

## Supplementary material

### S1. Projection procedure

It is convenient to use the generally accepted projection operator in order to evaluate the effective Hamiltonian in the framework of the perturbative approach assuming  $|t| \gg U$ . With accuracy up to second order corrections one can find:

$$\hat{H}'_e(S=0) = -\frac{1}{U} \sum_k |\psi_{kk}(S=0)\rangle \langle \psi_{kk}(S=0)| \quad (\text{S1.1})$$

The matrix elements are the following:

$$\begin{aligned} \langle \psi_{12} | \hat{H}'_e(S=0) | \psi_{12} \rangle &\approx -\frac{1}{U} \sum_{k=1,2} \langle \psi_{12} | \hat{H}_e(S=0) | \psi_{kk} \rangle^2 = -\frac{4t^2}{U}, \\ \langle \psi_{23} | \hat{H}'_e(S=0) | \psi_{23} \rangle &\approx -\frac{1}{U} \sum_{k=2,3} \langle \psi_{23} | \hat{H}_e(S=0) | \psi_{kk} \rangle^2 = -\frac{4t^2}{U}, \end{aligned} \quad (\text{S1.2})$$

$$\begin{aligned} \langle \psi_{12} | \hat{H}'_e(S=0) | \psi_{23} \rangle &= \langle \psi_{23} | \hat{H}'_e(S=0) | \psi_{12} \rangle \\ &\approx -\frac{1}{U} \langle \psi_{12} | \hat{H}_e(S=0) | \psi_{22} \rangle \langle \psi_{22} | \hat{H}_e(S=0) | \psi_{23} \rangle = -\frac{2t^2}{U}. \end{aligned}$$

Finally one obtains the following matrix for  $S=0$  states which incorporates the second order corrections:

$$\hat{\tilde{H}}_e(S=0) = \begin{pmatrix} \psi_{12}(0) & \psi_{13}(0) & \psi_{23}(0) \\ \delta - W - 4t^2/U & t & -2t^2/U \\ t & 0 & t \\ -2t^2/U & t & \delta + W - 4t^2/U \end{pmatrix}. \quad (\text{S1.3})$$

The accuracy of the perturbative approach for the parameters used in the text is illustrated in Figure S1.1.

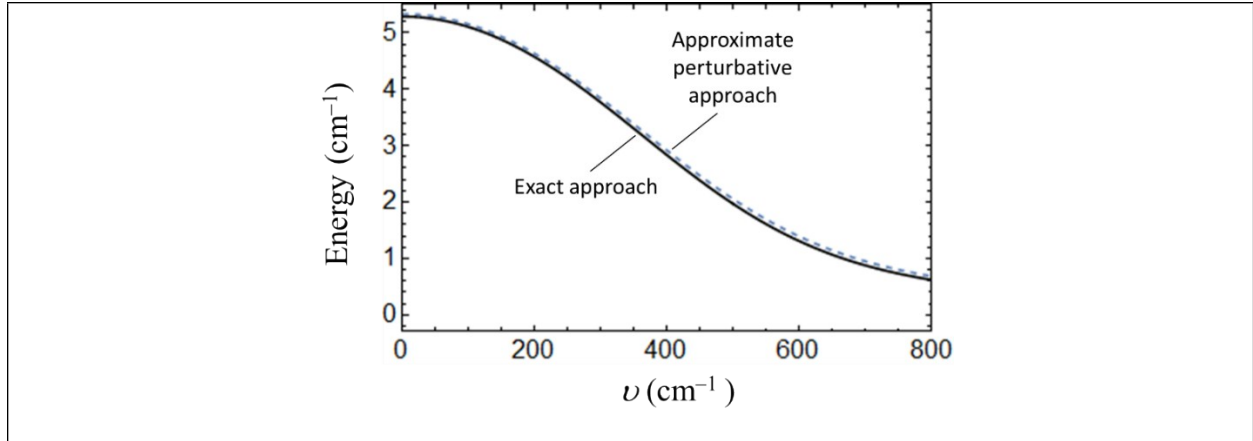


Figure S1.1. Comparison of the dependences of the singlet-triplet gap on the vibronic parameter calculated with the exact allowance for the excited doubly occupied orbitals (solid line) and the approximate (dashed line) perturbative approach based on the effective Hamiltonian, Eq. (S.3).

