Spin crossover transition of Fe(phen)$_2$(NCS)$_2$: periodic dispersion-corrected density-functional study

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Periodic dispersion corrected DFT calculations have been performed to study the spin-crossover transition of Fe(phen)$_2$(NCS)$_2$ in the molecular and in the crystalline state. We show that London dispersion interactions play a crucial role in the cohesion of the crystals. Based on calculations of vibrational eigenstates of the isolated molecule and of the crystalline phase in both the low- and high-spin states, the transition entropies and enthalpies have been calculated. We demonstrate that, due to the stabilization of the low-spin state by intermolecular dispersion forces, the transition enthalpy at the transition temperature is larger for the crystalline phase in comparison with an isolated molecule. The effective coordination number of the nitrogen atoms of the ligands around the iron atom has been identified as the order parameter driving the quasi-reversible low-spin to high-spin transition in the crystal. Finally, using constrained geometry relaxations at fixed values of the coordination number, we computed the energy barrier of the LS to HS transition and found it to be in a reasonable agreement with the experimental value.

1 Introduction

The spin-crossover (SCO) is a phenomenon, in which the spin state of some transition metal compounds can be changed by external stimuli such as variation of temperature, pressure, or light irradiation.$^{1-5}$ Such a controllable bistability can be used in designing devices$^{6,7}$ like pressure sensors and displays, and is widely studied both experimentally and theoretically. Depending on the nature of the interactions between individual constituents in the molecular crystal showing the SCO phenomenon, the spin transition can occur as an abrupt process, in which all molecules change their spin states in the same time, or as a continuous process, where the molecules change the spin state independently of each other. The cooperativity of SCO transitions has been studied recently by means of force-field simulations by Sinitskiy et al.$^8$ The abrupt SCO transition may exhibit hysteresis and theoretical studies of hysteretic behavior are reported in ref. 9 and 10. Crystalline cis-dithiocyanatobis(1,10-phenanthroline)iron(II) (Fe(phen)$_2$(NCS)$_2$)—the system studied in this work—is a prototype of SCO systems displaying an abrupt phase transition and a very small hysteresis in the thermally induced spin transition (0.15 K).$^{11}$ At low temperatures, the low spin (LS) singlet state ($S = 0$) is thermodynamically stable, the transition to the high spin (HS) quintet state ($S = 2$) occurs at $T = 176$ K.$^{11,12}$ The transition enthalpy and entropy for Fe(phen)$_2$(NCS)$_2$ determined by means of calorimetric measurements by Sorai and Seki$^{12}$ are $\Delta H_{\text{LS-HS}} = 9$ kJ mol$^{-1}$ and $\Delta S_{\text{LS-HS}} = 49$ J mol$^{-1}$ K$^{-1}$, respectively. About one third of the entropic increase is due to the change of the spin state.$^{12-14}$

$$\Delta S_{\text{el}} = R \ln \left( \frac{2S_{\text{HS}} + 1}{2S_{\text{LS}} + 1} \right) \approx 13.4 \text{ J mol}^{-1} \text{ K}^{-1},$$

the remaining entropy contribution ($\sim 36$ J mol$^{-1}$ K$^{-1}$) is due to vibrational degrees of freedom.

In this work we use computer simulations based on density functional theory (DFT) to study the structure of low- and high-spin phases of Fe(phen)$_2$(NCS)$_2$, as well as the mechanism and energetics of the corresponding phase-transition. From the computational point of view, the SCO phenomenon gives rise to several major challenges. In order to obtain correct relative energies for the LS and HS states one must take into account the strong correlation between the d-electrons of iron.$^{15}$ Standard (i.e. local and semi-local) DFT functionals are known to fail in this respect. Another difficulty is that the crystal structure of Fe(phen)$_2$(NCS)$_2$ is stabilized mainly by van der Waals interactions, more precisely by London-type dispersion interactions, which are not treated correctly by standard DFT functionals. To cope with these problems, two kinds of modifications of the standard DFT method have been applied in this work: a Hubbard-like term$^{16,17}$ has been added to the Kohn–Sham Hamiltonian to improve the treatment of the strongly correlated d-electrons of...
iron, and the DFT-D2 correction of Grimme has been used to account for the London dispersion interactions. The paper is organized as follows: in Section 2, the methodology and the computational details used in this study are described. Section 3 deals with the structures and the energetics of LS and HS states of the isolated Fe(phen)$_2$(NCS)$_2$ molecule, in Section 4, the structures and the energetics of the crystalline phases are detailed. Section 5 describes the mechanism and energetics of the spin-transition, and a summary of the most important results is given in Section 6.

