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## What is the nature of bonding in $[\text{Fe}(\text{CO})_3(\text{NO})]^-$ and $[\text{Fe}(\text{CO})_4]^{2-}$ ?

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Electronic supplementary material:

Energy Decomposition Analysis of  $[\text{Fe}(\text{CO})_3]^{2-}$  -- CO at SR-ZORA-BP86-D4/TZP and SR-ZORA-BHandHLYP/TZP level of theory; Energy Decomposition Analysis of  $[\text{Fe}(\text{CO})_3\text{--NO}]^-$  for different fragmentation patterns at SR-ZORA-BP86-D4/TZP level of theory; Energy Decomposition Analysis of  $[\text{Fe}(\text{CO})_3\text{--NO}]^-$  for different fragmentation patterns, at SR-ZORA-BHandHLYP/TZP level of theory;

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## Abstract

To shed new light on the electronic structure of  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  complex ion DFT based analysis of the nature of chemical bonding has been performed. For this purpose, the Extended Transition State Energy Decomposition Analysis alongside the Natural Orbital for Chemical Valence (EDA-NOCV) has been used and results compared to the nature and the strength of the interactions in isoelectronic  $[\text{Fe}(\text{CO})_4]^{2-}$  complex ion. Based on orbital contribution to the interaction energy and charge flow between the fragments, the ground state can be the best described as an open-shell singlet with zero formal oxidation state on iron and negative charge on the nitrosyl ligand. It is in agreement with the different nature of interactions when  $\text{NO}^+$  and CO ligands are bonded to  $\text{Fe}(-\text{II})$ .

## Keywords

Chemical bonding – Energy Decomposition Analysis – DFT – oxidation states – iron complexes

### 1. Introduction

In chemical compounds, iron can be found in various oxidation states (from -II to +VI) [1]. The most common ones are +II and +III, unusual oxidation states  $\text{Fe}(-\text{II})$ ,  $\text{Fe}(-\text{I})$ , and  $\text{Fe}(0)$  have been found in organometallic compounds [1–4]. The  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  has been the subject of interest in inorganic, organic, and physical chemistry, as well as in catalysis for many years [5–10]. Concerning its electronic structure, there is no general conclusion about the oxidation state of the central Fe atom and the resulting charge of the NO ligand, thus the determination of its ground electronic state.  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  is isoelectronic with  $[\text{Fe}(\text{CO})_4]^{2-}$  with the oxidation state of the iron unambiguously accepted to be -II [11, 12]. Accordingly, iron in the first complex is expected to be in -II oxidation state. On the other hand, these two species have different catalytic activity in various organic reactions pointing into a difference in their electronic structure [5, 6, 8, 9]. The combined experimental and theoretical study proposed that the electronic structure of  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  is best described as  $\text{NO}^-$  coordinated to  $\text{Fe}(0)$  [6]. More recent work gave different views on this subject more inline with the  $\text{Fe}(-\text{II})-\text{NO}^+$  bonding [7]. The vagueness of the nature of Fe-NO interaction in  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  is a consequence of both the diversity of the electronic structures of transition metal complexes in general [13–16] and non-innocence of the nitric oxide type ligand [17–23]. Energies of iron 3d orbitals and  $\pi^*$  orbitals of NO are of comparable energies, complicating the determination of the oxidation state of iron as well as the nature of nitric oxide type ligand –  $\text{NO}^+$ , NO radical or  $\text{NO}^-$ .

In  $[\text{Fe}(\text{CO})_4]^{2-}$  iron is in a tetrahedral environment with formally  $d^{10}$  electronic configuration. All five molecular orbitals (MOs) with dominant d-character are completely filled, giving singlet as the ground state. Excellent  $\pi^*$ -accepting properties of the CO assist in the stability of the  $d^{10}$  complex. When the isoelectronic  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  is considered in the same way, i.e.,  $\text{Fe}(-\text{II})$  and  $\text{NO}^+$ , naturally closed-shell singlet is again the ground state. In the other

situation, when there is an interaction between Fe(0) and NO<sup>-</sup>, there are two unpaired electrons on the iron center (d<sup>8</sup> electronic configuration) and two unpaired electrons on nitrosyl anion. This leads either to the quintet or to the open-shell singlet state. Consequently, the nature of the bonding of nitrosyl ligand to the iron center must be different depending on the electronic structure. And the role of  $\pi^*$  orbitals of the nitric oxide is different.

