | SCF | CCSD | CCSD(T) |
|---|---|---|---|
| POL | 2.311 | 1.513 | 1.393 |
| ANO[4321] | 2.296 | 1.517 | 1.378 |
| ANO[5432] | 2.301 | 1.541 | 1.396 |
| ANO[5432] – no adapt. | 2.301 | 1.505 | 1.353 |
| ANO[5432] – full adapt. | 2.301 | 1.541 | 1.398 |
| ANO[5432] – no adapt., semican. | – | – | 1.357[b] |
| ANO[6543] | 2.303 | 1.544 | 1.399 |
| aug-cc-pVTZ | 2.302 | 1.540 | 1.398 |
| aug-cc-pCVTZ – all el. corr. | 2.302 | 1.547 | 1.399 |
| aug-cc-pVQZ | 2.303 | 1.559 | 1.412 |
| aug-cc-pVQZ – all el. corr. | 2.303 | 1.568 | 1.418 |
| aug-cc-pV5Z | 2.303 | 1.565 | 1.417 |
| Effect of the DDVV spin adapt. | | | 0.043 |
| Effect of the inner shell corr.[c] | | | 0.001; 0.006 |
| ANO[5432] vibr. aver. corr. | | | –0.006 |
| aug-cc-pV5Z + core corr. + vibr. aver.[d] | | | 1.417 |
| Experimental value ($v$ = 0) | | | 1.45 ± 0.08[e] |

[a] The polarity is $C^{(+)}N^{(-)}$, the dipole moment is calculated at experimental bond distance, $r_e = 1.1718 \cdot 10^{-10}$ m (ref.[34]); [b] CCSD(T) calculation with semicanonical orbitals, ref.[12]; [c] from aug-cc-pCVTZ and aug-cc-pVQZ calculations, respectively; [d] included CCSD(T) core correlation (calculated with the aug-cc-pVQZ basis set) and vibration correction (calculated with the ANO[5432] basis set); [e] ref.[53].

The effects of spin adaptation, core correlation and vibration averaging are slightly larger in NS than in NO. Basis set effect is less smooth in the former case (Fig. 1). ANO and aug-cc basis sets seem to converge to dipole moments which differ by about 0.015 D, but still less than error bars of experiment. The $T_1$ diagnostic (Table IX) is higher for NS than that for NO and the same holds for largest excitation amplitudes, with the exception of the $t_1^{\alpha\alpha}$ amplitude. In NS both single ($t_1^{\alpha\alpha}$) and double ($t_2^{\alpha\beta\alpha\beta}$) excitation amplitudes are large. These facts allow us to conclude that the accuracy of our CCSD(T) result for NS is lower than that for NO, with error bars about ±0.02 D. Recent theoretical value for NS is the DFT calculation of Chong[39] who used the Local Density Approximation (LDA). He obtained $\mu_0 = 1.848$ D, in good agreement with our calculations. We note, however, that the similar DFT calculation[39] for NO, $\mu_0 = 0.235$ D, deviates from experiment by as much as 0.08 D which certainly cannot be considered as a spectacular agreement with experiment. MR-CI calculations on low-lying states of NS were performed by Lie *at al.*[43]. Their dipole moment for the ground state is by about 0.1 D too high ($\mu_0 = 1.951$ D).

### *PO and ClO Radicals*

The PO radical, Table III, has been studied much less frequently[39,44,45] than its isovalent counterparts NO and (partly) NS. All three radicals have the same valence electronic structure, $\sigma^2\pi^4\pi^*$. The striking difference is that the polarity is $P^{(+)}O^{(-)}$ in contrast to

