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Analytic UHF-CCSD(T) second derivatives: implementation and application to the calculation of the vibration-rotation interaction constants of NCO and NCS*

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Abstract. An implementation of analytic open-shell UHF-CCSD(T) second derivatives is presented. To demonstrate applicability and test the accuracy of the UHF-CCSD(T) approach for the determination of spectroscopical parameters, vibration-rotation interaction constants were calculated for the ground ($1^2\Pi$) and first electronically excited ($1^2\Sigma$) states of the NCO and NCS radicals. In addition, harmonic vibrational frequencies for both states, the Renner-Teller parameter for the ground state, as well as the $1^2\Pi \rightarrow 1^2\Sigma$ excitation energy are reported. While the computed values are in good agreement with reliable experimental information for NCO, most of the data presented for NCS are predictions of quantities not well known from experiment.

Key words: Coupled-cluster theory – Analytic second derivatives – High-spin open-shell systems – Vibration-rotation interaction constants – Renner-Teller-effect

1 Introduction

The coupled-cluster singles and doubles method (CCSD) [1], especially when augmented by a non-iterative correction for triple excitations [CCSD(T)] [2], represents one of the highest computational levels which can be applied routinely in quantum chemical calculations. The method has proven very accurate for the calculation of a large range of properties such as, for example, geometries, force fields, and heats of formation (see, for example, [3]). Though the CCSD(T) approach has been applied mainly to the study of closed-shell systems, similar accuracy has been achieved for high-spin open-shell systems. Spin contamination is a potential problem, but general experience is that the residual effects are small in most cases.

One of the most important applications of quantum chemical calculations is the determination of spectroscopic constants. When comparing calculated values with experiment, it is important to realize that an analogously accurate treatment is required for the nuclear motion in order to fully exploit the accuracy achieved for the electronic part by means of the CCSD(T) method. Therefore, it is essential to go beyond the harmonic approximation for vibrations and the rigid rotor approximations for rotations, which so far is used in most calculations, and to consider explicitly anharmonic effects.

Consideration of anharmonic effects, however, poses a challenge for electronic structure calculations, as determination of the required parts of the potential energy surface is severely hampered by the fact that the required number of energy points grows rapidly with the dimension of the system. Analytic derivative techniques are, therefore, of great importance (see, for example, [4]). While the availability of analytic first derivatives is an essential requirement for any routinely used quantum chemical method, analytic second and higher derivatives have been only recently implemented for highly correlated methods [5]. The main reasons for the rather late development of analytic second derivatives are (1) the large programming effort associated with higher derivative techniques and (2) the fact that the cost of both analytic and numerical derivatives (based on numerical differentiation of gradients) approaches scales linearly with the number of perturbations. There are, however, situations where analytic approaches are clearly preferred. These include:

1. Evaluation of magnetic properties, where numerical approaches require determination of complex wave function parameters (see, for example, [6] and [7]).

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* Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

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2. Cases where numerical differentiation is hampered by instabilities of the reference function – a common problem in the study of open-shell systems [8].

3. Calculation of higher derivatives, where numerical accuracy can be significantly improved by use of analytic second derivatives (see, for example, [9]).

In a previous paper [5], implementation of geometrical second derivatives for closed-shell CCSD and CCSD(T) has been reported along with an application to the calculation of vibrational effects on rotational constants. As discussed there, the required cubic force constants ($\phi_{rrs} = \partial^3 E/\partial^2 Q_r \partial Q_s$, with Q_r and Q_s as normal coordinates) can be calculated efficiently by numerical differentiation of analytically evaluated second derivatives with respect to the totally symmetric normal coordinate Q_s [5, 9]. The rotational constants A_0, B_0, C_0 and the vibration-rotation interaction constants α_r computed in [5] within the CCSD(T) approximation are in excellent agreement with experiment.

In the present paper, we report an extension of the CCSD(T) analytic second derivative implementation to high-spin open-shell systems described by unrestricted Hartree-Fock (UHF) reference functions and present an application to the NCO and NCS radicals. Both NCO and NCS were first identified in the 1950s [11] and their vibrational spectra were assigned in the 1960s [12–14]. The rotational states of NCO are well known for the ground ($1^2\Pi$) as well as first ($1^2\Sigma$) and second ($2^2\Pi$) excited states [15–20], while information for the same states of NCS is very limited [14, 21–23]. The UHF-CCSD(T) method is applicable to the ground and $1^2\Sigma$ excited states and vibration-rotation interaction constants will be calculated for these two states within the current work. While insights regarding the accuracy of the UHF-CCSD(T) calculations might be obtained by comparison with the reliable experimental data for NCO, results for NCS provide useful information for future spectroscopic investigations.

