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Theoretical Study of the Fe(phen)$_2$(NCS)$_2$ Spin-Crossover Complex with Reparametrized Density Functionals

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The theoretical study of spin-crossover compounds is very challenging as those parts of the experimental findings that concern the electronic structure of these compounds can currently hardly be reproduced because of either technical limitations of highly accurate ab initio methods or because of inaccuracies of density functional methods in the prediction of low-spin/high-spin energy splitting. However, calculations with reparametrized density functionals on molecules of the thermal spin-crossover type can give improved results when compared with experiment for close-lying states of different spin and are therefore important for, e.g., transition metal catalysis. A classification of transition metal compounds within hybrid density functional theory is given to distinguish standard, critical, and complicated cases. From the class of complicated cases we choose the prominent spin-crossover compound Fe(phen)$_2$(NCS)$_2$ and show in a first step how the electronic contribution to the energy splitting can be calculated. In a second step, the vibrational effects on the spin flip are investigated within the harmonic force-field approximation of the isolated-molecule approach. A main result of the study is the necessity of exact-exchange reduction in hybrid density functionals to arrive at reasonable electronic energy splittings. The study resolves problems that originated from the use of standard density functionals, which are not able to reproduce the electronic contribution to the low-spin/high-spin splitting correctly, and demonstrates to which extent reparametrized density functionals can be used for the prediction of the spin-crossover effect.

1. Introduction

The spin crossover in transition metal complexes has been discussed in great detail in many excellent reviews[1−8] in which the wealth of results obtained from various experimental techniques is compared and analyzed in terms of semiquantitative models for the spin transition. We start with our discussion at the innermost core of the phenomenon, which is the electronic contribution of each individual molecule. Subsequently, the intramolecular vibrations are considered.

The theoretical analysis of the thermal spin-crossover phenomenon requires an accurate calculation of the electronic structure and a reliable modeling of cooperativity in the condensed phase, which induces a sharp thermal spin flip. While the former electronic part of such an analysis can safely be carried out in the isolated-molecule approach of quantum chemistry, this is not the case for the latter, the vibrational part. However, an applicability study of the isolated-molecule approach to this vibrational part of the problem is worth being analyzed as the vibrational frequencies can be calculated within the quantum chemical harmonic force field without the assumption of any model parameters. Furthermore, the isolated molecule is the kernel of several subsequent models (e.g., ref 9) that treat the spin crossover on the basis of a collection of intramolecular harmonic

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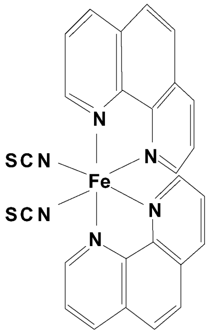

Figure 1. Structure of the Fe(phen)$_2$(NCS)$_2$ spin-crossover complex.

oscillators as is done in the standard quantum chemical harmonic force field that is used here.

Large molecules such as the spin-crossover complex Fe(phen)$_2$(NCS)$_2$ (Figure 1) can currently only be studied quantum chemically with methods of density functional theory (DFT). This is particularly true if extended quantum chemical calculations (structure optimizations and the calculation of vibrational frequencies) are needed. Today, even the most advanced ab initio methods of sufficient accuracy and high practicality with respect to computer resources and time—like the very recently developed sophisticated MR-MP2 code by Grimme and Waletzke[10]—are hardly able to cope with single-point calculations on systems such as Fe(phen)$_2$(NCS)$_2$.

As we have demonstrated in refs 11 and 12, the electronic energy splitting between spin states *a* and *b*, $\Delta E^{e}_{a/b}$, is governed by the amount of exact exchange admixture $E_{\mathrm{ex.ex.}}$ in the energy functional. A main result was that adjustment of the exact exchange admixture is necessary since pure density functionals tend to favor low-spin states, while hybrid functionals like B3LYP usually give the high-spin state as the lowest-energy state if the low-spin/high-spin energy splitting $\Delta E^{e}_{\mathrm{LS/HS}}$ is not too large.

Exact exchange has been introduced into DFT by Becke,[13] whose parametrization led to the development of hybrid functionals such as B3LYP[14]

$$E_{xc}^{\mathrm{B3LYP}} = E_x^{\mathrm{LSDA}} + c_1 E_x^{\mathrm{B88}} + c_2 E_c^{\mathrm{LYP}} + (1 - c_2) E_c^{\mathrm{VWN}} + c_3[E_{\mathrm{ex.ex.}} - E_x^{\mathrm{LSDA}}] \quad (1)$$

where E_x^{LSDA} is the Slater exchange, E_x^{B88} is Becke's gradient correction to the local spin density approximation (LSDA) for exchange,[15] and E_c^{VWN}[16] and E_c^{LYP}[17] are correlation functionals. The parameters c_i were fixed to be $c_1 = 0.72$, $c_2 = 0.81$, and $c_3 = 0.20$. We found that a reduction of c_3 to 0.15 yields a functional, dubbed B3LYP*, which is the only one capable of reproducing ground-state multiplicities for iron−sulfur complexes.[11] This result was then found to be transferable to other transition metal complexes as well, and the accuracy of B3LYP* thermochemistry is as high as the original B3LYP.[12]