2 Methodology

Periodic DFT calculations have been performed using the VASP code. The Kohn–Sham equations have been solved variationally in a plane-wave basis set using the projector-augmented-wave (PAW) method of Blochl, as adapted by Kresse and Joubert. The exchange–correlation energy was described by the functional of Perdew, Burke and Ernzerhof (PBE) based on the generalized gradient approximation. The treatment of strong correlation between the d electrons of iron has been improved by adding a Hubbard-like term to the Kohn–Sham Hamiltonian, the values of the parameters $U$ and $J$ (the on-site Coulomb and exchange potentials) were set to 2.5 eV and 0.95 eV, respectively. This setting has been found to yield reasonable energetics for spin-crossover systems such as Fe(phen)$_2$(NCS)$_2$ and Fe(bpy)$_2$(NCS)$_2$H$_2$O. In order to account for van der Waals interactions, the correction proposed by Grimme (PBE-D2) has been used, as implemented recently in the VASP code. The PBE-D2 approach was recently shown to improve substantially the predictions of the structure, energetics, and elastic properties for a wide range of dispersion bound materials. In all our calculations, a plane-wave cutoff of 600 eV was used, and the Brillouin zone sampling has been restricted to the $I$-point. The convergence criterion for the electronic self-consistency cycle, measured by the change in the total energy between successive iterations, was set to $10^{-7}$ eV per cell. The cutoff radius for the pair-potential describing the dispersion forces was set to 40 Å.

The structural optimizations have been performed using the program GADGET based on delocalized internal coordinates. GADGET is interfaced to VASP and allows one to perform atomic and lattice optimizations with arbitrary geometric constraints. The relaxations were terminated when the maximal component of gradient was smaller than $5 \times 10^{-4}$ au and the energy change in two subsequent cycles was less than $1 \times 10^{-5}$ au. In order to reduce undesired interactions between the periodically repeated images, the simulations of an isolated molecule have been performed using an orthorhombic supercell with $a = 18$ Å, $b = 17$ Å, $c = 16$ Å. In such a setting, the shortest intermolecular distance was at least 7 Å. The harmonic vibrational frequencies have been computed numerically using the finite difference technique. Molecular dynamics (MD) simulations in an NVT ensemble have been performed using an Andersen thermostat with a collision frequency of 0.02 fs$^{-1}$. The equations of motion have been integrated using the leap-frog algorithm with an integration step of 1 fs. The total simulation time for the MD runs discussed in Section 5 was 10 ps. The Born–Oppenheimer approximation has been applied in all calculations presented in this work.

3 Isolated molecule

The physical properties of the isolated molecule are important for understanding the properties of a molecular crystal. If the intermolecular interactions are weak, their effect can be neglected in a first approximation for the study of optical, magnetic and other properties of the constituent units. Indeed, the isolated molecule has been used as a basis for a number of theoretical studies on spin crossover systems. In this section, we briefly summarize the structure, energetics, and vibrational properties of the isolated Fe(phen)$_2$(NCS)$_2$ molecule. Fig. 1 shows the Fe(phen)$_2$(NCS)$_2$ molecule and defines the labeling of atoms used throughout this work.

The spin state of the Fe(phen)$_2$(NCS)$_2$ molecule affects most significantly the local geometry of the first coordination sphere of the iron atom. In Table 1, selected structural parameters computed for isolated LS and HS molecules are presented and compared with the corresponding values measured experimentally for the crystalline phase. For the LS state, the numerical values of the computed and the measured parameters are rather similar: the lengths of the three non-equivalent Fe–N bonds differ by 0.02–0.03 Å, and the parameter $\Sigma$ defined as the sum of the deviations of the dozen N–Fe–N angles from the value of 90° characteristic for an ideal octahedron measuring the deformation.