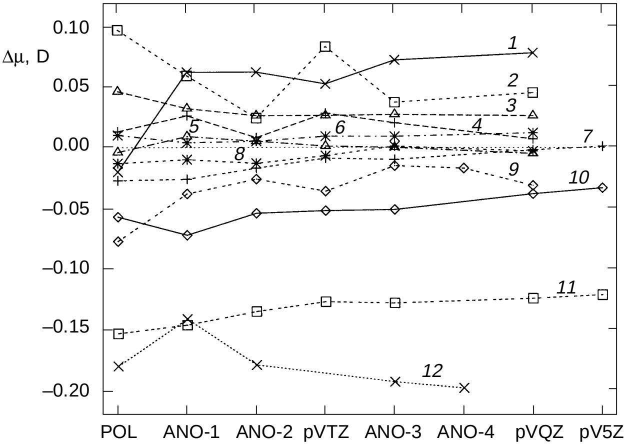

FIG. 1

Differences, $\Delta\mu = |\mu_{theor}| - |\mu_{exp}|$, between theoretical and experimental dipole moments. Contractions for ANO basis sets (see Table I). ANO-1 [5421/4321/321]; ANO-2 [6532/5432/432]; ANO-3 [7643/6543/543]; ANO-4 [6543/5432] for NS; [7743/7643] for O and Li atoms in LiO; pVXZ is a shorthand notation for aug-cc-pVXZ basis sets. Lines: *1* PO; *2* $ClO_2$; *3* SF; *4* ClO; *5* NO; *6* $NO_2$; *7* OH, $X^2\Pi$; *8* SO; *9* NS; *10* CN; *11* OH, $A^2\Sigma^+$; *12* LiO

$N^{(-)}O^{(+)}$ and $N^{(-)}S^{(+)}$, which naturally follows from negativities of participating atoms. The spin adaptation in PO is almost negligible, like in NO, and effect of the core correlation and vibration averaging is similar to that in NS. Our final dipole moment $\mu_0$ = 1.959 D favor a value at the upper limit of rather large error bars of experiment. Kanata *et al.*[45] stressed the importance of the availability of accurate dipole moment in their Stark effect microwave spectroscopic study. This is related to attempts to detect the PO radical in interstellar space by using radio telescopes. The basis set dependence for PO is not so smooth as for NO. Yet the final CCSD(T) values with largest basis sets vary by only about 0.005 D. Electron correlation contribute significantly, but small change due to the spin adaptation and quite small excitation amplitudes allow to conclude that CCSD(T) should be reliable.

The ClO molecule is considered to be a "difficult" case[39,47]. According to Petersson *et al.*[47] the $X^2\Pi$ state of ClO is not very well described by a single-reference configuration. Really, their results were quite sensitive to the selection of the correlated method.

TABLE VI
Dipole moment (debye) of the LiO radical in its $^2\Pi_i$ ground state[a]

| Basis set[b] | SCF | CCSD | CCSD(T) |
|---|---|---|---|
| POL | 6.857 | 6.668 | 6.631 |
| ANO[4321] | 6.855 | 6.711 | 6.670 |
| ANO[5432/5332] | 6.838 | 6.676 | 6.633 |
| ANO[5432] | 6.840 | 6.675 | 6.632 |
| ANO[5432] – no adapt. | 6.840 | 6.672 | 6.629 |
| ANO[5432] – all el. corr. | 6.840 | 6.678 | 6.635 |
| ANO[6543] | 6.838 | 6.663 | 6.618 |
| ANO[7743/7643] | 6.835 | 6.659 | 6.613 |
| ANO[7743/7643] – all el. corr. | 6.835 | 6.663 | 6.617 |
| Effect of the DDVV spin adapt. | | | 0.003 |
| Effect of the inner shell corr. | | | 0.003 |
| ANO[5432] vibr. aver. corr. | | | 0.025 |
| ANO[7743/7643] – all el. + vibr. aver.[c] | | | 6.642 |
| Experimental value ($v = 0$) | | | 6.84 ± 0.03[d] |

[a] The polarity is $Li^{(+)}O^{(-)}$; the dipole moment is calculated at experimental bond distance, $r_e$ = 1.68822 . $10^{-10}$ m (ref.[55]); [b] contraction of the ANO basis is denoted as ANO[O/Li] if contraction for both atoms is not the same; [c] vibration correction calculated with the ANO[5432] basis set; [d] ref.[56].