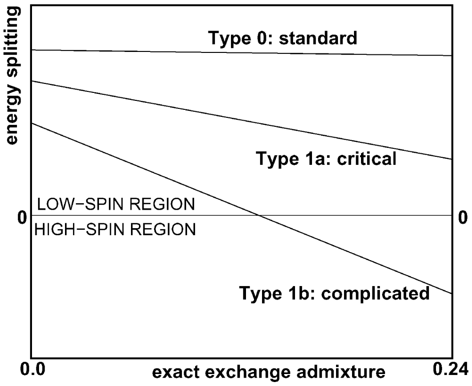

Figure 2. Reliability of DFT calculations: classification of compounds with respect to the variation of the energy splitting of states of different multiplicity $\Delta E^{e}_{a/b}$ with the exact exchange parameter c_3.

Table 1. Two Criteria That Define Three Classes of Transition Metal Compounds within Hybrid DFT

class	description	A[a]	B[b]
0	standard	negligible	no
1a	critical	large	no
1b	complicated	large	yes

[a] Denotes a descriptor for the absolute value of the slope of the function $\Delta E^{e}_{a/b} = \Delta E^{e}_{a/b}(c_3)$. [b] Logical flag for the check of crossing the zero-splitting horizontal line in the given interval of c_3.

We may classify the compounds, for which states of different multiplicities become significant in chemical processes, within hybrid DFT according to two criteria (Figure 2). These criteria are the absolute value of the slope of the dependence of the electronic energy splitting $\Delta E^{e}_{a/b}$ on c_3 and the crossing of the horizontal zero-splitting line, which marks a change of the ground-state multiplicity in such a hybrid DFT calculation. Table 1 gives a list of three classes—0, 1a, and 1b—and their correspondence to these criteria.

The first class contains all standard molecules for which the energy splitting of states of different multiplicities does only little depend on the exact exchange admixture parameter c_3. The slope of the linear relationship between $\Delta E^{e}_{a/b}$ and c_3 is not larger than approximately 0.5 kJ/mol for a change of 0.01 in c_3. For the B3LYP hybrid functional this means that we obtain a difference in energy splittings from B3LYP ($c_3 = 0.00$) and B3LYP ($c_3 = 0.20$) that is not larger than 10 kJ/mol. This classification is, of course, only meaningful if the splitting itself is much larger than 10 kJ/mol.

The second class 1a consists of those critical cases where the variation of the exact exchange parameter does not change the spin state of the ground state although the absolute value of the slope is large such that reaction energetics can significantly be affected, and wrong conclusions might be drawn on the basis of results from standard density functional calculations. We should repeat that the absolute value of the splitting must again be larger than the slope. Otherwise we would end up at class 1b.

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This third class 1b contains all complicated cases, for which the absolute value of the slope is very large such that pure and hybrid density functionals are even not conclusive on the true spin state of the ground state. In these cases it often does not matter how large the energy splitting itself is since we would find a spin flip upon variation of c_3 even for a splitting of 100 kJ/mol calculated with pure density functionals since the slope can be as large as 5 kJ/mol per 0.01 step in c_3 in these cases. The spin-crossover complexes, whose characteristic is their extremely small low-spin/high-spin energy splitting such that thermally induced spin flips can be observed experimentally, are obviously of this third class 1b.

Here, we analyze the spin-crossover compound Fe(phen)$_2$(NCS)$_2$ in the framework of hybrid DFT to demonstrate that DFT can approach chemical accuracy even in the case of molecules of type 1b, if the simple and surprisingly successful reparametrization of c_3 is taken into account. Although this reparametrization yields reliable energy splittings from DFT calculations for transition metal compounds that are of types 1a and 1b, the reparametrized functional B3LYP* need not necessarily be the optimum choice for the calculation of vibrational frequencies. In addition, the calculation of vibrational spectra even of an isolated molecule that is of the size of Fe(phen)$_2$(NCS)$_2$ is computer-resources demanding if approximations with respect to the quantum chemical method (no small basis sets, no effective core potentials) need to be reduced to the largest extent. However, a tailored methodology has been established particularly for this purpose[18] (see next section).

This work is organized as follows: in the following section 2, we describe the quantum chemical methodology in detail. Energy splittings, structural parameters, and vibrational frequencies are analyzed afterward, followed by a discussion of the spin-crossover phenomenon within the isolated-molecule approach.

2. Quantum Chemical Methodology

For all calculations the density functional and Hartree−Fock programs provided by the TURBOMOLE 5.1 suite[19] were used. We employ the pure density functionals by Becke and by Perdew dubbed BP86[15,20] and by Becke and by Parr et al. dubbed BLYP[15,17] as well as the hybrid functional B3LYP[13,14] as implemented in TURBOMOLE. Furthermore, the B3LYP* functional[11] (i.e., B3LYP with $c_3 = 0.15$) has been employed extensively.