The problem of the description of the electronic structure in [Fe(CO)<sub>3</sub>(NO)]<sup>-</sup> is clearly multireference [6, 7]. Closed-shell singlet state and high-spin quintet state can be adequately described by one Slater determinant, but this is not the case for the open-shell singlet state. This instantly leads to the conclusion that multideterminantal methodologies that are based on configuration interaction should be used. Unfortunately, such methods did not give equivocal findings [6, 7]. Adequate treatment of the dynamical correlation is also necessary. As a single determinant method, conventional Kohn-Sham Density Functional Theory (KS-DFT) cannot rigorously describe multideterminantal states. Noodleman's suggestion was the approach called the broken-symmetry (BS), which represents multideterminantal states with only one „antiferromagnetically coupled“ Slater determinant [13, 24–26]. Another drawback of all DFT-based methods is the dependence of the results on the choice of the Density Functional Approximations (DFA) employed. It is well known that the generalized gradient (GGA) functionals overestimate delocalization [27]. In contrast, hybrid functionals tend to localize electron, and the extent of the localization will be higher with a higher percentage of the exact Hartree-Fock (HF) exchange [28]. This situation occurs, e.g., in mixed-valence compounds [28], in homolytic dissociation [29, 30], charge transfer [31]. One of the solutions for this kind of problem is the use of long-range separated hybrid functionals [32, 33]. Alternatively, it is possible to tune the percentage of the exact exchange [28, 34], or to rely on some non-conventional DFT based methods like constrained DFT [35] or multiplet sum DFT method [36].

To shed new light on the problem of the electronic structure of [Fe(CO)<sub>3</sub>(NO)]<sup>-</sup> we performed DFT bond analysis in the framework of Extended Transition State Energy Decomposition Analysis [37–39] with Natural Orbital for Chemical Valence (EDA-NOCV) method [40, 41] and compared it to the nature and the strength of the interactions in [Fe(CO)<sub>4</sub>]<sup>2-</sup> complex ion. EDA based schemes have been proven to be compelling and trustworthy for understanding chemical bonding [39, 42–45].

## 2. Computational details

All calculations were done by DFT with the ADF program package (version 2019.302) [46–48]. The all-electron triple-zeta Slater-type orbitals plus one polarization function (TZP) basis set was used for all atoms. Relativistic effects were considered with the zeroth-order regular approximation to the Dirac Hamiltonian in the scalar-relativistic formulation (SR-ZORA) [49]. All calculations were performed on the complex ions from experimentally determined X-ray structures of [Fe(CO)<sub>3</sub>(NO)]<sup>-</sup> (CCDC 1266312)[50] and [Fe(CO)<sub>4</sub>]<sup>2-</sup> (CCDC 1217933)[11] with long-range separated hybrid CAMY-B3LYP [51–53]. Additionally, in

line with previously stated, to test the DFAs, 11 other functionals were used: GGAs in the form of BP86 [54–56] and OPBE [57]; meta-GGAs in the form of M06-L [58, 59], TPSS [60, 61], SCAN [62]; hybrid B3LYP\* [63], B3LYP [64], BHandHLYP functionals and meta-hybrid M06 [58, 59], M06-2X [58, 59] and TPSSh [60, 61]. Hybrid and meta-hybrid functionals used have a different amount of the exact exchange (ranging from 10% in TPSSh to 54% in M06-2X). All open-shell systems are treated with unrestricted formalism. Broken symmetry solutions are obtained from the high spin states with the spin-flip method. All calculations were performed with an increased numerical integration grid (“quality good” in ADF).