Most extensive MR-CI led to $\mu_0$ = 1.275 and $\mu_1$ = 1.252 D. The difference agrees completely with our ANO[6532/5432] values, $\mu_0$ = 1.223 and $\mu_1$ = 1.200 D but our values are by 0.05 D lower. Superficially one could trust MR-CI rather than the single determinant reference CCSD(T) calculation for ClO. The problem with MR-CI is that the reported[47] value of 1.275 D includes an *approximate* correction for quadruples. Without it, $\mu_0$ is 1.229 D (ref.[47]). In any case the vibration averaging seems to be reliable. Also basis set is not a problem because dipole moments with largest basis sets mutually agree quite well (see also Fig. 1). Our best dipole moment of 1.246 D agrees very well with experimental value46 from Stark effect of microwave spectrum, see Table III. Peterson *et al.*[47] present an experimental value $\mu_0$ = 1.2980, but their source of information is unfortunately not available to us. There are at least two facts for

TABLE VII
Dipole moments (debye) of the $NO_2$ radical in its $X^2A_1$ ground state and the $ClO_2$ radical in its $X^2B_1$ ground state[a]

| Basis set[b] | $NO_2$[c] | | | $ClO_2$[g] | | |
|---|---|---|---|---|---|---|
| | SCF | CCSD | CCSD(T) | SCF | CCSD | CCSD(T) |
| POL | 0.752 | 0.397 | 0.326 | 2.224 | 1.959 | 1.884 |
| A[5421/4321] | 0.735 | 0.396 | 0.320 | 2.211 | 1.935 | 1.846 |
| A[6532/5432] | 0.747 | 0.401 | 0.321 | 2.201 | 1.906 | 1.811 |
| A[6532/5432] – no adapt. | 0.747 | 0.400 | 0.325 | – | – | – |
| A[6532/5432] – full adapt. | 0.747 | 0.401 | 0.321 | 2.201 | 1.906 | 1.810 |
| A[6532/5432] – core el. corr.[d] | 0.747 | 0.403 | 0.322 | 2.201 | 1.912 | 1.816 |
| A[7643/6543] | 0.751 | 0.404 | 0.325 | 2.213 | 1.920 | 1.824 |
| aug-cc-pVTZ | 0.750 | 0.404 | 0.325 | 2.242 | 1.961 | 1.870 |
| aug-cc-pCVTZ –core el. corr.[d] | 0.750 | 0.404 | 0.325 | – | – | – |
| aug-cc-pVQZ | 0.750 | 0.408 | 0.328 | 2.223 | 1.928 | 1.832 |
| Effect of the DDVV spin adapt. | | | –0.004 | | | –0.001 |
| Effect of the core corr. | | | 0.001 | | | 0.005 |
| aug-cc-pVQZ + core corr. | | | 0.329 | | | 1.837 |
| Experimental value | | | 0.316[e]<br>0.303 ± 0.004[f] | | | 1.792[h] |

[a] The polarity is $N^{(+)}O_2^{(-)}$ and $Cl^{(+)}O_2^{(-)}$; [b] A[X/Y] means contractions of the ANO basis for X = Cl and Y = N, O; [c] calculated at experimental geometry, $r_e$ (NO) = 1.194 . $10^{-10}$ m (refs[60,61]) and $\Theta$ (ONO) = 133.8°; [d] 1s electrons of Cl were not correlated; [e] ref.[62]; [f] ref.[63]; [g] calculated at experimental geometry, $r_e$ (ClO) = 1.470 . $10^{-10}$ m and $\Theta$ (OClO) = 117.38° (ref.[64]); [h] ref.[65].

which the dipole moment of ClO deserves more careful discussion. First, the spin adaptation is as high as –0.032 D in this case (it is the same with the DDVV and full spin adaptation). Second, largest amplitudes are quite high, *i.e.* 0.197 for the $\pi \rightarrow \pi$ single excitation (Table IX). Double excitation amplitudes are, however, sufficiently small. Good agreement with experiment confirms the capability of ROHF-CCSD(T) with spin adapted amplitudes to manage this difficult case.