For the BP86 functional we apply the resolution-of-the-identity (RI) technique[21,22] since this increases the efficiency of the calculations largely. All results are obtained from all-electron restricted and unrestricted Kohn−Sham calculations. The TZVP basis set[23] featuring a valence triple-ζ basis set with polarization functions on all atoms was used throughout. Note that the TZVP basis set is considerably larger than all basis sets that have been applied in calculations on spin-crossover complexes so far.

We always ensured that the initial occupation in the case of C_2 symmetry corresponds to the ground-state configuration. Furthermore, singlet states have also been calculated as unrestricted singlets to find potential lower-lying open-shell singlet states. We found the Fe(phen)$_2$(NCS)$_2$ singlet to be closed-shell, which was also confirmed by stability analyses[24] revealing singlet and triplet stability in BP86/RI as well as in B3LYP calculations. The spin contamination of the quintet states is rather small: the $\langle S^2\rangle$ expectation value is 6.222 for BP86/RI, 6.076 for B3LYP*, and 6.040 for B3LYP.

For the frequency analyses, the program package SNF[18] was employed. The second derivatives of the total electronic energy of the harmonic force field are calculated numerically from analytic energy gradients, which were obtained from TURBOMOLE. From the vibrational frequencies ν_i of this normal-mode analysis, we calculate the contribution of (intramolecular) vibrations to the total entropy of a given state according to the well-known formula for a collection of harmonic oscillators:

$$S^{v}(T,\nu_i) = \sum_i \left\{ \frac{h\nu_i}{kT}\left[\exp\left(\frac{h\nu_i}{kT}\right) - 1\right]^{-1} - \ln\left[1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right]\right\} \quad (2)$$

An electronic contribution to the total entropy of a state is only apparent for the quintet state ($M_S = 5$, where M_S is the multiplicity, which is twice the spin quantum number plus one) given by the spin-only value of the 5-fold degenerate high-spin wave function

$$S^{el}(M_S) = R\ln(M_S) = R\ln(5) = 13.38\ (\mathrm{J/mol\ K}) \quad (3)$$

where we assume that the electronically excited states are higher in energy such that they cannot be thermally excited, and the total state is governed by the lowest-energy wave function only.

The translational contribution to the total entropy is computed according to the standard expression for an ideal gas. All total entropy values given in this work contain the translational contribution, while it cancels upon subtraction of the total entropies of different spin states. All $\Delta S(T)$ values calculated within this model do thus not contain any translational contribution. The rotation part of the total entropy of a given state is calculated classically according to

$$S^{rot}(T, J_i) = R[\ln(z^{rot}) + 3/2],\ z^{rot} = \frac{\sqrt{\pi}}{\sigma}\sqrt{\frac{T^3}{T_1T_2T_3}},\ T_i = \frac{h^2}{8k\pi^2 J_i} \quad (4)$$

where σ is the symmetry number, which is two in the case of C_2 and one in the case of C_1 symmetry, and J_i are the moments of inertia. S^{rot} is different for different spin states and does not cancel upon subtraction in contrast to the translational contribution because the moments of inertia change significantly upon spin transition from the LS to the HS state, which possesses increased Fe−N bond lengths. It should be noted that this entropy contribution from free rotation of a single molecule can be neglected for the spin-crossover phenomenon taking place in condensed phase where the complexes cannot rotate freely. However, the rotational contribution appears to be of the size of the contribution from low-frequency vibrations in the solid state[25] and is therefore included here.

3. Spin-Crossover Phenomenon

3.1. Dependence of $\Delta E^{e}_{LS/HS}$ on c_3. As has already been mentioned in the Introduction, energy splittings $\Delta E^{e}_{a/b}$ from

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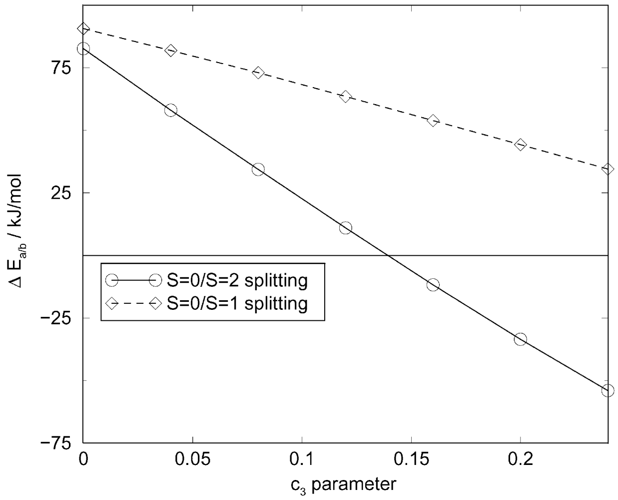

Figure 3. Dependence of $\Delta E^{\rm e}_{a/b}$ on c_3 for $Fe(phen)_2(NCS)_2$ (in kJ/mol; TZVP basis set was used).