**Fig. 1** Molecule of Fe(phen)$_2$(NCS)$_2$ and the labeling of selected atoms.

<table>
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<th>Parameter</th>
<th>Value (Å)</th>
<th>Value (Å)</th>
<th>Value (Å)</th>
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**Table 1** Selected parameters measuring the geometry of the FeN$_6$ octahedron in the Fe(phen)$_2$(NCS)$_2$ molecule: bond lengths between an iron atom and three nonequivalent N atoms (Fe–N), the parameter measuring the angular deformation of the FeN$_6$ octahedron ($\Sigma$), and the coordination number (cn) of iron with respect to nitrogen atoms (see eqn (4)). The parameter $\Sigma$ is defined as the sum of the deviations of twelve N–Fe–N angles from the value of 90° characteristic for an ideal octahedron.
of the FeN₆ octahedron differs by less than one degree. In the HS state, the computed Fe–N distances are 0.08–0.29 Å longer than those in the LS state, the parameters involving nitrogen atoms from the 1,10-phenanthroline group [i.e. the N(2) and N(3) atoms] are affected significantly more than the Fe–N bond with the nitrogen atom N(1) from the isothiocyanate group. Moreover, the value of Σ increases to 96.4° indicating that the FeN₆ octahedron in the HS molecule is less regular than that in the LS state. These results are in qualitative agreement with the experimental observations.³⁴ Compared to the experimental geometry, the computed Fe–N(2) and Fe–N(3) distances are 0.01–0.03 Å longer, while the Fe–N(1) bond is 0.08 Å shorter. The computed angular deformation parameter Σ is significantly larger than the experimental value, the difference being 27.5°. Apart from the internal parameters involving the central iron atom, the computed geometries of LS and HS molecules are rather similar: the root mean square (RMS) differences computed for bond lengths, bond and torsion angles are 0.005 Å, 0.8°, and 1.2°, respectively.

Calculations of the vibrational frequencies are complicated by the presence of several very soft vibrational modes (ν < 50 cm⁻¹). Note that even the use of stringent relaxation criteria (maximal force smaller than 10⁻⁴ au and the energy change between two subsequent optimization cycles of less than 10⁻⁷ au) did not ensure the absence of soft imaginary vibrational modes. In order to obtain vibrational spectra with satisfactory quality, several iterations consisting of geometry optimizations along the unstable directions, followed by full relaxation of the atomic positions and dynamical matrix calculations had to be performed. As shown in Fig. 2(a), the vibrational spectra computed for the molecules in the LS and HS states are rather similar and significant differences are observed only in the two spectral regions in which the frequencies of the HS state are significantly lower than those of the LS state: the interval 110 cm⁻¹ < ν₃ < 430 cm⁻¹ corresponding to the ligand–iron stretching vibrations,¹⁴ and the region around 2100 cm⁻¹ characteristic for the N–(CS) stretching vibrations.¹⁴ Similar results have been reported in a combined theoretical and experimental study of Brehm et al.¹⁴ The red-shift of the vibrational frequencies in the HS state has an important effect on the entropic stabilization of the HS state at elevated temperatures: the vibrational contribution to the entropy of transition ΔS_{LS→HS}^{vib} computed at the temperature at which the LS → HS transition occurs experimentally (T = 176 K) is 33.2 J mol⁻¹ K⁻¹, which together with the electronic ΔS_{LS→HS}^{el} = 13.4 J mol⁻¹ K⁻¹ and rotational ΔS_{LS→HS}^{rot} = 0.6 J mol⁻¹ K⁻¹ contributions (note that the translational entropy is identical for both LS and HS states) yields a value of 47.2 J mol⁻¹ K⁻¹ that is surprisingly close to the experimentally measured transition entropy (49 J mol⁻¹ K⁻¹).¹² A similar value of ΔS_{LS→HS} (48.8 J mol⁻¹ K⁻¹) has been reported in the DFT study of Reiher,¹³ in which the exchange-correlation functional of Becke and Perdue,⁵⁵,²⁸ (BP86/RI) has been used. Although such a good agreement with experiment is evidently fortuitous, this result suggests that the main contribution to the vibrational transition entropy in the crystalline phase is due to localized molecular vibrations. Not surprisingly, the dominant contribution to the value of ΔS_{LS→HS}^{vib} is due to modes from the spectral region that is most sensitive to the spin state: if only frequencies corresponding to the ligand–iron stretching vibrations (110 cm⁻¹ < ν₃ < 430 cm⁻¹) are considered, the computed value of ΔS_{LS→HS}^{vib} is 30.0 J mol⁻¹ K⁻¹, i.e. only 3.2 J mol⁻¹ K⁻¹ lower than the value computed using the complete vibrational spectra. A similar conclusion has been reached in the theoretical study of Brehm et al.¹⁴ who demonstrated that the dominant contribution to ΔS_{LS→HS}^{vib} is due to modes with a frequency below 420 cm⁻¹.