### *SO and SF Radicals*

SO, presented in Table IV, is the only species with the $^3\Sigma$ ground state in our set. It is really not a "problematic" radical. All corrections are small, convergence with extending the basis set is smooth (Fig. 1), agreement with experiment is excellent. Unfortunately error bars of the experimental[48] dipole moment from the Stark effect of

TABLE VIII
Dipole moment (debye) of the OH radical in its $X^2\Pi$ ground state and $A^2\Sigma^+$ excited state[a]

| Basis set[b] | OH $^2\Pi$ | | | OH $^2\Sigma$ | | |
|---|---|---|---|---|---|---|
| | SCF | CCSD | CCSD(T) | SCF | CCSD | CCSD(T) |
| POL | –1.757 | –1.634 | –1.620 | –1.967 | –1.798 | –1.780 |
| A[4321/321] | –1.747 | –1.636 | –1.620 | –1.958 | –1.807 | –1.786 |
| A[5432/432] | –1.755 | –1.647 | –1.630 | –1.968 | –1.818 | –1.796 |
| A[5432/432] – no adapt. | –1.755 | –1.647 | –1.629 | –1.968 | –1.818 | –1.795 |
| A[5432/432] – all el. corr. | –1.755 | –1.652 | –1.634 | –1.968 | –1.820 | –1.797 |
| A[6543/543] | –1.757 | –1.652 | –1.636 | –1.972 | –1.825 | –1.804 |
| aug-cc-pVTZ | –1.761 | –1.654 | –1.637 | –1.976 | –1.825 | –1.804 |
| aug-cc-pVQZ | –1.757 | –1.660 | –1.644 | –1.973 | –1.830 | –1.808 |
| aug-cc-pV5Z | –1.757 | –1.663 | –1.647 | –1.973 | –1.832 | –1.811 |
| Effect of the spin adapt. | | | –0.001 | | | –0.001 |
| Effect of the core corr. | | | –0.004 | | | 0.001 |
| Vibr. aver. corr. | | | –0.004 | | | –0.048 |
| aug-cc-pV5Z + core corr. + vibr. aver. | | | –1.655 | | | –1.859 |
| Experimental value ($v = 0$) | | | 1.65520 ± 0.00010[b] | | | 1.98 ± 0.08[c] |

[a] The polarity is $O^{(-)}H^{(+)}$, $r_e = 0.96966 \cdot 10^{-10}$ m and $r_e = 1.0121 \cdot 10^{-10}$ m for the ground state and for the excited state, respectively, ref.[34]; [b] ref.[68]; [c] refs[34,71].

microwave spectrum are quite large. Our results agree perfectly with the Restricted Active Space SCF (RAS SCF) calculations by Fülscher *et al.*[49] when their largest active space and the ANO[6s5p4d3f/5s4p3d2f] basis set is considered. Our final $\mu_0 = 1.547$ D is slightly closer to experiment than Fülscher's *et al.* result ($\mu_0 = 1.540$ D), but both are within the experimental error bars. The CAS SCF dipole moment $\mu_0 = 1.607$ published by Peterson and Woods[50] is only slightly higher than experiment, but their CI-SD is higher by as much as 0.44 D. Our $\mu_0$ and $\mu_1$ directly calculated with the ANO[6532/5432] basis set are 1.5554 and 1.5594 D and $\mu_1 - \mu_0$ agrees with previous theoretical calculations very well.

In the SF radical (Table IV) we observe only small effect of the spin adaptation, core correlation and vibration correction. Basis set dependence converges smoothly towards the experimental value[51] (Fig. 1). Thus, the correct dipole moment of SF is obtained in a very straightforward and well-controlled way. We note a large deviation of the DFT value[39] from experiment (underestimation by more than 0.167 D). CEPA calculations[52] overestimate the experimental value significantly.