Table 2. Low-Spin/High-Spin Splittings $\Delta E^{\rm e}_{\rm LS/HS}$ of $Fe(phen)_2(NCS)_2$ Calculated with Different Methods[a]

method	$\Delta E^{\rm e}_{\rm LS/HS}$
B3LYP ($c_3 = 0.00$)	82.6
BP86/RI	66.0
BLYP	48.1
B3LYP ($c_3 = 0.12$)	11.0
B3LYP ($c_3 = 0.13$)	5.5
B3LYP ($c_3 = 0.14$)	−0.3
B3LYP ($c_3 = 0.15$)	−6.1
B3LYP	−33.4
HF	−407.5
B3LYP/3-21G[26]	−35.5

[a] In kJ/mol; TZVP basis set.

hybrid density functionals such as B3LYP show a strong dependence on the exact exchange admixture expressed by the value of the c_3 parameter in B3LYP. Figure 3 shows the dependence of the energy splittings $\Delta E^{\rm e}_{a/b}$ on c_3 of three states in $Fe(phen)_2(NCS)_2$: (1) the $\Delta E^{\rm e}_{\rm LS/HS}$ splitting of the singlet and quintet and (2) the energy splitting of the low-spin singlet and the triplet state. While this triplet state has experimentally not been found to be of importance for the thermal spin transition, it becomes important in the case of photoinduced spin crossover (e.g., ref 5).

We note that the dependence of $\Delta E^{\rm e}_{\rm LS/HS}$ on c_3 is linear, which is a remarkable feature already described for transition metal complexes in refs 11 and 12 as a consequence of the explicitly considered Fermi correlation in the exact exchange expression $E_{\rm ex.ex.}$. Furthermore, the triplet state is always higher in energy than the low-spin singlet and the high-spin quintet, which is in agreement with experiment. The negative slope of the curves shows that the exact exchange admixture favors the triplet and quintet states with respect to the singlet state. The slope is larger the greater the difference of the spins (i.e., the bigger the $\Delta\langle S^2\rangle$ expectation value difference is).

From Figure 3 we deduce that the exact exchange admixture in B3LYP needs to be reduced from $c_3 = 0.20$ to $c_3 \approx 0.14$ to arrive at an electronic energy splitting that is reasonable for the description of the spin transition. Table 2 lists $\Delta E^{\rm e}_{\rm LS/HS}$ values obtained from the pure density functionals BP86/RI, BLYP, and B3LYP ($c_3 = 0.00$), from various variants of B3LYP, and from Hartree−Fock.

The general feature of the pure density functionals is their preference of singlet states resulting in large positive values for $\Delta E^{\rm e}_{\rm LS/HS}$. On the opposite side, we find the Hartree−Fock splitting of −407.5 kJ/mol, which is far from being reasonable. An energy splitting of this size, which is the reason why correlated methods based on Hartree−Fock wave functions (like Møller−Plesset perturbation theory of second order or like the standard coupled-cluster approach) are not capable of the description of spin transitions in transition metal complexes, has also been found for the manganocene spin-crossover compound.[12] B3LYP yields $\Delta E^{\rm e}_{\rm LS/HS} = -33.4$ kJ/mol, which is much too small. Only values of c_3 around 0.14 give reasonable energy splittings for $Fe(phen)_2(NCS)_2$. Already B3LYP ($c_3 = 0.13$) yields an appropriate description of $Fe(phen)_2(NCS)_2$ because the singlet state is the ground state, and the splitting is in the range of $3RT$ such that the thermal spin transition is electronically possible. It should be noted that the energy splitting of 11.0 kJ/mol for B3LYP ($c_3 = 0.12$) gives the closest resemblance within our theoretical model, which is discussed in detail in section 3.3 and in which the electronic energy splitting is given by $\Delta E^{\rm e}_{a/b} = T\Delta S(T_{1/2}) - \Delta E^{\rm v}_{a/b}(T_{1/2}) = 176 \times 0.0398 - 5.1 = 12.1$ kJ/mol (see below).

In our previous studies we identified B3LYP ($c_3 = 0.15$), dubbed B3LYP*, as a significantly improved variant of B3LYP. In this case, B3LYP* favors the quintet state by −6.1 kJ/mol, which is comparatively small in view of the error of the method (ca. 10 kJ/mol)[12] and which is significantly better than B3LYP. Although B3LYP* still favors the high-spin state that is in contrast with the experimental finding, this hybrid functional is still recommended for general use in DFT calculations on transition metal compounds because it is applicable to a wide range of transition metal complexes[12] and represents the smallest modification to the original B3LYP functional. The improvement of the density functional for the calculation of spin-crossover complexes such as $Fe(phen)_2(NCS)_2$ should not be the reduction of c_3 from 0.15 in B3LYP* to 0.13 or 0.12 but the consideration of improved exchange and correlation functionals, which enter the definition of the hybrid energy functional in eq 1.