## S2. Derivation of the two-mode vibronic Hamiltonian

The three local coordinates  $q_1, q_2, q_3$  can be transformed to the new collective symmetry adapted coordinates are found as (Eq.(5) in the main text):

$$q'_g = \frac{1}{\sqrt{3}}(q_1 + q_2 + q_3), \quad q_g = \frac{1}{\sqrt{6}}(2q_2 - q_1 - q_3), \quad q_u = \frac{1}{\sqrt{2}}(q_1 - q_3), \quad (\text{S2.1})$$

where  $q'_g$  is the full-symmetric molecular vibration corresponding to the simultaneous (in-phase) compression and expanding of the three active sites. The reverse unitary transformation from the local full-symmetric coordinates to the symmetry adapted coordinates is given by:

$$q_1 = \frac{1}{\sqrt{3}}q'_g - \frac{1}{\sqrt{6}}q_g + \frac{1}{\sqrt{2}}q_u, \quad q_2 = \frac{1}{\sqrt{3}}q'_g + \frac{2}{\sqrt{6}}q_g, \quad q_3 = \frac{1}{\sqrt{3}}q'_g - \frac{1}{\sqrt{6}}q_g - \frac{1}{\sqrt{2}}q_u. \quad (\text{S2.2})$$

By substituting Eq. (S2.2) into Eqs. (3) and (4) in text we obtain:

$$\begin{aligned}
\hat{H}_\omega + \hat{V} &= \left[ \frac{\hbar\omega}{2} \left( q_g'^2 - \frac{\partial^2}{\partial q_g'^2} \right) + \frac{2\nu}{\sqrt{3}} q_g' \right] \hat{I} \\
&+ \frac{\hbar\omega}{2} \left( q_g^2 + q_u^2 - \frac{\partial^2}{\partial q_g^2} - \frac{\partial^2}{\partial q_u^2} \right) \hat{I} + \nu \begin{pmatrix} \psi_{12}(S) & \psi_{13}(S) & \psi_{23}(S) \\ \frac{1}{\sqrt{6}} q_g + \frac{1}{\sqrt{2}} q_u & 0 & 0 \\ 0 & -\frac{2}{\sqrt{6}} q_g & 0 \\ 0 & 0 & \frac{1}{\sqrt{6}} q_g - \frac{1}{\sqrt{2}} q_u \end{pmatrix}, \tag{S2.3}
\end{aligned}$$

where  $\hat{I}$  is the  $3 \times 3$  unit matrix. One can see that the contribution associated with the full-symmetric vibration is proportional to the unit matrix which means that this part of the Hamiltonian commutes with all remaining electronic and vibronic interactions. Thus, this separable part of the Hamiltonian can be ruled out from the further consideration. Then one can apply the shift transformation to the full-symmetric coordinate

$$q_g' = q_g - \frac{2\nu}{\hbar\omega\sqrt{3}}. \tag{S2.4}$$

As a result one obtains the following Hamiltonian that describes the free harmonic oscillations around the new equilibrium position  $\tilde{q}_g'$ :

$$\frac{\hbar\omega}{2} \left( q_g'^2 - \frac{\partial^2}{\partial q_g'^2} \right) + \frac{2\nu}{\sqrt{3}} q_g' = -\frac{2\nu^2}{3\hbar\omega} + \frac{\hbar\omega}{2} \left( \tilde{q}_g'^2 - \frac{\partial^2}{\partial \tilde{q}_g'^2} \right). \tag{S2.5}$$

The energy of the system is shifted down by the value  $-2\nu^2/3\hbar\omega$  which is the gain of the electron-vibrational energy due to relaxation of the system in the new equilibrium position  $\tilde{q}_g'$ . In fact, the position  $q_g' = 0$  corresponds to the minimum of the energy of the  $\text{Fe}^{\text{II}}\text{-Fe}^{\text{II}}\text{-Fe}^{\text{II}}$  system without two extra holes. The shift to the new equilibrium position  $\tilde{q}_g'$  of the full symmetric mode can be interpreted as compression of the system due to mean field of the two holes whose density is equally distributed over three sites. This disposition of the atoms is assumed to be a reference configuration when considering the vibronic effects interrelated with the remaining two vibrations  $q_u$  and  $q_g$  which are active in the JT and pseudo JT interactions.