2 Theory and implementation

The second derivative of the CCSD and CCSD(T) energy with respect to perturbations x and y can be cast in the following form [5]:

$$
\begin{aligned}
\frac{d^2E}{dxdy} = & \sum_{\mu\nu} D_{\mu\nu} \left\{ \frac{\partial^2 h_{\mu\nu}}{\partial x \partial y} + \sum_{\sigma\rho} D^{\mathrm{SCF}}_{\sigma\rho} \frac{\partial^2 \langle \mu\sigma || \nu\rho \rangle}{\partial x \partial y} \right\} \\
& + \sum_{\mu\nu} I_{\mu\nu} \frac{\partial^2 S_{\mu\nu}}{\partial x \partial y} + \sum_{\mu\nu\sigma\rho} \Gamma_{\mu\nu\sigma\rho} \frac{\partial^2 \langle \mu\nu || \sigma\rho \rangle}{\partial x \partial y} \\
& + \sum_{\mu\nu} D_{\mu\nu} \sum_{\sigma\rho} \frac{\partial D^{\mathrm{SCF}}_{\sigma\rho}}{\partial y} \frac{\partial \langle \mu\sigma || \nu\rho \rangle}{\partial x} \\
& + \sum_{\mu\nu} \frac{\partial D_{\mu\nu}}{\partial y} \left\{ \frac{\partial h_{\mu\nu}}{\partial x} + \sum_{\sigma\rho} D^{\mathrm{SCF}}_{\sigma\rho} \frac{\partial \langle \mu\sigma || \nu\rho \rangle}{\partial x} \right\} \\
& + \sum_{\mu\nu} \frac{\partial I_{\mu\nu}}{\partial y} \frac{\partial S_{\mu\nu}}{\partial x} + \sum_{\mu\nu\sigma\rho} \frac{\partial \Gamma_{\mu\nu\sigma\rho}}{\partial y} \frac{\partial \langle \mu\nu || \sigma\rho \rangle}{\partial x} \qquad (1)
\end{aligned}
$$

with $h_{\mu\nu}$, $S_{\mu\nu}$, and $\langle \mu\nu || \sigma\rho \rangle$ denoting one-electron Hamiltonian, overlap, and antisymmetrized two-electron integrals in the atomic orbital (AO) representation. Here and below, AO basis functions are denoted by Greek indices, while molecular orbitals are labeled by Latin indices $(p, q, r \ldots)$. In Eq. (1), $D^{\mathrm{SCF}}_{\sigma\rho}$ represents the SCF density matrix, while $D_{\mu\nu}$ and $\Gamma_{\mu\nu\sigma\rho}$ represent effective one- and two-particle CC density matrices [24, 25] as given, for example, for CCSD in [6] and for CCSD(T) in [7]. Finally, $I_{\mu\nu}$ are elements of what is often referred to as the energy-weighted density matrix (see, for example [26]). The required derivatives of these quantities are given by [5]:

$$
\begin{aligned}
\frac{\partial D_{\mu\nu}}{\partial y} = & \sum_{pq} c^*_{\mu p} \frac{\partial D_{pq}}{\partial y} c_{\mu q} + \sum_{pqr} U^{y\,*}_{rp} c^*_{\mu r} D_{pq} c_{\nu q} \\
& + \sum_{pqr} c^*_{\mu p} D_{pq} c_{\nu r} U^y_{rq} \qquad (2)
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial I_{\mu\nu}}{\partial y} = & \sum_{pq} c^*_{\mu p} \frac{\partial I_{pq}}{\partial y} c_{\mu q} + \sum_{pqr} U^{y\,*}_{rp} c^*_{\mu r} I_{pq} c_{\nu q} \\
& + \sum_{pqr} c^*_{\mu p} I_{pq} c_{\nu r} U^y_{rq} \qquad (3)
\end{aligned}
$$