Paulsen, Trautwein and co-workers[26] have recently conducted an extensive study of nine spin-crossover complexes using different basis sets and density functionals. Their results show the same pattern, which has been discussed so far, namely, that B3LYP favors, in general, the high-spin state while all pure density functionals favor the low-spin state. However, they did not trace this failure back to the role of Fermi correlation, which is explicitly taken into account in a hybrid functional through the exact exchange contribution as explained in detail in ref 11. It is surprising that the B3LYP value for $\Delta E^{\rm e}_{\rm LS/HS}$ of −35.5 kJ/mol obtained in ref

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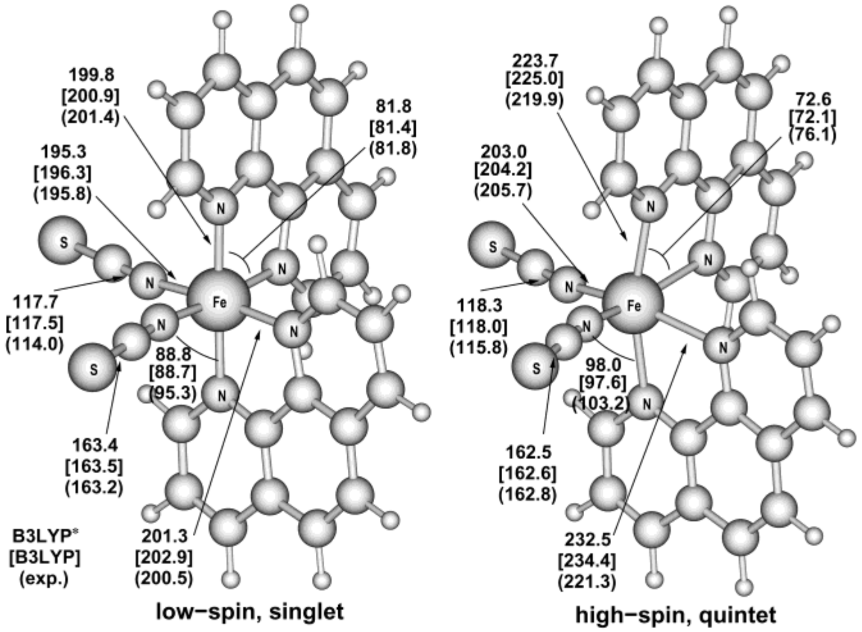

Figure 4. Structures of LS- and HS-Fe(phen)$_2$(NCS)$_2$ as obtained with B3LYP*/TZVP and B3LYP/TZVP in brackets as compared with the experiment (in parentheses)[27].

26 (Table 2) deviates only little from the one reported here (−33.4 kJ/mol), although the 3-21G basis set used in ref 26 is extremely small and does not contain any polarization functions.

3.2. Effect on Structural Parameters and Vibrational Frequencies. We briefly discuss effects of the exact exchange parameter on bond lengths. Figure 4 gives an overview of selected bond lengths and angles calculated with B3LYP and B3LYP* and compared with the experimental values from ref 27. For a comparison with structural parameters from BP86/RI calculations, we refer to ref 25. Notice that the symmetry reduction from C_2 to C_1 observed in BP86/RI calculations on the high-spin state in ref 25 is neither observed for B3LYP nor for B3LYP*, which both possess C_2 symmetric high-spin states (as is the case in HF and BLYP calculations). However, as was already mentioned in ref 25, the energy gain by reducing the symmetry in the BP86/RI calculation, which did not appear to be an artifact of a wrong initial occupation of the molecular orbitals in the two irreducible representations of C_2, is less than 10 kJ/mol and thus of the order of the accuracy of current DFT methods.

The well-known increase of metal−ligand bond lengths upon spin flip from singlet to quintet, which may be rationalized in terms of a one-particle picture as an occupation of molecular orbitals with antibonding character, is well-reproduced in the calculation. We find a better agreement for metal−nitrogen(phenanthroline) distances with experiment for the singlet state than for the quintet state. It is noteworthy that the N−C bond lengths of the NCS ligands are about 3 pm larger for B3LYP and B3LYP* (independent of the spin state) than the experimental value, whereas the C−S bond distances are in excellent agreement. While we found in previous studies on Fe(II)−S complexes that B3LYP does not yield satisfactory bond lengths for Fe(II)−S and that B3LYP* performs slightly better,[11] this is also the case for HS-Fe(phen)$_2$(NCS)$_2$ but not for LS-Fe(phen)$_2$(NCS)$_2$.

The octahedral nitrogen atom environment of Fe(II) is largely distorted in HS-Fe(phen)$_2$(NCS)$_2$, which is in agreement with the experimental finding in ref 27, where this was identified as the main structural feature indicating a prominent role of the short-range (i.e., local and nonlattice) structural changes.

The calculated IR absorption spectra for the low-spin and high-spin states of Fe(phen)$_2$(NCS)$_2$ are depicted in Figure 5 , and Table 3 lists a comparison of calculated wavenumbers for selected normal modes of the NCS ligands with experiment (see ref 25 for a detailed discussion of all normal modes in comparison to the experimental IR and Raman spectra).