The computed energy difference between the LS and HS states is ΔH_{LS→HS} = 10.2 kJ mol⁻¹. Although the Fe(phen)₂(NCS)₂ molecule is relatively large, the contribution of London dispersion interactions to the value of ΔH_{LS→HS} is only 1.7 kJ mol⁻¹. The energy difference between the LS and HS states computed by Reiher¹³ using the BP86 functional is 66 kJ mol⁻¹, the value obtained with the modified B3LYP functional is 48 kJ mol⁻¹.
both values being too large compared to the experiment.\textsuperscript{12} The contribution of the change in the vibrational modes to the transition enthalpy $\Delta H_{\text{LS-HS}}^{ vib}$ computed for $T = 176$ K (measured spin-flip temperature) is $-5.7$ kJ mol$^{-1}$. As the rotational and the translational degrees of freedom do not contribute to the transition enthalpy (the terms $H_{\text{rot}}^0$ and $H_{\text{trans}}^0$ depend only on the temperature and are therefore identical for both spin states), $\Delta H_{\text{LS-HS}}$ can be expressed as the sum of electronic and vibrational contributions, which is $4.5$ kJ mol$^{-1}$. Once again, this number is surprisingly close to the transition enthalpy of $9$ kJ mol$^{-1}$ measured for Fe(phen)$_2$(NCS)$_2$ in the crystalline phase.\textsuperscript{12}

\section*{4 Crystalline phase}

The pioneering work on the structural characterization of cis-dithiocyanatobis(1,10-phenanthroline)iron(II) has been made by Gallois \textit{et al.}\textsuperscript{39} who performed X-ray measurements at $T = 130$ K (LS) and $293$ K (HS). More recently, low temperature (32 and 15 K) X-ray measurements of this system have been reported by Legrand \textit{et al.}\textsuperscript{34} the formation of the low temperature high-spin state (termed HS-2 in ref. 34) has been achieved by laser excitation. As our simulations correspond to zero temperature, we use the measurements of Legrand \textit{et al.}\textsuperscript{34} performed at $T = 15$ K as the experimental reference in this work. Cis-dithiocyanatobis(1,10-phenanthroline)-iron(II) crystallizes in the space group \textit{Pbnm}, the crystallographic unit cell is orthorhombic and contains four formula units ($Z = 4$).

The experimentally determined lattice parameters for the LS state are $a = 12.762$ Å, $b = 10.024$ Å, $c = 17.090$ Å and the unit cell volume is $2186.2$ Å$^3$. Due to the LS $\rightarrow$ HS transition, the parameter $a$ increases by $0.4$ Å, while the parameters $b$ and $c$ change only by a few hundredths of Å (see Table 2). The system also undergoes a moderate expansion of the unit cell, the cell volume increases by $61$ Å$^3$ ($i.e.$ by $\sim 3\%$).