### *CN Radical*

The CN radical certainly belongs among "difficult" cases. It is well known as being heavily spin contaminated when calculated with the unrestricted Hartree–Fock (UHF)

TABLE IX
Largest excitation amplitudes and the $T_1$ diagnostics[a]

| Radical | $t_1^{\alpha\alpha}$ | $t_1^{\beta\beta}$ | $t_2^{\alpha\alpha\alpha\alpha}$ | $t_2^{\beta\beta\beta\beta}$ | $t_2^{\alpha\beta\alpha\beta}$ | $T_1$ |
|---|---|---|---|---|---|---|
| NO | 0.0321 | 0.0694 | 0.0181 | –0.0381 | –0.0645 | 0.0230 |
| NS | 0.0281 | –0.1014 | 0.0259 | –0.0529 | –0.1156 | 0.0309 |
| PO[b] | 0.0497 | –0.0814 | –0.0197 | 0.0312 | –0.0674 | 0.0281 |
| ClO | 0.0229 | –0.1967 | 0.0186 | 0.0439 | 0.0460 | 0.0377 |
| SO | 0.0204 | 0.0722 | –0.0207 | –0.0660 | –0.0277 | 0.0201 |
| SF[c] | –0.0174 | 0.0648 | 0.0214 | 0.0177 | –0.0363 | 0.0197 |
| CN | 0.0275 | 0.1980 | –0.0221 | –0.0331 | –0.0628 | 0.0469 |
| LiO | –0.0148 | –0.0274 | –0.0141 | –0.0117 | 0.0257 | 0.0173 |
| $NO_2$ | –0.0666 | 0.0848 | –0.0176 | 0.0453 | –0.0848 | 0.0259 |
| $ClO_2$ | –0.0384 | 0.0557 | –0.0094 | –0.0295 | –0.0337 | 0.0248 |
| OH $^2\Pi_i$ | –0.0141 | –0.0230 | –0.0149 | 0.0117 | –0.0302 | 0.0143 |
| OH $^2\Sigma^+$ | 0.0204 | –0.0230 | –0.0150 | –0.0150 | –0.0329 | 0.0167 |

[a] In most calculations the DDVV spin adaptation and the ANO[5432] and ANO[6532] for first and second row atoms, respectively, was used; [b] full adaptation; [c] ANO[7643/6543] basis.

method. Is was investigated previously by one of us with Watts and Bartlett[12]. Our resulting dipole moment was 1.357 D, that is, it was by 0.09 D lower than the experimental value (1.45 D). Since extending the basis set led only to marginal increase, we agreed with Langhoff and Bauschlicher[54] (their MR-CI $\mu_0$ was 1.317 D) that the experimental value must be too high. This would have some consequences in the astrophysical detection of this radical. Previous calculation[12] was a result with ROHF-CCSD(T) using semicanonical orbitals, without spin adaptation. Our present result shows that previous suspicion concerning the underestimation of the experimental value was perhaps premature. The DDVV spin adaptation increases the dipole moment by as much as by 0.043 D and brings the ROHF-CCSD(T) value within rather large error bars of experiment. Full adaptation differs from the DDVV adaptation by only 0.002 D and demonstrates the usefulness of the simple approach. Inner shell correlation effect and the vibration correction for $v = 0$ are both very small. Basis set effects are more important but not dramatic (see Fig. 1). The final CCSD(T) value with vibration correction ($v = 0$) and estimated effect from the inner shell correlation, and with our largest aug-cc-pV5Z basis is 1.417 ± 0.005 D. The change of the dipole moment due to the basis set extension from aug-cc-pVQZ to aug-cc-pV5Z was only 0.005 D. We note that the aug-cc-pV5Z basis set for CN contains 254 contracted Gaussians and that further extension has no practical meaning when one considers the use of the present investigations to larger molecules. Most important point is perhaps the fact, that the spin adaptation in the CCSD(T) calculation of the dipole moment of CN is the most important effect of the spin adaptation on any physical quantity observed so far (see also Li and Paldus[22]).

We note that the Johnson's *et al.*[40] DFT results with the 6-31G* basis set vary from 1.009 to 1.149 D depending on the actual selection of the functional. B3LYP value of Barone[57] is slighly low (1.398 D) and the Oliphant and Bartlett's[21] result with the B-LYP functional and the polarized triple zeta basis is too high (1.695 D). Corresponding CCSD(T) value of Oliphant and Bartlett is 1.334 D. Clearly, the accuracy of CCSD(T) can be kept under control much better than DFT results.