The nature of the metal-ligand bonding was analyzed with the Extended Transition State Energy Decomposition scheme (EDA) [37–39]. The interaction energy,  $E_{\text{int}}$ , between chosen fragments is decomposed into three chemically significant components i) the quasi-classical electrostatic interaction between the fragments ( $E_{\text{elst}}$ ); ii) the repulsive Pauli interaction ( $E_{\text{Pauli}}$ ); iii) the orbital stabilizing contribution due to the covalency, i.e., charge transfer, and polarization ( $E_{\text{orb}}$ ). In addition to the  $E_{\text{int}}$ , the preparation energy  $E_{\text{prep}}$ , the energy required to bring separated fragments from their equilibrium geometry to the geometry they adopt in complex ions, is considered. Furthermore, natural orbitals for chemical valence (NOCV)[40, 41] decomposition of the electron density deformation was performed to elucidate different density transfer channels and to quantify their importance as an energy contribution to the  $E_{\text{orb}}$ . Charge flow between the fragments was quantified with the Hirshfeld charge analysis[65]. For  $[\text{Fe}(\text{CO})_4]^{2-}$  the interaction between  $[\text{Fe}(\text{CO})_3]^{2-}$  and CO was analyzed. For  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  three possibilities were considered: i) interaction between closed-shell  $[\text{Fe}(\text{CO})_3]^{2-}$  and  $\text{NO}^+$  ii) interaction between  $[\text{Fe}(\text{CO})_3]^-$  and NO iii) interaction between  $[\text{Fe}(\text{CO})_3]$  and  $\text{NO}^-$ . In cases ii) and iii), spin-unrestricted fragments were used.  $[\text{Fe}(\text{CO})_3]^-$  and NO fragments are considered in doublet states, while  $[\text{Fe}(\text{CO})_3]$  and  $\text{NO}^-$  fragments in triplet states.

### 3. Results and Discussion

As we stated in the Introduction, determination of the spin ground state with DFT is a delicate task, and strongly depend on the choice of the DFA. Therefore, we examined 12 different functionals (GGAs, meta-GGAs, hybrid functionals, as well as long-range, and meta-hybrid functionals) and their performance on the spin ground state for both complexes under study (Table 1). GGA and meta-GGA functionals always give closed-shell singlet as the ground state, with triplet higher in energy. The performance of hybrid and meta-hybrid functionals depends on the percentage of the exact HF exchange. The high spin states are more stabilized as the percentage of the exact exchange is higher. The closed-shell singlet state is still the ground state with functionals having low (TPSSh with 10%, B3LYP\* with 15%) to moderate (B3LYP with 20%, M06 with 27%) amount of the HF exchange. BHandHLYP and M06-2X favor the broken symmetry solution. This is due to a large amount of the exact exchange (50% in BHandHLYP, and 54% in M06-2X) leading to the artificial symmetry breaking [6, 66]. The most reasonable results have been obtained with long-range separated hybrid CAMY-B3LYP: the ground state of  $[\text{Fe}(\text{CO})_4]^{2-}$  is a closed-shell singlet

with a broken symmetry singlet state approx. 70 kcal/mol higher in energy, in accordance with previous findings [11, 12], while in the case of  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  closed-shell singlet and open-shell singlet are similar in energy, later being more stable for 0.8 kcal/mol.

**Table 1** Spin-state energy differences in  $[\text{Fe}(\text{CO})_4]^{2-}$  and  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  with different DFAs at X-ray geometries (CCDC 1217933 [11], 1266312 [50]); energies are given in kcal/mol relative to the closed-shell singlet states.