and

$$
\begin{aligned}
\frac{\partial \Gamma_{\mu\nu\sigma\rho}}{\partial y} = & \sum_{pqrs} c^*_{\mu p} c^*_{\nu q} \frac{\partial \Gamma_{pqrs}}{\partial y} c_{\sigma r} c_{\rho s} + \sum_{pqrst} U^{y\,*}_{tp} c^*_{\mu t} c^*_{\nu q} \\
& \times \Gamma_{pqrs} c_{\sigma r} c_{\rho s} + \sum_{pqrst} c^*_{\mu p} U^{y\,*}_{tq} c^*_{\nu t} \Gamma_{pqrs} c_{\sigma r} c_{\rho s} \\
& + \sum_{pqrst} c^*_{\mu p} c^*_{\nu q} \Gamma_{pqrs} U^y_{tr} c_{\sigma t} c_{\rho s} \\
& + \sum_{pqrst} c^*_{\mu p} c^*_{\nu q} \Gamma_{pqrs} c_{\sigma r} U^y_{ts} c_{\rho t} \qquad (4)
\end{aligned}
$$

with the U^y_{pq} obtained by solving the coupled-perturbed HF (CPHF) equations. We note that the second derivatives in Eq. (1) are given in an asymmetric form. Computational advantages and disadvantages of this approach have been discussed in [27].

The implementation of UHF-CCSD(T) second derivatives based on Eq. (1) to Eq. (4) is very similar to that for the closed-shell RHF case [5]. Thus, the scheme outlined in Fig. 1 of [5] is also valid for the UHF case. Instead of repeating this, we discuss in the following the actual computation of the various quantities appearing in the above equations. The first three terms on the right-hand side of Eq. (1) are the same as those appearing in the expression for the first derivative of the CC energy, except that second derivative rather than first derivative integrals are used. The fourth term in Eq. (1) requires the perturbed SCF density matrix, which can be computed from the perturbed MO coefficients (U^y_{pq}) obtained by solving the CPHF equations. The last three terms in Eq. (1) again have a similarity to the first derivative expression, but now the unperturbed density matrices are replaced by the corresponding derivatives. The MO counterparts of these density matrices require knowledge of perturbed amplitudes $\partial t/\partial y$ and $\partial \lambda/\partial y$, i.e. the perturbed CC and Λ equations need to be solved. The corresponding equations can be found in [6]. Special attention has to be paid to triple excitation corrections included in CCSD(T), since the large number of triple excitation amplitudes prohibits their storage on disk. Optimal strategies including usage of perturbed canonical orbitals are discussed, for example, in [5].

The above analysis readily allows an estimate of computational cost for second derivative calculations: since perturbed CCSD and Λ equations need to be solved for all n_{pert} perturbations, the computational time is roughly $(n_{\text{pert}} + 1)$ times the cost of gradient calculations. For CCSD(T), the analysis is somewhat more involved, as the non-iterative n^7 steps are the most time-consuming. Perturbed triple excitation amplitudes as well as corresponding contributions to perturbed density matrices are calculated roughly with twice the cost as the corresponding unperturbed quantities. In addition, the required recalculation of the unperturbed triple excitation amplitudes needs to be considered and renders the whole calculation even more expensive, with the total cost of an analytic CCSD(T) second derivative calculation being about $2n_{\text{pert}}$ to $3n_{\text{pert}}$ times that of a corresponding gradient calculation. It thus appears that numerical differentiation of CCSD(T) gradients might be somewhat cheaper than full analytic differentiation. However, we consider this less severe considering the improved accuracy provided by the full analytic approach.

Finally, some comments on the use of symmetry in these calculations are warranted. The use of symmetry-adapted perturbations allows full exploitation of point group symmetry in the whole calculation, and translational symmetry can be used to reduce the number of perturbations by three. The importance of the former lies not only in the reduced computational demands, but also that calculations on excited states belonging to different irreducible representations than the ground state can now easily be carried out. This applies, for example, for the $1^2\Sigma$ states considered in this work.

To make calculations with about 150–250 basis functions feasible, the storage requirement must be reduced. Therefore, MO quantities with four virtual indices (either the integrals or density matrices) are never explicitly calculated in our implementation: the corresponding integral contributions are directly obtained from AO integrals, while corresponding contributions involving density matrices are directly calculated from t and λ amplitudes [6].

The UHF-based CCSD and CCSD(T) second derivatives have been implemented in a local version of the ACESII program system [28].