The structures reported in ref. 34 have been used as starting geometries for our periodic calculations. As shown in Table 2, the PBE+U approach without dispersion corrections does not yield an accurate description of the structures of Fe(phen)$_2$(NCS)$_2$: the error with respect to the experimental lattice parameters is as large as 20%. The quality of the structural predictions improves substantially if the dispersion corrections proposed by Grimme\textsuperscript{18} are used. The lattice parameters computed using the PBE+U-D2 method differ only by $\sim 2.5\%$ or less from the experimental values (see Table 2). The dispersion corrected calculations reproduce the observed volume expansion for the

The intermolecular interactions in the cis-dithiocyanatotris(bis(1,10-phenanthroline)iron(II) crystal affect the internal geometry of the Fe(phen)$_2$(NCS)$_2$ molecules only moderately. In the crystalline LS state, the angular deformation of the FeN$_6$ octahedron ($\Sigma$) is 4.4$\%$ smaller and the lengths of the Fe–N bonds are almost identical to the values computed for isolated molecules. The structural modifications for the HS state are more significant: bonds between iron and nitrogen atoms of the thiocyanate group (Fe–N(1)) are elongated by 0.05 Å, the Fe–N(3) bonds are shortened by 0.03 Å and $\Sigma$ is decreased to 83.5$\%$—all these parameters are closer to the experimental values than those computed for an isolated molecule.

As described in Section 3, an accurate vibrational analysis of molecular Fe(phen)$_2$(NCS)$_2$ is problematic due to the presence of soft degrees of freedom that require a very precise minimization of all residual forces on the atoms. The number of such soft degrees of freedom is even larger for Fe(phen)$_2$(NCS)$_2$ in the crystalline phase. Moreover, the dispersion of the phonon frequencies should, in principle, be taken into account when computing the vibrational contributions to enthalpy and entropy of the crystalline phases. As such calculations are prohibitively costly in terms of the simulation time, we performed only a semi-quantitative analysis of $\Delta S_{\text{LS-HS}}$, and $\Delta H_{\text{LS-HS}}^{ vib}$ where the vibrational eigenstates are calculated only at the $\Gamma$-point and their dispersion in the Brillouin zone is neglected. This assumption is well justified for localized intra-molecular vibrations which, as demonstrated above, determine 90% of the transition entropy. This assumption seems to be well justified also for the vibrational enthalpy, which according to its definition,

\begin{equation}
H_{\text{ vib}}^{ vib} = \sum_{i=1}^{N_{\text{e}}} \left( \frac{1}{2} \hbar \omega_i + \frac{\hbar \omega_i e^{-\beta \hbar \omega_i / 2k_B T}}{1 - e^{-\beta \hbar \omega_i / 2k_B T}} \right),
\end{equation}

increases monotonically with increasing vibrational frequency. It is therefore reasonable to expect that the dominant contribution to $\Delta H_{\text{LS-HS}}^{ vib}$ is due to high-frequency modes such as the stretching vibrations that have usually only a small dispersion. The delocalized acoustic and soft optical phonons, on the other hand, can be expected to contribute only little. The neglect of the phonon dispersion is at first sight less well justified for the vibrational entropy, where contribution of vibrational modes decreases with increasing frequency:

\begin{equation}
S_{\text{ vib}}^{ vib} = \sum_{i=1}^{N_{\text{e}}} \frac{\hbar \omega_i}{T} \frac{1}{e^{\beta \hbar \omega_i / k_B T} - 1} - k_B \ln(1 - e^{-\beta \hbar \omega_i / k_B T}).
\end{equation}