$[\text{Fe}(\text{CO})_4]^{2-}$				$[\text{Fe}(\text{CO})_3\text{NO}]^-$		
GGA	BP86-D4		OPBE	BP86-D4		OPBE
Singlet	0.00		0.00	0.00		0.00
Triplet	73.01		77.79	56.43		55.66
Quintet	152.89		155.41	110.24		105.75
Open-shell Singlet	73.82 <sup>a</sup>		79.24 <sup>a</sup>	65.69 <sup>a</sup>		65.86 <sup>a</sup>
Meta-GGA	M06-L	TPSS	SCAN	M06-L	TPSS	SCAN
Singlet	0	0	0	0	0	0
Triplet	81.09	76.22	74.27	53.28	54.49	49.85
Quintet	155.09	154.83	148.9	98.51	106.18	94.15
Open-shell Singlet	86.30 <sup>a</sup>	77.03 <sup>a</sup>	76.51 <sup>a</sup>	64.43 <sup>a</sup>	64.41 <sup>a</sup>	61.07 <sup>a</sup>
Hybrid	B3LYP*	B3LYP	BHandHLYP	B3LYP*	B3LYP	BHandHLYP
Singlet	0	0.00	0.00	0	0.00	0.00
Triplet	69.10	67.55	57.57	48.14	44.54	23.31
Quintet	145.06	141.4	115.03	93.16	85.73	39.73
Open-shell Singlet	69.56 <sup>a</sup>	68.67 <sup>a</sup>	-1.9	65.28 <sup>a</sup>	56.23 <sup>a</sup>	-17.95
Meta-Hybrid	TPSSh	M06	M06-2X	TPSSh	M06	M06-2X
Singlet	0	0	0	0	0	0
Triplet	74.63	75.92	50.17	48.69	46.53	18.33
Quintet	149.75	147.13	107.06	94.18	86.2	40.13
Open-shell Singlet	77.03 <sup>a</sup>	75.12 <sup>a</sup>	-3.33	64.66 <sup>a</sup>	64.90 <sup>a</sup>	-18.06 <sup>a</sup>
Long-range	CAMY-B3LYP			CAMY-B3LYP		
Singlet	0.00			0.00		
Triplet	68.94			40.57		
Quintet	141.26			78.82		
Open-shell Singlet	69.33 <sup>a</sup>			-0.84		

<sup>a</sup> “non-aufbau” occupation of KS-MOs

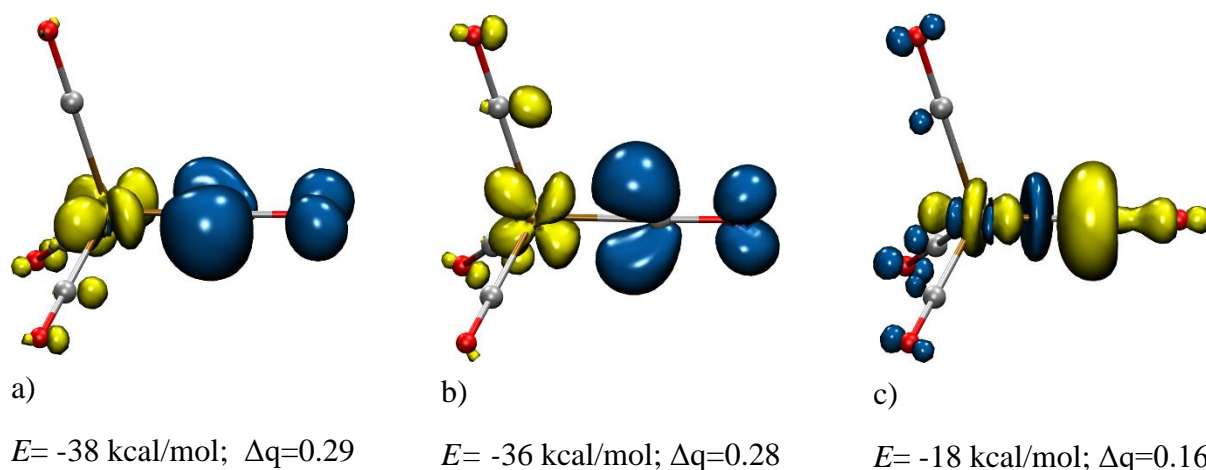
EDA analysis with CAMY-B3LYP provides insight into the nature of the Fe-CO bond (Table 2). The attractive interactions ( $E_{\text{elst}}$  and  $E_{\text{orb}}$ ) are the indications of ionic vs. covalent bonding, respectively. It is clear from Table 2 that Fe-CO bonding can be described as 50% ionic and 50% covalent in line with transfer of charge from  $[\text{Fe}(\text{CO})_3]^{2-}$  fragment to CO. The same picture is obtained with other DFA’s (Table S1 in SI).