3 Applications

For linear molecules, the vibrational dependence of rotational constants can be expanded in a Taylor series:

$$B_v = B_e - \sum_r \alpha_r \left(v_r + \frac{d_r}{2} \right) + \cdots \tag{5}$$

where the α_r are known as vibration-rotation interaction constants and v_r denotes the quantum number for the rth vibrational normal mode with degeneracy d_r. The vibration-rotation interaction constants [10] depend on the equilibrium structure and the potential energy surface of the molecule and can be related via perturbation theory to the frequency ω_r of the normal mode Q_r, the equilibrium moment of inertia I, its derivatives a_r with respect to the normal modes, elements of the Coriolis zeta matrices $\zeta_{r,s}$ and cubic force constants ϕ_{rrs} in terms of dimensionless normal coordinates [10]:

$$\alpha_s = -\frac{2B_e^2}{\omega_s}\left[\frac{3a_s^2}{4I} + \sum_t (\zeta_{s,t})^2 \frac{(3\omega_s^2 + \omega_t^2)}{(\omega_s^2 - \omega_t^2)} + \pi\left(\frac{c}{h}\right)^{1/2} \sum_{s'} \phi_{sss'} a_{s'} \left(\frac{\omega_s}{\omega_{s'}^{3/2}}\right)\right] \tag{6}$$

and

$$\alpha_t = -\frac{2B_e^2}{\omega_t}\left[\frac{1}{2}\sum_s (\zeta_{s,t})^2 \frac{(3\omega_t^2 + \omega_s^2)}{(\omega_t^2 - \omega_s^2)} + \pi\left(\frac{c}{h}\right)^{1/2} \sum_{s} \phi_{stt} a_{s} \left(\frac{\omega_t}{\omega_{s}^{3/2}}\right)\right]. \tag{7}$$

Eq. (6) is appropriate for non-degenerate vibrations, while Eq. (7) is the corresponding expression for degenerate modes [29]. The various terms in Eqs. (6) and (7) account for (1) the non-vanishing mean-square displacement $\langle Q_r^2 \rangle$, (2) Coriolis interactions, and (3) anharmonic effects on $\langle Q_r \rangle$, with the first contribution missing in Eq. (7) due to symmetry reasons. Computation of the first two terms requires knowledge of the molecular geometry and harmonic force field. However, the third term, which is generally of comparable magnitude to the other two terms, depends upon the cubic force constants ϕ_{rrs}. The latter can conveniently be obtained by numerical differentiation of analytically calculated harmonic force constants with respect to totally symmetric normal coordinates as described, for example, in [5].

The treatment of vibronic energy levels in linear radicals is complicated due to spin-orbit interactions and the so-called Renner-Teller effect [30]. In the usual description (see, for example, [31]), rotational constants (B) are assumed to be independent of the total angular momentum and, consequently, the experimental energy levels of different components of the same vibronic state are fitted to the same B. Thus, neglect of spin-orbit interaction is not expected to be a serious problem in our treatment.[1] On the other hand, different rotational constants generally are assumed for different vibronic components corresponding to the same vibrational quantum numbers [31]. This means that Renner-Teller interactions in principle influence the rotational constants. In the usual treatment of Renner-Teller interaction, however, the degenerate harmonic bending potential corresponding to the frequency ω_2 is used as the zeroth-order approximation (see for example, [34]) and the splitting is treated as a perturbation. Therefore,

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[1] Calculations of the spin-orbit splitting for NCO and NCS have been reported in [32]

the effect of the Renner-Teller interaction on the rotational constants of the vibrational ground state appears in higher than second-order perturbation theory and is neglected in the current treatment. To our knowledge, no explicit formula for the dependence of the rotational constants on the Renner-Teller interaction has so far been given in the literature.

A further comment is warranted with respect to the treatment of the Renner-Teller effect in our calculations. Within the usual procedures, the potential energy surfaces along the bending coordinates of a linear molecule correspond to the symmetric and asymmetric Renner-Teller surfaces with $K = 0$, where K is the quantum number for the z component of the total angular momentum (given as the sum of the angular momenta of electrons and nuclei). Thus, harmonic force field calculations based on these surfaces directly yield the nondegenerate vibrational frequencies ω_2^+ and ω_2^- on these $\mathrm{K} = 0$ surfaces. (For details see, for example, [33].) As Renner-Teller interactions are neglected in the calculation of vibration-rotation interaction constants, the corresponding calculations need to be carried out for the degenerate situation with ω_2 as the frequency for both bending modes. This frequency as well as the corresponding Renner-Teller parameter ϵ are easily calculated from ω_2^+ and ω_2^- using the equations

$$\omega_2^+ = \omega_2\sqrt{1+\epsilon} \tag{8}$$

and

$$\omega_2^- = \omega_2\sqrt{1-\epsilon}\ . \tag{9}$$

The cubic force constants required for the determination of the vibration-rotation interaction constants [compare Eqs. (6) and (7)] are then obtained by differentiating a Hessian averaged with respect to both bending modes.