### *LiO Radical*

LiO molecule is another difficult case in a sense that in this highly polar molecule there is observed the largest difference between theoretical and experimental dipole moments. In fact, both experimental and theoretical treatments[58] are difficult. The bond in LiO is rather ionic and the molecule dissociates into neutral fragments which seems to indicate a possibility of problems in using the single determinant CCSD(T) approach. This resembles another highly ionic molecule, the closed shell BeO molecule, which is notoriously known as a difficult case[13,15]. It was BeO in which the importance of a careful consideration of excitation amplitudes was stressed[13]. One has to expect a crossing of covalent and ionic terms and consequently high CCSD excitation amplitudes for LiO. The low lying excited state, $A^2\Sigma^+$, lies 2 400 $cm^{-1}$ above the ground state[34]. Yet around the equilibrium distance the excitation amplitudes are quite small, see Table IX. In fact, they belong among the smallest ones in our series of radicals. They cannot deteriorate the CCSD(T) calculation of $\mu_e$ in the vicinity of the equilibrium distance but one cannot exclude problems at larger distances needed for vibration averaging. The vibration correction for LiO is quite large, 0.025 D, but not large enough to explain the discrepancy between the theory and experiment. Moreover at distances which we have used for the vibration averaging the amplitudes still remained to be reasonably small. Our theoretical value agrees very well with the CASSCF result (6.616 D calculated at $r_e = 1.676$) of Fowler and Sadlej[59].

Spectroscopic measurements on this radical seem to be rather rare. Even if the experimental dipole moment of LiO (ref.[56]) concerns the $^2\Pi_{3/2}$ ($v = 0$) state and our calculation without spin orbit effects cannot distinguish the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ components one can hardly expect the difference as high as 0.2 D due to this effect. Considering all this we conclude that there exists a space for improvement both at the theoretical and experimental sides to bring both values into a better agreement. We believe, however, that our theoretical value cannot be in error as large as 0.2 D.

### *$NO_2$ and $ClO_2$ Radicals*

$NO_2$ dipole moment approaches the experimental value in a similar way as NO: spin adaptation and core correlation are almost negligible, and, moreover, results are almost stable with changes of the basis set. We note that DFT values appear to be stable for $NO_2$ as well[41] and oscillate between 0.291 an 0.299 D. Theorists[41] usually refer to the experimental value of Hodgeson *et al.*[62] (0.316 D) which we have used as well. A new Stark experiments carried out on a supersonic molecular beam by high resolution laser spectroscopy[63] lead to the dipole moment for the $X^2A_1$ ground state of 0.303 ± 0.004 D. Our value agrees better with the former microwave experiment[62]. However, one has to keep in mind that our theoretical value for $NO_2$ is not vibrationally corrected. Still, the agreement with experiment is reasonable.

The experimental value of the dipole moment for $^{35}ClO_2$ in its ground state appears to be very accurate[65], 1.79195 ± 0.00010 D. The agreement of our theoretical data with experiment is not as good as one would like. The bottleneck appears to be a basis set effect, which manifests itself in large oscillations with the basis set, see Fig. 1. Since the spin adaptation, $T_1$ diagnostic and excitation amplitudes are small (Table IX), we are unable to recognize any indication of problems with CCSD(T) for $ClO_2$. MR-CI value published by Peterson and Werner[66] ($\mu_e = 1.852$ D) is also a bit too high. Even if some DFT results with aug-cc-pVTZ basis[67] (especially with non-hybrid functionals) are in a reasonable agreement with our results and with experiment, the problem is that some other functionals, like hybrid B3LYP ($\mu_e = 1.962$ D) deviate from experiment as much as by 0.17 D. At the same time B3LYP hybrid functional appears to have the best overall performance for other properties of a series of chlorine-oxygen compounds[67].

### *OH Radical in the $X^2\Pi$ Ground State and the $A^2\Sigma^+$ Excited State*

The convergence of the dipole moment for the ground state with the basis set (see Table VIII and Fig. 1) is very smooth leading to perfect agreement with the most accurate experimental result[68]. Previous theoretical calculations (see *e.g.* refs[22,69,70]) also provide results in good agreement with our calculations. Also the vibration correction, 0.004 D, as it follows from scaled vibrationally averaged dipole moments[69] for $v = 0$ and $v = 1$ agrees with our correction very well. Both spin adaptation and core correlation affect the result very little. In fact, excitation amplitudes and the $T_1$ diagnostic is the smallest one for $^2\Pi$ OH from among all our molecules, which indicates that this is a well behaved system.