**Table 2** Energy Decomposition Analysis of  $[\text{Fe}(\text{CO})_3]^{2-} \cdots \text{CO}$  at SR-ZORA-CAMY-B3LYP/TZP level of theory; energy components are given in kcal/mol relative to the chosen fragments;  $\Delta Q$  is Hirshfeld charge, transferred between fragments;  $E = E_{\text{int}} + E_{\text{prep}}$ .

	$E_{\text{Pauli}}$	$E_{\text{elst}}$	$E_{\text{orb}}$	$E_{\text{int}}$	$E_{\text{prep}}$	$E$	$\Delta Q$
$[\text{Fe}(\text{CO})_3]^{2-} \cdots \text{CO}$	121.79	-104.05	-102.62	-84.88	14.42	-70.46	0.45 <sup>a</sup>

<sup>a</sup> charge is transferred from  $[\text{Fe}(\text{CO})_3]^{2-}$  fragment to CO fragment

NOCV scheme reveals three dominant electron density flow channels and clarifies the covalent character of the bonding, Fig. 1. The most important contribution is  $\pi^*$ -back-donation from Fe d-orbitals (Fig. 1a and Fig. 1b). The  $\pi^*$ -accepting properties of coordinated ligands are crucial for bonding in  $d^{10}$  complexes [43]. Another important contribution is  $\sigma$ -donation from the lone pair of CO ligand and the charge accumulation in the bonding region (Fig. 1c). The other contributions are mainly polarization because of small Hirshfeld charge transfer,  $\Delta q$ , indicating the intra-fragment character of density transfers.



**Fig. 1** Most important density deformation channels from EDA-NOCV analysis of  $[\text{Fe}(\text{CO})_3]^{2-} \cdots \text{CO}$  interaction: a) and b)  $\pi^*$ -back-donation c)  $\sigma$ -Fe-CO bond. Their relevance is given by their energy contribution  $E$  to  $E_{\text{orb}}$  and by Hirshfeld charge transferred between the fragments  $\Delta q$ . Charge outflow/inflow is represented by yellow/blue color (isovalue=0.005 a.u.)

Calculations on  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  were performed considering different oxidation state of the central Fe atom and the resulting charge of the nitric oxide: i) Fe(-II) ( $d^{10}$  electronic configuration) and  $\text{NO}^+$ , giving closed-shell singlet as the ground state; ii) Fe(-I) and  $\text{NO}$ , with one unpaired electron on the iron center ( $d^9$  electronic configuration) and one unpaired electron on the neutral nitrosyl ligand giving open-shell singlet as the ground state; iii) Fe(0) and  $\text{NO}^-$  with two unpaired electrons on both centers, leading to the open-shell singlet state, as the ground state. Because of the covalent character of bonding with nitrosyl ligand, the open-shell singlet states prepared as in ii) and iii), according to our calculations, converge to

the same electronic distribution. It has been previously shown [6, 7], and our calculations proved it, that determination of the ground state is influenced by the chosen DFA (Table 1). High spin states (triplet in the case ii) and quintet in the case iii)) are always much higher in energy. Looking only at the ground state energies will not give an unambiguous conclusion on the electronic structure. Therefore, we performed EDA analysis with a different selection of fragments, i.e., choices i), ii), and iii), Table 3. To compare three different decisions, energy  $E_{\text{rel}}$  is stated as the energy difference relative to the most stable relaxed fragment pairs ( $[\text{Fe}(\text{CO})_3]^-/\text{NO}$ ).

**Table 3** Energy Decomposition Analysis of  $[\text{Fe}(\text{CO})_3\text{--NO}]^-$  for different fragmentation patterns, i), ii) and iii) at SR-ZORA-CAMY-B3LYP/TZP level of theory; energy components are given in kcal/mol relative to the chosen fragments;  $E_{\text{rel}}=E_{\text{int}}+E_{\text{prep}}$  relative to the relaxed  $[\text{Fe}(\text{CO})_3]^-/\text{NO}$  pair;  $\Delta Q$  is Hirshfeld charge, transferred between fragments.