NCO is one of the most often investigated free radicals, partially because Renner-Teller interactions, Fermi resonances, and spin-orbit interactions can be observed and studied in detail for this molecule. For a review of the extensive research on NCO, we refer the interested reader to [35]. Here, we focus on measurements of the rotational transitions and their analysis. Techniques such as optical absorption spectroscopy [16], electron paramagnetic resonance [15], dispersed fluorescence [36], microwave spectroscopy [17, 18], and stimulated emission pumping (SEP) spectroscopy [19, 20] have been used in recent years to obtain accurate molecular constants for the ground ($1^2\Pi$) as well two low-lying excited states ($1^2\Sigma$, $2^2\Pi$) of NCO. Experimental investigations have provided a consistent set of data and enabled the assignment of the lower vibrational states, so that derived molecular constants can be considered reliable. Comparison of computed and experimental numbers can therefore be used to evaluate the performance of the UHF-CCSD(T) method in the accurate prediction of molecular properties.

The CCSD(T) method based on an UHF reference has been used in all calculations. As already mentioned, the ground state ($1^2\Pi$) and the first excited $1^2\Sigma$ state can be treated without problems by the CCSD(T) method, while the other excited states would necessitate an explicit excited state treatment and cannot be studied with UHF-CCSD(T). According to recent experience with closed-shell systems [5], two basis sets were used in the present calculations: a triple-zeta quality basis with two polarization functions (TZ2P) [37] has been used for the computation of the vibration-rotation interaction constant, while the much larger cc-pVQZ set [38] including g functions has been used to obtain accurate values for equilibrium geometry and B_e. Estimates for B_0 and B_{v_1,v_2,v_3} were then obtained from B_e computed with the cc-pVQZ basis and the α_τ values computed with the TZ2P basis. The combined use of the two basis sets allows a significant reduction in the computational requirement, while the loss in accuracy is expected to be small.

Table 1 lists the calculated molecular parameters, while a comparison of experimental and theoretical results is presented in Table 2 [39]. The overall agreement is very encouraging. The calculated rotational constants turn out to be systematically too high by about $5\text{–}8 \times 10^{-4}\,\mathrm{cm}^{-1}$, very similar to what was observed for the closed-shell molecule cyclopropenylidene at the same level of theory in [5]. Harmonic vibrational frequencies and Renner-Teller parameters are also in excellent agreement with corresponding values derived from experiment, thus indicating that our potential energy surface is reasonably good. The unusually small difference

Table 1. Spectroscopic constants of NCO as calculated at the CCSD and CCSD(T) levels of theory

State	$1^2\Pi$			$1^2\Sigma$		
Method	CCSD	CCSD(T)	CCSD(T)	CCSD	CCSD(T)	CCSD(T)
Basis	TZ2P		cc-pVQZ	TZ2P		cc-pVQZ
r_{CN} (Å)	1.2255	1.2329	1.2272	1.1803	1.1883	1.1839
r_{CO} (Å)	1.1747	1.1801	1.1741	1.1757	1.1834	1.1775
B_e (cm^{-1})	0.39168	0.38757	0.39135	0.40626	0.40089	0.40443
T_{00} (cm^{-1})	–	–		23215	22948	
ω_1 (cm^{-1})	1290	1258		1374	1328	
ω_3 (cm^{-1})	1933	1936		2403	2356	
ω_2 (cm^{-1})	549	529		708	679	
ϵ	0.1393	0.1452		–	–	
α_1 (cm^{-1})	0.00127	0.00128		0.00131	0.00137	
α_2 (cm^{-1})	−0.00098	−0.00103		−0.00063	−0.00061	
α_3 (cm^{-1})	0.00344	0.00336		0.00300	0.00307	