Here we use our result presented in Section 3 that the dominant contribution to the vibrational transition entropy comes from localized ligand–iron vibrations in the interval $110 < \nu_{\text{LS}} < 430$ cm$^{-1}$. Importantly, the vibrational spectra ($\Gamma$-point phonons) computed for the crystalline LS and HS states are qualitatively similar to those for isolated molecules. As shown in Fig. 2(b), the spectral regions sensitive to the spin
state are essentially the same as those for the isolated molecule. In order to determine the localized vibrational modes, the dynamical matrix computed for all atomic degrees of freedom has been projected onto the space of internal coordinates corresponding to intramolecular degrees of freedom. In such a way, the modes corresponding to translational and rotational motions of the rigid molecules in the crystal have been effectively projected out. Using the localized vibrational modes, the vibrational contribution to $\Delta S_{\text{LS}}^{\text{el}}$ computed for the transition temperature (176 K) is 25.1 J mol$^{-1}$ K$^{-1}$, i.e., $\sim 8$ J mol$^{-1}$ K$^{-1}$ lower than that computed for isolated molecules. Combined with the electronic contribution $\Delta S_{\text{LS}}^{\text{el}} = 13.4$ J mol$^{-1}$ K$^{-1}$, we estimate transition entropy of 38.5 J mol$^{-1}$ K$^{-1}$, which is $\sim 9$ J mol$^{-1}$ K$^{-1}$ lower than the experimental value.\textsuperscript{12}

The energy difference between the LS and HS states computed for the crystalline phases ($\Delta H_{\text{LS}}^{\text{el}}$) is 21.9 kJ mol$^{-1}$. This value is $\sim 11$ kJ mol$^{-1}$ higher than the result computed for an isolated molecule. A large part of this difference is due to London dispersion interactions which play a more significant role in the crystal than for the isolated molecule: the LS state is stabilized in comparison to the HS state, dispersion corrections contribute 15.9 kJ mol$^{-1}$ to the total energy difference. A qualitatively similar result, i.e., a stabilization of the LS phase due to the intermolecular interactions, has been predicted by a macroscopic model based on the analysis of molecular data by Kepenekian et al.\textsuperscript{8,10} The term $\Delta H_{\text{LS}}^{\text{el}}$ computed for the transition temperature is $-4.7$ kJ mol$^{-1}$, the total transition enthalpy is therefore 17.2 kJ mol$^{-1}$, which is $\sim 8$ kJ mol$^{-1}$ higher compared to the experimental value.\textsuperscript{12} Altogether, taken into account the number of approximations that had to be made at various states of our simulation, we consider the agreement between the experiment and our theoretical results for structure and energetics of crystalline Fe(phen)$_2$(NCS)$_2$ as satisfactory. The energy difference between the HS and LS states has been reported also in the periodic LDA DFT study of Matar and Létard.\textsuperscript{40}

Although the vibrational contribution to $\Delta H_{\text{LS}}^{\text{el}}$ has not been taken into account in ref. 40, the computed value of 69 kJ mol$^{-1}$ is definitely too large compared to experiment.\textsuperscript{12}

5 Mechanism of spin-transition

As already mentioned, the LS $\rightarrow$ HS transition can be induced by thermal excitation. In our case this transition occurs abruptly at a temperature of 176 K and shows only very small hysteresis (0.15 K).\textsuperscript{11} This result suggests that the transition path for the spin transition of Fe(phen)$_2$(NCS)$_2$ is almost independent of the direction of transformation and hence it can be considered as a (quasi-)reversible process (note that a hysteresis would occur only if the LS $\rightarrow$ HS and HS $\rightarrow$ LS transitions followed two different transformation paths). The observed abrupt change from the LS to the HS state is a sign of high cooperativity, i.e., all molecules in the crystal change their spin simultaneously.\textsuperscript{8} These observations indicate that a single order parameter is enough to characterize the reversible transformation between the LS and HS states. As explained in Section 4, the LS $\rightarrow$ HS transformation is accompanied by a modest change of the cell volume ($\Delta V = 79$ Å$^3$). Unfortunately, the volume alone is not a suitable order parameter for the transition in this case, since the variation of volume leads to only modest changes in the intermolecular distances while the intramolecular degrees of freedom, essential for the phase transition, are left almost unaffected. If the volume is varied in the interval between 2117 and 2196 Å$^3$ (corresponding to the equilibrium volumes for the LS and HS states, respectively), the change in the intermolecular spacing induces only a modest variation of the energy and the low-spin phase remains lower in energy at all volumes than the corresponding high-spin state. A similar behavior has been found for the lattice parameter $a$, the only lattice parameter that has significantly different values for the LS and HS states (see Table 2). It has been pointed out in Sections 3 and 4 that the LS $\rightarrow$ HS transformation is accompanied by significant structural changes in the first coordination sphere of the iron atom in the Fe(phen)$_2$(NCS)$_2$ molecules, in particular, the Fe–N distances increase considerably. The order parameter describing the transition should affect all the three nonequivalent Fe–N distances, but should not depend critically upon changes of individual distances. A suitable order parameter should be coupled to macroscopic quantities such as the temperature that can be used to stimulate the spin transition. Moreover, it is desirable that the order parameter be a continuous analytical function. For similar purposes, a function measuring the coordination number of atoms is often used in the literature.\textsuperscript{41–44} In this work we define a function $cn$ as