		$E_{\text{Pauli}}$	$E_{\text{elst}}$	$E_{\text{orb}}$	$E_{\text{int}}$	$E_{\text{prep}}$	$E_{\text{rel}}$	$\Delta Q$
i)	$[\text{Fe}(\text{CO})_3]^{2-}\text{--NO}^+$	105.95	-210.78	-324.34	-447.17	86.07	-65.17	1.25 <sup>a</sup>
ii)	${}^2[\text{Fe}(\text{CO})_3]^- \text{--} {}^2\text{NO}$	160.12	-93.37	-156.68	-89.94	23.95	-65.99	0.46 <sup>b</sup>
iii)	${}^3[\text{Fe}(\text{CO})_3] \text{--} {}^3\text{NO}^-$	195.04	-178.47	-122.76	-106.19	4.22	-65.99	0.28 <sup>c</sup>

i) closed-shell singlet  $[\text{Fe}(\text{CO})_3\text{NO}]^-$  ii) and iii) open-shell singlet  $[\text{Fe}(\text{CO})_3\text{--NO}]^-$

<sup>a</sup> charge is transferred from  $[\text{Fe}(\text{CO})_3]^{2-}$  fragment to  $\text{NO}^+$  fragment

<sup>b</sup> charge is transferred from  $[\text{Fe}(\text{CO})_3]^-$  fragment to  $\text{NO}$  fragment

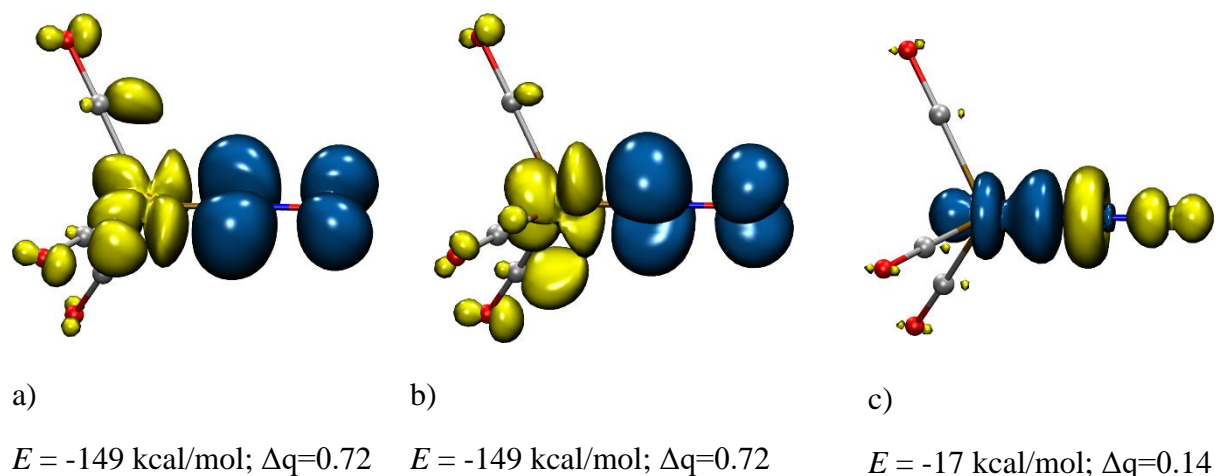
<sup>c</sup> charge is transferred from  $\text{NO}^-$  fragment to  $[\text{Fe}(\text{CO})_3]$

Energy differences between three possible fragmentation choices are small and in line with DFT calculations, showing that the broken-symmetry solution is more stable for approx. 0.8 kcal/mol. However, energy components are entirely different, indicating the importance of the fragment choice. Different fragment alternatives reflect the diverse nature of the interaction between fragments. The model, which is the closest to the physical reality, is the one with the lowest absolute value of  $E_{\text{orb}}$  [67]. Orbital interaction takes into account the significance of the charge transfer between the fragments. Thus,  $[\text{Fe}(\text{CO})_3\text{--NO}]^-$  choice of fragments, iii), is the most similar to the final electronic structure of the complex anion, Table 3. Moreover, in the situation i)  $\Delta Q$  is very large, showing a tendency to reduce  $\text{NO}^+$ . It is noteworthy that even different DFAs, that give different ground states, in EDA analysis give the same trends (Tables S2 and S3 in Supplementary material).