The situation with the $^2\Sigma$ state is different. Also for this state is the spin adaptation and core correlation very small and the dependence on changes of basis sets is very smooth. Only the vibration correction, 0.048 D, is large. Excitation amplitudes and the $T_1$ diagnostic are almost as small as for the ground state, yet the deviation from experiment[71] for the $^2\Sigma$ state is as large as 0.121 D. Unfortunately we were unable to find a more reliable experimental value (see also data from ref.[72]). Theoretical correlated dipole moment obtained by Meyer[73] is 1.88 D. Slightly lower values, 1.825 D for $v = 0$ and 1.939 D for $v = 1$, were obtained by Langhoff *et al.*[72]. Considering small excitation amplitudes and $T_1$ diagnostic and a small basis set dependence we believe that our theoretical CCSD(T) dipole moment is close to the correct value.

## DISCUSSION

The performance of the CCSD(T) method in calculations of dipole moments appears to be very good in general. Our set of molecules can be divided into three groups according to the absolute deviation of the theoretical value from experiment: (i) For most radicals the deviation is about 0.03 D or smaller; for NO, SO, ClO, and OH $X^2\Pi$ it is less than 0.01 D; (ii) Dipole moments of the two radicals, $ClO_2$ and PO, differ from experiment by more than 0.03 D but less than 0.08 D; (iii) Dipole moments of LiO and OH $A^2\Sigma^+$ differ by more than 0.1 D from experimental data known to us. Very different error bars of experimental measurements for specific radicals complicate the discussion of the accuracy of theoretical values. This is a reason why we do not present the average deviation of theoretical and experimental data. For PO, which is in our group (ii), error bars are as large as ±0.07 D so that our theoretical value is actually at the edge of the upper limit of error bars. On the other hand, the experimental value for $ClO_2$, which is in the same group, is accurate to five decimals and the deviation of the theoretical value from experiment, 0.045 D, is certainly caused by the deficiency of the theoretical approach, most probably by the basis set effect. LiO and OH $A^2\Sigma^+$ are specific cases which will be discussed later.

Another important factor is the convergence of dipole moments following the sequence of the ANO and aug-cc-pVXZ basis sets. We can conclude that further extension of the basis set would affect the final result by less than 0.005 D in most cases. Less regular behaviour and thus reduced accuracy with respect to the basis set extension is observed for NS and $ClO_2$. We have to keep in mind, however, that we paid an attention mainly to the size of generally available basis sets and not to a selection of additional basis functions for the dipole moment of a specific radical. Useful comparisons of the performance of different basis sets in CC calculations of one electron properties can be found in ref.[20]. It follows from the work of Halkier *et al.*[20] that further extension of the basis set beyond aug-cc-pVQZ affects final results very little. The same concerns doubly augmented basis sets and basis sets aug-cc-pCVXZ if basis is larger than triple zeta. We have to stress a good performance of the POL basis set in comparison with much larger ANO and aug-cc-pVXZ basis sets. With the exception of $ClO_2$, PO, and NS the POL results differ from largest basis sets results by less than 0.04 D. POL basis sets appear to be a good choice for calculations of larger molecules. The average absolute difference (maximum difference) between results with POL basis set and results with the largest basis set was 0.025 (0.063) D. Analogous differences for the ANO[6532/5432/432] basis set were 0.011 (0.021) D and those for aug-cc-pVTZ were 0.012 (0.038) D. Last two basis sets have the same size.

Other than basis set issues are the following: (i) Relativistic effects; (ii) More accurate treatment of vibration averaging; and, (iii) Even more sophisticated treatment of the electron correlation, including possible problems with quasi degeneracy.

