

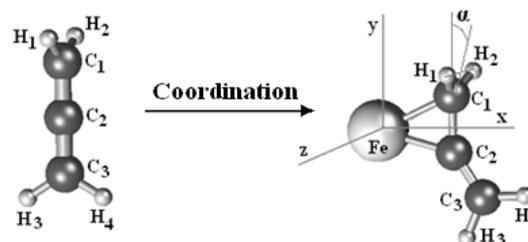
JAHN-TELLER AND PSEUDO JAHN-TELLER ORIGIN OF STRUCTURAL DISTORTIONS OF COORDINATED MOLECULES

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A new approach based on an approximate evaluation of the Jahn-Teller effect (JTE), pseudo JTE, and Renner-Teller effect (RTE) in systems with fractional charges is employed to reveal the origin of structural distortions of coordinated formaldehyde and allene molecules in comparison with their structure as a free system. It is shown that the orbital charge transfers to formaldehyde in the $\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\eta^2\text{-CH}_2\text{O})$ and $\text{Fe}(\text{PH}_3)_4(\eta^2\text{-CH}_2\text{O})$ complexes induce the pseudo Jahn-Teller interaction in CH_2O molecule leading to the out-of-plane bending of the latter. The changes in allene geometry by coordination are shown to be due the common action of the JT and PJT effects induced by the orbital charge transfers.



INTRODUCTION

A large number of the experimental and theoretical studies indicate that small molecules coordinated to the metal centers or adsorbed on the surfaces undergo, as a rule, structural changes leading to distortion of their high-symmetry nuclear configurations. As examples can be mentioned the *cis*-distortion of η^2 -coordinated acetylene and ethylene molecules and their derivatives,¹⁻⁹ the bending of coordinated or adsorbed carbon dioxide,^{9,10-12} the out-of-plane distortion of coordinated formaldehyde molecule,¹³⁻¹⁷ the in-plane bending of the C-C-O moiety of ketenes in the metal-ketene complexes,^{9,18} the bending of coordinated allene,¹⁹⁻²¹ etc. Moreover, one and the same coordinated molecule is strongly distorted in some complexes, in others it is distorted weaker, and in some complexes it is not distorted at all.

Up until now, among the models for description of the metal-ligand bonding the Dewar-Chatt-Duncanson diorbital scheme²² for unsaturated hydrocarbons is more conventional. However, this

scheme is only qualitative in nature and does not explain the different distortions of the same molecule in different complexes. Moreover, the metal-ligand bonds may be not only diorbital, but also a mono- or multiorbital ones, which occurs, for example, in the metal-cyclic molecule systems.

A more general definition of the ligand bonding, in which mono-orbital, diorbital and multiorbital metal-ligand bonds are distinguished, was suggested by Bersuker in his monograph.²³ In the MO terminology "the multiplicity of the orbital bonding (mono-, di-, and multiorbital) equals the number of complex-ligand bonding MOs uncompensated by the antibonding orbitals".²³ It follows from this definition that the electron charge transfers to and from the ligand is due to formation of such uncompensated bonding molecular orbitals of the entire complex. The values of the orbital charge transfers depend on the nature of the metal and the geometry of ligand coordination. They may have opposite signs ($\Delta q_i < 0$ means the electron density transfer from *i*-th MO of the ligand to the metal, and $\Delta q_i > 0$ in the

opposite case) compensating each other and giving a small value of the total charge transfer. However, their effect on ligand activation may be additive. In the particular case of diorbital bonding the scheme of mutually compensating charge transfers²³ is qualitatively the same as the Dewar-Chatt-Duncanson one.²²

We have proposed a new approach to handle instabilities and structural changes in coordinated and adsorbed molecules.²⁴ It is based on an approximate evaluation of the Jahn-Teller effect (JTE), pseudo JTE (PJTE), and Renner-Teller effect (RTE) induced by the orbital charge transfers (OCTs) in such systems. The efficiency of the proposed theory has been demonstrated by several examples showing how the OCTs influence the JTE, PJTE, and RTE in coordinated molecules, leading to distortion of their high-symmetry nuclear configurations.²⁴

In the present paper, in the framework of the above approach, we analyze the structural distortions of formaldehyde (CH₂O) and allene (C₃H₄) molecules by their coordination in transition metal complexes. The out-of-plane distortion of formaldehyde molecule coordinated in the Fe(CO)₂(PH₃)₂(η²-CH₂O) and Fe(PH₃)₄(η²-CH₂O) complexes is explained as due to the PJTE. The changes in allene geometry by coordination are shown to be due the common action of the JT and PJT effects induced by the OCTs.

THEORETICAL MODEL AND COMPUTATIONAL DETAILS

When any small molecule is coordinated to the metal, one to several binding molecular orbitals are formed between this molecule and the complex. Due to formation of these bonding MOs the orbital charge transfers (OCT) to and from the coordinated molecule take place. The main idea of the proposed approach is that the influence of these small OCTs ($\Delta q \ll ne$, where n is the number of electrons in the molecule) can be considered as a small perturbation to the integer-electron system. In other words, in the first order of perturbation theory, we can assume that the additional charge

$$F'_Q = F_{Q_0} + \Delta F = \sum_i (q_i + \Delta q_i) f_Q^i = \sum_i q_i f_Q^i \neq 0, \quad (5)$$

and the system is distorted. A similar JTE emerges when the charge Δq_i is removed from a fully

occupies the LUMO or frees the HOMO without changing significantly the MO wavefunctions. Consider now how the OCTs influence the JTE and the PJTE in coordinated molecules leading to the instability and distortion of their high-symmetry nuclear configurations.