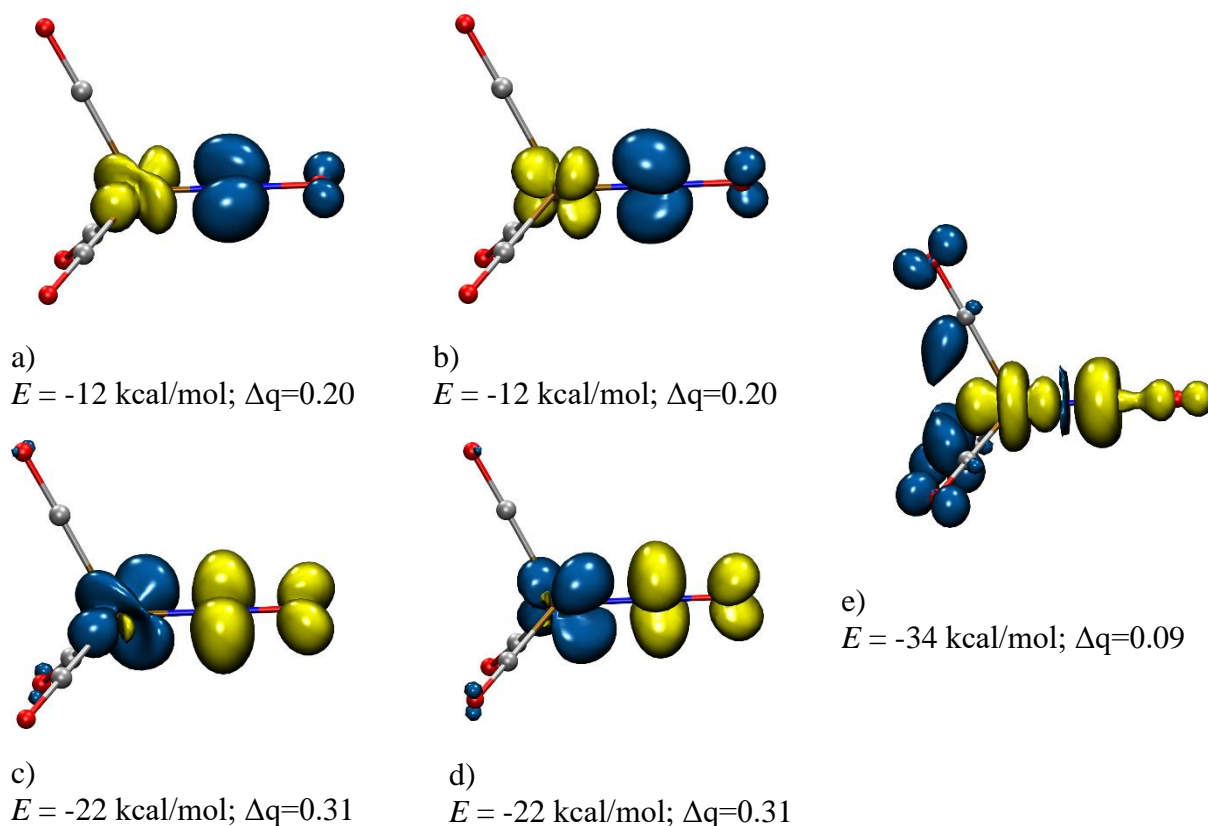
NOCV analysis for the first fragmentation scheme reveals almost exclusive  $\pi^*$ -back-donation to the  $\text{NO}^+$  (Fig. 2a and Fig. 2b). These two, most dominant electron density flows contribute more than 90% to  $E_{\text{orb}}$  and include the transfer of 1.4 electrons, oxidize iron, and suggest that iron cannot be in the -II oxidation state, supplementing previous arguments. The third density flow channel is clear  $\sigma$ -donation but is of minor importance (Fig. 2c). The same analysis on the broken symmetry  $[\text{Fe}(\text{CO})_3\text{--NO}]^-$  also shows the importance of  $\pi$  bonding between the fragments (Fig. 3). Four most dominant density flow channels correspond to the  $\alpha$ - $\pi^*$ -back-donation (Fig. 3a and Fig. 3b) and  $\beta$ - $\pi^*$ -donation (Fig. 3c and Fig. 3d).  $\sigma$ -type interaction