The first recording of the high-frequency N−(CS) modes dates back to the early 1960s.[28,29] König and Madeja[30,31] conducted the assignment of vibrations in the range of 300−4000 cm^{-1}. Their detailed analysis has been extended by Sorai and Seki in 1974,[32] who were able to record IR spectra temperature-dependent down to 30 cm^{-1} and analyzed the spin flip in terms of a phenomenological theory based on heterophase fluctuations. Takemoto and Hutchinson[33−35] made the first assignment of Fe−N stretching vibrations in the complex region between 100 and 600 cm^{-1} by the

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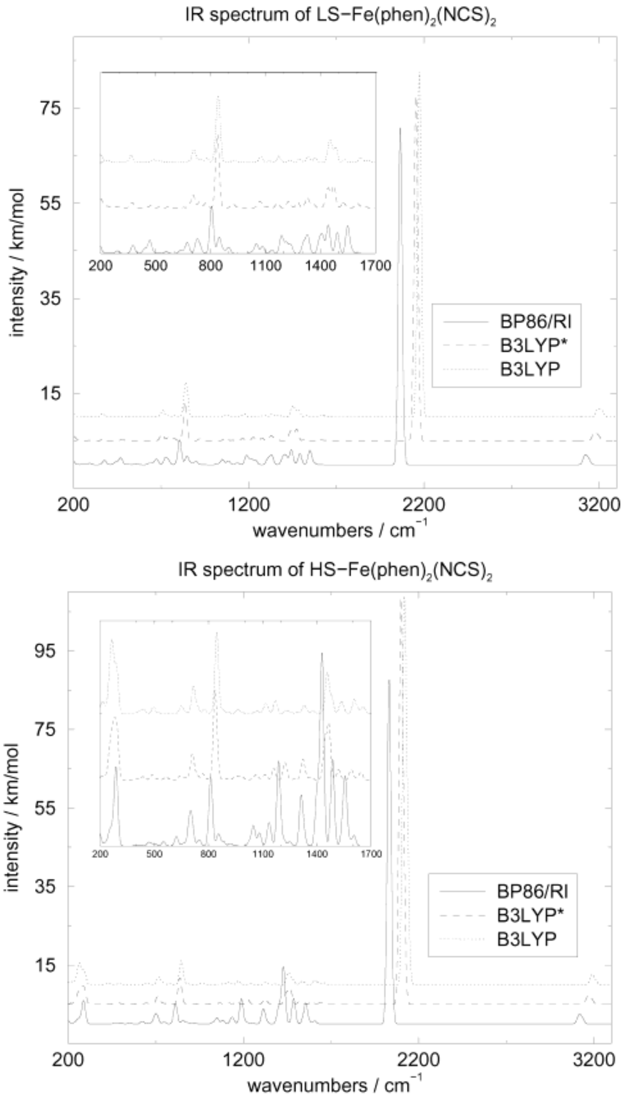

Figure 5. Calculated IR spectra of low-spin (top) and high-spin (bottom) Fe(phen)$_2$(NCS)$_2$ (top line: B3LYP; middle line: B3LYP*; bottom line: BP86/RI).

application of ^{54,57}Fe isotope techniques. Recently, Bousseksou et al. estimated the vibrational contributions to the entropy change by means of Raman spectroscopy.[36] The latest very accurate temperature-dependent FT-IR and Raman spectra have been recorded by Brehm et al.[25] down to 60 cm^{-1}.

The bending vibrations of the NCS ligands are difficult to extract from the calculations as the coupling with the phenanthroline ligands is rather strong. The pair of symmetric and asymmetric normal modes at wavenumbers around 840 cm^{-1} is well-reproduced by all density functionals bearing in mind that they have been calculated within the harmonic approximation. The deviations are much larger for the pair of stretching modes around 2100 cm^{-1}. This larger deviation for the high-frequency modes may partially be attributed to large anharmonicities, which are not taken into account in the quantum chemical model. However, the differences between harmonic frequencies obtained with different functionals for these modes are as large as 109 cm^{-1}. For these two high-frequency modes, the dependency on the functional can thus be as large as the contribution from the anharmonicity of the potential energy surface. These large deviations are exceptional and not found for most of the other modes. Furthermore, the high-frequency modes contribute only very little to the vibrational entropy such that these deviations do not affect the calculation of the entropy.