$$cn = \sum_i \frac{1 - \left(\frac{r_{Fe-N_i}}{R_0}\right)^M}{1 - \left(\frac{r_{Fe-N_i}}{R_0}\right)^N}$$

measuring the coordination number of iron surrounded by nitrogen atoms. In eqn (4), the summation is over all intramolecular Fe–N distances. The value of parameter $R_0$ is set to 1.9 Å, which is close to the shortest Fe–N distance found in the low-spin state of crystalline Fe(phen)$_2$(NCS)$_2$. For the exponents $M$ and $N$ we choose the values 9 and 14, respectively. We note that there is a certain arbitrariness in the choice of $M$ and $N$—the values used in this study appear to be a reasonable compromise between two opposite requirements—the difference $N - M$ should be as large as possible in order to ensure that $cn$ takes distinctly different values for the LS and HS states, while it should be small enough to ensure that $cn$ remains sensitive to changes in $r_{Fe-N_i}$ for distances larger than $R_0$. The values of $cn$ computed for the molecules in the LS and HS states are listed in Table 1. As the Fe–N distances increase with increasing temperature, the function $cn$ decreases and is therefore naturally coupled to the macroscopic parameter driving the spin transition. In order to demonstrate the sensitivity of $cn$ to $T$, NVT molecular dynamics simulations of the molecule in the LS state have been performed at two different temperatures (100 K and 500 K). The computed probability distributions $P(cn)$ are shown in Fig. 3. The value of $cn$ in the relaxed molecule representing zero-temperature is 3.61, while the average value of $cn$ computed for $T = 100$ K is 3.57 and 3.30 at $T = 500$ K.

The change of the total energy as a function of the order parameter ($cn$) has been determined by performing a set of constrained relaxations, in which the values of $cn$ for all the four molecules present in the simulation cell have been fixed, while all the other geometry parameters (including the cell shape and volume) have been relaxed. Fig. 4 shows the energy...
profiles computed for both the LS and the HS states. As expected, the energy increases with \( cn \) for the HS state and decreases for the LS state, the two curves cross at the point where \( cn = 2.98 \). The high-spin state is therefore energetically stable if the coordination number of the Fe atoms is \(< 2.98\), the low spin state is more favorable otherwise. In the crossing point, the energies for HS and LS phases are equal and therefore the spin transition is energetically favored. This can happen without hysteresis only if the LS and HS states are structurally similar at the crossing point. As shown in Fig. 5, the volume and the lattice parameter \( a \) decrease monotonically and approximately linearly with increasing \( cn \), irrespective of the spin state of Fe(phen)$_2$(NCS)$_2$, the volumes of the LS and HS states are almost identical at all values of \( cn \). This remarkable result indicates that the volume at a given value of \( cn \) is essentially independent of the spin state. At the crossing point, the cell parameter \( a \) computed for the HS and LS states differs only by 0.08 Å. Note that the remaining lattice parameters change only slightly during the LS \( \rightarrow \) HS transition (see Table 2). Altogether, the structures of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Probability distribution functions of \( cn \) for the LS state of non-interacting molecule of Fe(phen)$_2$(NCS)$_2$ computed using molecular dynamics for two different temperatures: \( T = 100 \text{ K} \) and \( T = 500 \text{ K} \).}
\end{figure}