between the fragments (Fig. 3e) contributes around 27% to the  $E_{\text{orb}}$ , but a minimal amount of charge is transferred between the fragments (0.09 electrons).



**Fig 2** Most important density deformation channels from EDA-NOCV analysis of  $[\text{Fe}(\text{CO})_3]^{2-} \text{--} \text{NO}^+$  interaction: a) and b)  $\pi^*$ -back-donation c)  $\sigma$ -donation. Their relevance is given by their energy contribution  $E$  to  $E_{\text{orb}}$  and by Hirshfeld charge transferred between the fragments  $\Delta q$ . Charge outflow/inflow is represented by yellow/blue color (isovalue=0.005 a.u.)



**Fig 3** Most important density deformation channels from EDA-NOCV analysis of  $[\text{Fe}(\text{CO})_3]^- \text{--} \text{NO}^-$  interaction: a) and b)  $\alpha$ - $\pi^*$ -back-donation c) and d)  $\beta$ - $\pi^*$ -donation e)  $\sigma$ -polarization. Their relevance is given by their energy contribution  $E$  to  $E_{\text{orb}}$  and by Hirshfeld charge transferred between the

fragments  $\Delta q$ . Charge outflow/inflow is represented by yellow/blue color (isovalue=0.005 a.u. in a), b, c), d) and isovalue= 0.0025 a.u. in e))

#### 4. Conclusions

With the approach of combined Energy Decomposition Analysis and Natural Orbital for Chemical Valence, new insights into the electronic structure of the  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  has been gained. The results are also compared with the  $[\text{Fe}(\text{CO})_4]^{2-}$ , where iron is in the formal oxidation state -II. DFT calculations did not give an obvious conclusion about the oxidation state of the iron atom and the resulting charge of the nitric oxide ligand. The computed ground state depends on the chosen functional. With GGA, meta-GGA, hybrid and meta-hybrid functionals with a lower percentage of the exact exchange, the electronic structure of  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  correspond to the  $[\text{Fe}(\text{CO})_4]^{2-}$ , i.e., Fe(-II) ( $d^{10}$  electronic configuration) and  $\text{NO}^+$ . On the other hand, hybrid and meta-hybrid functionals with a higher percentage of the exact exchange (e.g., BHandHLYP and M06-2X), as well as long-range separated CAMY-B3LYP gave the open-shell singlet with Fe(0) and  $\text{NO}^-$ .

However, it has been shown that the trends in EDA are irrespective of the chosen functional. The choice of fragments in EDA is a clear indication of actual bonding in analyzed complexes. The orbital contribution is an indicator of how well the chosen fragments represent the real picture. The lowest absolute value of  $E_{\text{orb}}$  suggests that the electronic state of  $[\text{Fe}(\text{CO})_3(\text{NO})]^-$  is the best described with iron in zero formal oxidation state bounded to the nitrosyl anion. Furthermore, NOCV analysis on  $[\text{Fe}(\text{CO})_3]^{2-}--\text{NO}^+$  fragments show large charge flow from iron to  $\text{NO}^+$  ligand, confirming that iron cannot be in -II oxidation state. Comparison with its analog  $[\text{Fe}(\text{CO})_4]^{2-}$  showed that the nature of bonding is different.

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