Table 3. Wavenumbers $\tilde{\nu}$ in cm^{-1} for the Vibrations of the NCS Ligands of Fe(phen)$_2$(NCS)$_2$ in Its Singlet and Quintet State[a]

normal mode	irrep	BP86/ RI[25]	B3LYP* this paper	B3LYP this paper	exp refs 30,31/ref 32/ref 25
			Low-Spin State		
N−(CS) sym stretch	*a*	2069.8	2159.8	2179.0	2116/2114/2110
N−(CS) asym stretch	*b*	2060.4	2150.1	2169.5	2108/2107/2107
(NC)−S sym stretch	*a*	848.0	835.6	833.0	809/−/845
(NC)−S asym stretch	*b*	844.3	832.2	830.0	807/−/842
NCS bending	*b*	438.7	466.8	478.8	476/−/467, 475, 477, 479
	a	448.7	476.5	486.8	
	b	467.9	479.7	487.6	
	a	469.0	479.9	489.9	
			High-Spin State		
N−(CS) sym stretch	*a*	2040.0	2111.9		2075/2074/2072
N−(CS) asym stretch	*b*	2028.5	2096.5		2063/2062/2062
(NC)−S sym stretch	*a*	853.4	848.1		809/−/847
(NC)−S asym stretch	*b*	852.7	846.2		809/−/847
NCS bending	*b*	462.1	479.1		473,483/−/473, 484
	b	463.8	483.6		
	a	468.8	483.7		
	b	469.8	487.1		
	b	473.7	489.0		
	a	478.4	489.9		
	a		490.7		
	b	491.4			

[a] The bending modes of the low-spin complex calculated with BP86/RI show a stronger coupling with the phenanthroline ligands than the modes calculated with B3LYP* and B3LYP. Note that the minimum structure of the high-spin state is of C_1 symmetry with BP86/RI, while it is C_2 for B3LYP* and B3LYP.

The comparison of the normal modes demonstrates that the hybrid density functional B3LYP*, which is most appropriate for the calculation of the electronic structure, need not be the optimum choice for the calculation of vibrational spectra. In the case of Fe(phen)$_2$(NCS)$_2$, we find that harmonic BP86/RI wavenumbers are in better agreement with fundamental (anharmonic) experimental ones than harmonic B3LYP* and B3LYP wavenumbers are. This better agreement is due to an error compensation for BP86/RI as anharmonicities are completely neglected in the quantum chemical model.[37,38] Consequently, the harmonic frequencies from B3LYP and B3LYP* calculations may actually compare better with harmonic frequencies recalculated from the experimental values. However, since we aim at the experimental values, which are needed for a discussion of the vibrational entropy contribution, we recommend the BP86/RI values for this purpose.

3.3. Entropy Contributions and the Spin-Flip Temperature. The most challenging task for the quantum chemical calculation of the spin-crossover phenomenon would be the prediction of the spin-flip temperature $T_{1/2}$. One would expect that this is hardly possible within the standard isolated-

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molecule approach of molecular quantum chemistry because the spin crossover is induced in condensed phase mainly by low-frequency vibrations of the crystal lattice, which contribute most to the total entropy of a given state. However, it is worthwhile to have a closer look upon the calculation of the spin-flip temperature within the isolated-molecule approach.

At the spin-flip temperature $T_{1/2}$, the Gibbs free enthalpy change $\Delta G(T)$ would be zero such that we may calculate from

$$\Delta G(T_{1/2}) = 0 = \Delta H(T_{1/2}) - T_{1/2}\Delta S(T_{1/2}) \tag{5}$$

the spin-flip temperature:

$$T_{1/2} = \frac{\Delta H(T_{1/2})}{\Delta S(T_{1/2})} \tag{6}$$

The main drawback of this equation is that the enthalpy and entropy depend on the spin-flip temperature to be calculated. The low-spin/high-spin energy splitting at 0 K $\Delta E^0_{a/b}$ can be obtained from the electronic energy splitting by adding the difference in zero-point energy of both spin states:

$$\Delta E^0_{a/b} = \Delta E^{\mathrm{e}}_{a/b} + \Delta ZPE. \tag{7}$$

At the finite spin-flip temperature $T_{1/2}$ we add to the electronic splitting $\Delta E^{\mathrm{e}}_{a/b}$ the temperature-weighted vibrational contribution of all harmonic oscillators (normal modes):

$$\Delta H(T_{1/2}) = \Delta E^{\mathrm{e}}_{a/b} + \Delta H_{\mathrm{res}}(T_{1/2}) = \Delta E^{\mathrm{e}}_{a/b} + \Delta E^{\mathrm{v}}_{a/b}(T_{1/2}) \tag{8}$$

Note that the translational and rotational contributions, which are estimated classically as $3RT$ each, cancel upon subtraction and need not to be taken into account (i.e., the residual enthalpy $\Delta H_{\mathrm{res}}(T_{1/2})$ contains only the vibrational part $\Delta E^{\mathrm{v}}_{a/b}$).