\begin{figure}[h]
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\caption{Variation of electronic enthalpy with the coordination number of nitrogen atoms on iron (\( cn \)) for the low- and high-spin crystals of Fe(phen)$_2$(NCS)$_2$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5}
\caption{Variation of volume (above) and lattice parameter \( a \) (below) with the change of the order parameter \( cn \) (eqn (4)) for the low-spin (LS) and high-spin (HS) states of the Fe(phen)$_2$(NCS)$_2$ crystal.}
\end{figure}
the LS and HS states are remarkably similar to each other at the crossing point and hence the spin transition can take place easily at the crossing point. The existence of a single point at which the transition occurs, irrespective of the direction of the transformation, is in line with the very small hysteresis observed experimentally. Legrand et al.\textsuperscript{11} reported a thermal activation energy of ($E_{\text{HS} \rightarrow \text{LS}}$) for the relaxation of the HS state excited by laser at $T = 15$ K to the ground state (LS), the measured value of $E_{\text{HS} \rightarrow \text{LS}}$ is $\sim 11$ kJ mol$^{-1}$. Our simulations can be used to estimate this quantity: neglecting thermal and quantum effects, $E_{\text{HS} \rightarrow \text{LS}}$ can be computed as the energy difference between the stable HS state and the crossing point (see Fig. 4). The computed value of 16 kJ mol$^{-1}$ compares well with the above-mentioned experimental result.

6 Conclusions

The spin-crossover transition for cis-dithiocyanatobis(1,10-phenanthroline)iron(II) has been studied by means of dispersion (van der Waals) corrected density functional theory. In order to appreciate the role of intermolecular interactions, periodic structural models of the LS and HS states of cis-dithiocyanatobis(1,10-phenanthroline)iron(II) crystals have been employed. It has been shown that London dispersion interactions play a crucial role in the stabilization of the structure of the Fe(phen)$_2$(NCS)$_2$ crystals: while the standard PBE functional significantly overestimates the lattice parameters (even if a Hubbard correction to account for the strong correlation between the Fe d electrons is used), dispersion corrected PBE calculations predict cell parameters in very good agreement with experiment. The properties of crystalline phases of Fe(phen)$_2$(NCS)$_2$ are largely determined by the properties of their constituent units: intramolecular structure, vibrational properties, and energetics computed for an isolated molecule are qualitatively similar to those determined for a periodic crystal. The intermolecular interactions play an important role in the stabilization of the crystalline phases: the computed $\Delta H_{\text{LS} \rightarrow \text{HS}}$ increases from 11 to 17 kJ mol$^{-1}$ for isolated molecules to 22 kJ mol$^{-1}$ for the solid state. The value of $\Delta H_{\text{LS} \rightarrow \text{HS}} = 17$ kJ mol$^{-1}$ computed for the flipping temperature ($T = 176$ K) compares reasonably with the experimental value of 9 kJ mol$^{-1}$.\textsuperscript{12} A semi-quantitative analysis of the transition entropy has been performed, using the assumption that only localized molecular vibrational modes contribute significantly to $\Delta S_{\text{LS} \rightarrow \text{HS}}$. The entropy of transition estimated for the experimental transition temperature is 38.5 J mol$^{-1}$ K$^{-1}$, only $\sim 9$ J mol$^{-1}$ K$^{-1}$ lower than the experimental value.\textsuperscript{12}

The mechanism of LS $\rightarrow$ HS transition has been studied by means of constrained geometry relaxations. It has been shown that the order parameter describing the transition is the coordination number of the nitrogen atoms around iron. The remaining degrees of freedom, including the cell volume and lattice geometry, follow adiabatically the change in the order parameter. Moreover, it has been demonstrated that the LS and HS geometries are very similar at the crossing point on the $E$ vs. $cn$ curves. This result is in line with the observation that the spin transition in crystalline Fe(phen)$_2$(NCS)$_2$ occurs with only a very small hysteresis $^{11}$ (0.15 K). The lattice volume has been found to change approximately linearly with the order parameter; its actual value being almost independent of the spin state. The computed barrier for the HS $\rightarrow$ LS transition is 16 kJ mol$^{-1}$, in reasonable agreement with the experimental estimate of 11 kJ mol$^{-1}$.\textsuperscript{34}

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