Table 2. Comparison of calculated and experimental molecular constants of NCO

	$1^2\Pi$		$1^2\Sigma$	
	Experiment	Calculations[a]	Experiment	Calculations[a]
B_{000} (cm^{-1})	0.3895139[b]	0.39006	0.402163[c] 0.402161[d]	0.40282
B_{100} (cm^{-1})	0.38802[e] 0.38769[f]	0.38878	0.401489[d]	0.40145
B_{010} (cm^{-1}) ($^2\Sigma$)	0.3904802[b]	0.39109	–	–
B_{010} (cm^{-1}) ($^2\Delta$)	0.3905459[b]	0.39109	–	–
B_{020} (cm^{-1})	0.391601[b] 0.39233[e] 0.39143[f]	0.39212	0.4025183[d]	0.40404
B_{001} (cm^{-1})	0.386178[g]	0.38670	0.399083[d]	0.39975
ω_1 (cm^{-1})	1254.64[e]	1258	–	1328
ω_3 (cm^{-1})	–	1936	–	2356
ω_2 (cm^{-1})	532.69	529	–	679
ϵ	0.1436[c]	0.1452	–	–
T_{00} (cm^{-1})	–	–	22754.4495[c]	22757

[a] Rotational constants obtained from CCSD(T)/cc-pVQZ equilibrium value with CCSD(T)/TZ2P vibration-rotation interaction constant; T_{00} is obtained from the CCSD(T)/cc-pVQZ minimum-to-minimum energy difference with zero-point energy correction from CCSD(T)/TZ2P calculations; all other values from CCSD(T)/TZ2P calculations

[b] From [17] and [18]

[c] From [16]

[d] From [19]; a fit using SEP data together with data from [12]

[e] From [20]; a fit using SEP data together with data from [36]

[f] From [36]

[g] From [15]

of 4 cm^{-1} between experimental and theoretical excitation energy for the $1^2\Pi \rightarrow 1^2\Sigma$ transition, however, should be considered fortuitous (partial cancelation of correlation and basis set incompleteness errors). In conclusion, the correspondence between our computational results and those derived experimentally suggests that useful predictions can be made from calculations at the UHF-CCSD(T) level of theory for the related molecule NCS.

Table 3. Spectroscopic constants of NCS as calculated at the CCSD(T) level of theory

State	$1^2\Pi$		$1^2\Sigma$	
Basis	tz2p	cc-pVQZ	tz2p	cc-pVQZ
r_{CN} (Å)	1.1757	1.1738	1.1909	1.1869
r_{CS} (Å)	1.6568	1.6419	1.6073	1.5979
B_e (cm^{-1})	0.20037	0.20295	0.20640	0.20845
T_{00} (cm^{-1})	–	–	27848	–
ω_1 (cm^{-1})	2018	–	2076	–
ω_3 (cm^{-1})	708	–	788	–
ω_2 (cm^{-1})	372	–	476	–
ϵ	0.1661	–	–	–
α_1 (cm^{-1})	0.00046	–	0.00117	–
α_2 (cm^{-1})	−0.00054	–	−0.00016	–
α_3 (cm^{-1})	0.00099	–	0.00099	–

The existence of the sulfur analog of NCO, NCS, was first reported together with the discovery of NCO [11], and it has been of interest in molecular spectroscopy ever since. Dixon and Ramsay were the first [14] who achieved a resolution required to assign rotational structure in the $1^2\Pi \rightarrow 2^2\Pi$ band of the absorption spectrum. The resolution was, however, not good enough to resolve the rotational structure in $1^2\Pi \rightarrow 1^2\Sigma$ band system. More recent experiments by Northrup and Sears [21, 22] using SEP and laser-induced fluorescence techniques, as well as a microwave study by Amano and Amano [23], also did not resolve all questions. Hence, the reported uncertainties of the molecular constants (except B_0) are much larger than for NCO. For the $1^2\Sigma$ state, only one (rather speculative) experimental value, the B_{001} constant, is available. Thus, the present theoretical investigation might provide important insights for future spectroscopic investigations of NCS. The calculations are performed at a similar level as for NCO: the CCSD(T) method based on a UHF reference together with tz2p [40] and cc-pVQZ [38] basis sets was used in the calculations. The results are documented in Table 3, while the theoretical values are compared with the available experimental information in Table 4. The calculated B_0 value for the ground state seems to support the most recent experimental value of B_0 (0.20369 cm^{-1}) [23], though the discrepancy between the calculated and measured values is somewhat larger than for NCO. The B_{100} value is also in fair agreement with our predictions, although the actual value might be somewhat lower than the measured one. Concerning the experimental rotational constants for the $^2\Sigma$ and $^2\Delta$ vibronic states corresponding to $v = (0, 1, 0)$, it is interesting to note that the two values differ only by 6×10^{-5} cm^{-1} for NCO, while they are very different for NCS. In the latter case, the corresponding vibration-rotation interaction constants even have opposite signs. Since the Renner-Teller parameter is just slightly higher for NCS than for NCO, the model we use (i.e. neglect of the Renner-Teller effect on the rotational constants) should work equally well for both systems. There are two possibilities to explain this discrepancy: either neglect of Renner-Teller effects on B is not justified or the interpretation of the experiment on NCS needs to be reconsidered. This question is, how-