While the change in the nuclear contribution to the enthalpy $\Delta E^{\mathrm{v}}_{a/b}$ upon spin transition is almost the same for different density functionals (namely, −5.1 kJ/mol for BP86/RI, −7.5 kJ/mol for B3LYP*, and −6.3 kJ/mol for B3LYP), it has a negative sign, which must be compensated by the electronic contribution $\Delta E^{\mathrm{e}}_{a/b}$. Therefore, the electronic energy splitting $\Delta E^{\mathrm{e}}_{a/b}$ needs to be calculated with high accuracy before the validation of the harmonic approximation for vibrational enthalpy contributions is possible. However, this accuracy can currently not be achieved with DFT. For BP86/RI we would obtain from eq 6 a temperature of 1530 K (BP86/RI: $\Delta S(176\ \mathrm{K}) = 39.8$ J/(mol K), $\Delta H(176\ \mathrm{K}) = 60.9$ kJ/mol), which is an order of magnitude too large, while it is impossible to calculate a spin-flip temperature from the hybrid DFT functionals as $\Delta H(176\ K)$ and thus $T_{1/2}$ are negative.

The maximum contribution to the entropy comes according to eq 2 from vibrations with very small frequencies. But especially these lowest frequencies are subject to deviations from the harmonic approximation and, furthermore, are affected by numerical limitations of the semi-numerical approach for the calculation of the second derivatives of the total electronic energy. Therefore, the absolute values for the entropy at a given temperature differ largely for different methods, and their difference cannot be used for a prediction of the spin-flip temperature. However, the BP86/RI results are closest to the experimental value of 48.78 ± 0.71 J/(mol K).[32]

To summarize, while the reparametrized hybrid density functional is able to produce the currently best electronic and vibrational energy splittings, the entropy contribution is due to an error compensation best estimated from harmonic BP86/RI wavenumbers. It is thus advisable to use both functionals for the study of the spin-crossover phenomenon.

4. Conclusion

This work has demonstrated how the electronic contribution $\Delta E^{\mathrm{e}}_{a/b}$ to a low-spin/high-spin energy splitting at 0 K, $\Delta E^0_{a/b}$, or at finite temperature, $\Delta H(T_{1/2})$, can be calculated from quantum chemical calculations with reparametrized hybrid density functionals. Since a small electronic energy splitting is a boundary condition for a thermal spin crossover, the reparametrized functional B3LYP* is capable of identifying potential spin-crossover complexes.

Because DFT is at present the only quantum chemical method to optimize large molecular structures such as the Fe(II) complex studied, for which vibrational analyses can then be performed to get the vibrational frequencies needed for enthalpies and entropies, it is decisive that DFT describes the electronic structure correctly. In previous work,[11,12] we have demonstrated that the low-spin/high-spin energy splitting of several metal complexes (including the manganocene spin-crossover complex) can be calculated within the precision of the method by adjusting the admixture parameter for exact exchange in B3LYP from 0.20 to 0.15 (B3LYP*). A scan of this parameter from 0.00 to 0.24 for $\mathrm{Fe(phen)_2(NCS)_2}$ shows the same linear dependence of the energy splitting on this parameter observed earlier for other transition metal complexes.[11,12] At about $c_3 = 0.14$ the zero-splitting line is crossed, and the high-spin state is slightly favored at $c_3 = 0.15$, while the low-spin state is the ground state at $c_3 = 0.13$. Although the low-spin state is the ground state in the case of $\mathrm{Fe(phen)_2(NCS)_2}$, we still recommend using the B3LYP* functional with $c_3 = 0.15$, as the slope of the curve is not too large such that the error introduced is in the range of the method (i.e., smaller than about 10 kJ/mol). This has the advantage that the well-recognized reliability of B3LYP is maintained,[12] and the deficiencies of B3LYP for the prediction of energy splittings of states of different multiplicities are reduced to a maximum extent.

The benefit of the reduction of c_3 to 0.15 is that the electronic contribution, which should be close to zero to enable a vibrationally induced spin flip, can be reliably estimated, and a potential spin crossover can be predicted. It should thus be possible to identify a priori to measurement those complexes that show a temperature-dependent spin flip. This is, in general, not possible without reparametrization of the B3LYP functional since B3LYP underestimates in the case of Fe(phen)$_2$(NCS)$_2$ the splitting by ca. −33 kJ/mol, while the pure density functionals such as BP86 and BLYP give a splitting that is by more than 48 kJ/mol too large. However, the prediction of the spin-flip temperature, which is strongly dependent on the entropy contribution of low-frequency vibrations in condensed phase, is hardly possible within the harmonic approximation for the vibrations of an isolated molecule.

While B3LYP* can help to identify potential spin-crossover complexes and its value for a better description of close-lying spin states in transition metal catalysis is obvious, a recommended general protocol for systems in which spin flips may occur on increasing temperature is as follows: a scan of the c_3 parameter should be carried out for the smallest molecule out of a homogeneous series to be studied to verify the validity of B3LYP* by comparison with the energy splitting from experimental reference data or from extensive correlated ab initio methods such as MR-MP2.

To conclude, we have demonstrated how DFT hybrid functionals can be reparametrized to obtain reliable electronic energy splittings, which are comparable to experimental results. This study resolves the difficulties in DFT studies on spin-crossover complexes. Furthermore, the results presented here will also be of great value to the study of reaction mechanisms in transition metal catalysis, where states of different multiplicities get close in energy.

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