We have estimated relativistic effects using the first order mass–velocity and Darwin (MVD) method. For systems containing only first and second row atoms this approach yields sufficiently accurate relativistic corrections to electric properties[74]. For all relativistic corrections finite field perturbation treatment with standard POL basis sets was used. Relativistic contributions were found to be very small but not negligible (in D): –0.005 (NS), 0.005 (PO), 0.006 (ClO), 0.007 (SO), 0.011 (SF), and 0.009 ($ClO_2$). With the exception of NS and SO these relativistic corrections, if used in connection with large basis sets, lead to the increase of the deviation of theoretical and experimental results, even if mostly not beyond experimental error bars. Unfortunately we are unable at present to calculate the spin–orbit splitting at the spin adapted ROHF-CCSD(T) level. This may affect mainly $^2\Pi$ states, but the two components, $J = 1/2$ and $J = 3/2$ cannot be resolved experimentally either, at least not in most cases. We have already mentioned the spin–orbit splitting in the NO molecule. Another example is the OH radical in its $^2\Pi$ ground state[65] but the difference between the two states is only 0.0003 D. Theoretical relativistic calculations[75], which include the magnetic part of the Breit interaction term, lead to the same value. Surely, for other radicals it can be larger.

Our main concern is the assessment of the reliability of the electron correlation in the dipole moment calculations. Our theoretical tool, CCSD(T), normally provides excellent molecular data[5–8,19–23]. Stanton has recently presented a new insight into its background[76]. One has to realize that CCSD(T) is merely an approximation, even if very successful in many applications, to the iterative CCSDT, and that connected quadruples important in quasi-degenerate situations are not considered at all. It is then important to be able to estimate the applicability of the ROHF-CCSD(T) with a single determinant reference. One can also ask a question in which radicals a significant contribution from spin adaptation can be expected. Our idea was to link the importance of the spin adaptation in CCSD(T) with the spin contamination of the generally available UHF SCF wave function, but this proved to be not the case. From our data, Table IX, one can easily deduce that the effect of the spin adaptation is related to largest excitation amplitudes and to the $T_1$ diagnostic. The first three largest amplitudes are found for CN, ClO (single excitation amplitudes), and NS (both single and double excitation amplitudes). For the same radicals there was found the largest influence of the spin adaptation on dipole moments (0.043, –0.032, and –0.015 D). For all other radicals the spin adaptation was lower than 0.005 D. Even if largest amplitudes for CN and ClO were approaching a value of 0.2 and those for NS were slightly larger than 0.1, the agreement with experiment was at least satisfactory, as was discussed in the preceding part. Certainly, these radicals are difficult cases, but still manageable by CCSD(T).

Now, let us return to LiO and $A^2\Sigma^+$ OH. Considering the previous experience and discussion and the fact, that the amplitudes for both species belong among the smallest ones and the same is valid for the $T_1$ diagnostic, there is no doubt about the reliability of our CCSD(T) data. There is no similarity with other difficult cases.

## CONCLUSIONS

To summarize, in the quality assessment of the CCSD(T) dipole moment calculations one can consider the following steps:

*1*. Inspect the basis set convergence, or rely on one of the basis sets used in this work considering the accuracy required and computational resources available.

*2*. Inspect the largest single and double excitation amplitudes. Amplitudes larger than 0.1 may indicate lower accuracy. However, amplitudes as large as 0.2 still do not mean meaningless results. We have to note, however, that the size of excitation amplitudes may change with the rotation of the orbital space. More detailed discussion can be found in Bartlett's and our reviews[5,25] and papers[13,15].

*3*. Inspect the $T_1$ diagnostic. Values larger than 0.03 may indicate lower accuracy.

*4*. The importance of the spin adaptation appears to be linked with large amplitudes and large value of the $T_1$ diagnostic.

*5*. Additional steps may include considerations of a more sophisticated version of the CC approach, like approximate or full iterative CCSDT (not available to us with the spin adaptation within the ROHF framework so far). Also some other classes of theoretical methods, as multireference methods, and a comparison of CCSD(T) results to the hierarchy of these alternative methods can be useful.

*6*. Consider other effects, as relativistic effects (including the spin–orbit splitting) and the vibration averaging.

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