Table 4. Comparison of calculated and experimental molecular constants of NCS

	$1^2\Pi$		$1^2\Sigma$	
	Experiment	Calculations[a]	Experiment	Calculations[a]
B_{000} (cm^{-1})	0.2036[b] 0.2039[c] 0.206[d] 0.203694951[e]	0.20277	–	0.20753
B_{100} (cm^{-1})	0.204[b]	0.20231		0.20636
B_{010} (cm^{-1})($^2\Sigma$)	0.2033[g]	0.20331	–	–
B_{010} (cm^{-1})($^2\Delta$)	0.20491[g]	0.20331	–	–
B_{020} (cm^{-1})	0.2084[g]	0.20385	–	0.20785
B_{001} (cm^{-1})	0.210[b] 0.1984[g]	0.20178	0.201[f]	0.20654
ω_1 (cm^{-1})	–	2018	–	2076
ω_3 (cm^{-1})	735.41[g]	708	–	788
ω_2 (cm^{-1})	375.96[g]	372	–	476
ϵ	0.1598[g]	0.1661	–	–
T_{00} (cm^{-1})	–	–	26054.56[g]	27327

[a] Rotational constants obtained from CCSD(T)/cc-pVQZ equilibrium value with CCSD(T)/tz2p vibration-rotation interaction constants; T_{00} is obtained from the CCSD(T)/cc-pVQZ minimum-to-minimum energy difference with zero-point energy correction from CCSD(T)/tz2p calculations; all other values from CCSD(T)/tz2p calculations

[b] From [14]

[c] From [21]; new fit of the data from [14]

[d] From [21]; a fit using LIF data together with data from [14]

[e] From [23]

[f] From [21]

[g] From [22]

ever, beyond the goals of the present study. The experimental B_{020} appears too high according to our calculations and in fact is inconsistent with the B_{010} values derived from the same experiment. A possible explanation might be a Fermi resonance which has been considered in the analysis of the experimental data but not considered in our treatment. None of the two rather different experimental B_{001} agrees with the calculated value. Considering the good agreement for NCO and for the other parameters for NCS, it appears that this theoretical prediction may be more reliable than the inferred values from experiment. As for NCO, very good agreement is found for the Renner-Teller parameter ϵ and the harmonic bending frequency ω_2. On the other hand, ω_3 is somewhat lower than the experimentally obtained value, but agreement is still reasonable. Concerning the $1^2\Sigma$ state, calculations do not support the experimentally derived value for B_{001}. However, the observed excitation energy is in satisfactory agreement with the computed value.

4 Conclusions

An implementation of analytic CCSD and CCSD(T) second derivatives for the treatment of high-spin open shell systems starting from a UHF reference function is reported. The power of this technique is demonstrated by an investigation of vibration-rotation interactions in the ground ($1^2\Pi$) and $1^2\Sigma$ excited states of the radicals NCO and NCS. For NCO, comparison with the available and reliable experimental data demonstrates the high accuracy which can be achieved in the calculation of spectroscopic constants. Very good agreement has been found for the rotational constants of several low-lying vibrational levels of both states as well as for harmonic frequencies, the Renner-Teller parameter, and the $1^2\Pi \rightarrow 1^2\Sigma$ transition. In case of NCS, much less experimental information is available. For the ground state, calculated rotational constants (B_0, B_{100}, B_{010}), harmonic frequencies, and the Renner-Teller parameter agree reasonably well with the sparse experimental observations. Larger discrepancies found for B_{001} and B_{020} point to certain inconsistencies in the experimental set of data. We also make predictions for rotational constants in the $1^2\Sigma$ excited state which have not yet been obtained from experiment.

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