In the JTE which refers to polyatomic systems with degenerate electronic states the force, acting upon the nuclear framework, distorts it in the direction Q , and the distortion magnitude is

$$Q_0 \sim F_Q / K_0 \quad (1)$$

where K_0 is the primary force constant (the force constant without the JTE), and F_Q is the diagonal constant of the linear vibronic coupling

$$F_Q \equiv F_{\Gamma\gamma}^{(\Gamma\gamma)} = \langle \Gamma\gamma | (\partial H / \partial Q_{\Gamma\gamma})_0 | \Gamma\gamma \rangle \quad (2)$$

It has the physical meaning of the force with which the electrons in state $\Gamma\gamma$ distort the nuclear framework in the direction of symmetrized coordinate $Q_{\Gamma\gamma}$. In the MO approximation the total distortion force (2) equals the sum of the orbital vibronic coupling constants (OVCC) f_Q^i multiplied by the MO occupation numbers q_i :^{23,25}

$$F_Q = \sum_i q_i f_Q^i, \quad (3)$$

where the diagonal orbital vibronic coupling constant (OVCC) f_Q^i is defined as the matrix element of the derivative of the Hamiltonian H with respect to nuclear displacements on the molecular orbitals $|i\rangle$:

$$f_Q^i \equiv f_Q^{(i,i)} = \langle i | (\partial H / \partial Q)_0 | i \rangle \quad (4)$$

Assume that before the charge transfer the system is stable in the high-symmetry configuration Q_0 . It means that in this configuration the total distortion force $F_{Q_0} = 0$. Suppose, further, that the only one MO takes part in the charge transfer with the additional charge Δq_i occupying a degenerate orbital. For this latter, in accordance with the JTE, $f_Q^i \neq 0$ in the direction of the JT active coordinate Q . Hence, the force with which the electrons affect the nuclear framework, is not equal to zero,

occupied degenerate orbital (which does not produce distortions without the charge transfer).

In the PJTE the problem of the stability or instability of molecular nuclear configuration may be reduced to the consideration of the curvature K of the adiabatic potential energy surface (APES) in the direction of Q . In²⁴ it was shown that in this case we can write the following expression for the curvature K of coordinated molecule along the distortion coordinate:

$$K^{coord} = K^{free} - \sum_{i,j} (q_i - q_j) \left| f_Q^{(i,j)} \right|^2 / \Delta. \quad (6)$$

Here q_i and q_j are the occupations of molecular orbitals $|i\rangle$ and $|j\rangle$, and

$$f_Q^{(i,j)} = \langle i | (\partial H / \partial Q)_0 | j \rangle \quad (7)$$

is the off-diagonal OVCC between them.

Thus, in order to clarify whether any coordinated molecule is stable ($K^{coord} > 0$) or unstable ($K^{coord} < 0$) with respect to symmetrized coordinate of nuclear displacements Q , we need to calculate the curvature of the AP of free molecule (K^{free}), to evaluate the PJT coupling constants $f_Q^{(i,j)}$, and to estimate the orbital charge transfers induced by coordination.

To do this the electronic structure of free CH_2O and C_3H_4 molecules and in the coordinated state was evaluated. All calculations were performed with the GAMESS quantum chemistry package.²⁶ The geometry optimization of all considered species was carried out by means of the DFT (B3LYP) method²⁷ using the 6-31G* basis set.

To estimate the values of the orbital charge transfers to and from coordinated molecules following the scheme explained above in Section 2, the calculated MOs of the complexes are rewritten in the basis of the eigenfunctions of the

free molecules and the atomic orbitals (AO) of other atoms. Then the changes in the occupations of MOs of coordinated molecules in the complex are estimated from the difference in Mulliken populations of the corresponding orbitals.

RESULTS AND DISCUSSION

Pseudo Jahn-Teller Effect in coordinated formaldehyde molecule

The metal-formaldehyde complexes have been postulated to be the pivotal intermediates in the catalytic activation of carbon monoxide. Some formaldehyde complexes were synthesized and structurally identified,¹³⁻¹⁵ in which the η^2 -coordinated CH_2O molecule is distorted to a nonplanar (C_s) shape. We apply the above theory to explain the origin of distortion of the molecule as due to the PJTE induced by the OCTs by coordination.

To do this, we performed *ab initio* calculations of the free CH_2O molecule and the two model complexes of iron, $\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\eta^2\text{-CH}_2\text{O})$ **I** and $\text{Fe}(\text{PH}_3)_4(\eta^2\text{-CH}_2\text{O})$ **II**. A general view of the complexes (**I**) and (**II**) along with the used coordinate system is shown in Fig. 1. The geometry optimization was carried out under the assumption that the spatial nuclear configuration of these compounds corresponds to the C_s point group of symmetry. Calculated values of the C-O distances (1.33 Å in the **I**, and 1.37 Å in **II**) and the angles between the CH_2 plane and the C-O bond (31.3° and 39.4° for the **I** and for the **II** complexes, respectively) agree well with the data of the work.¹⁷

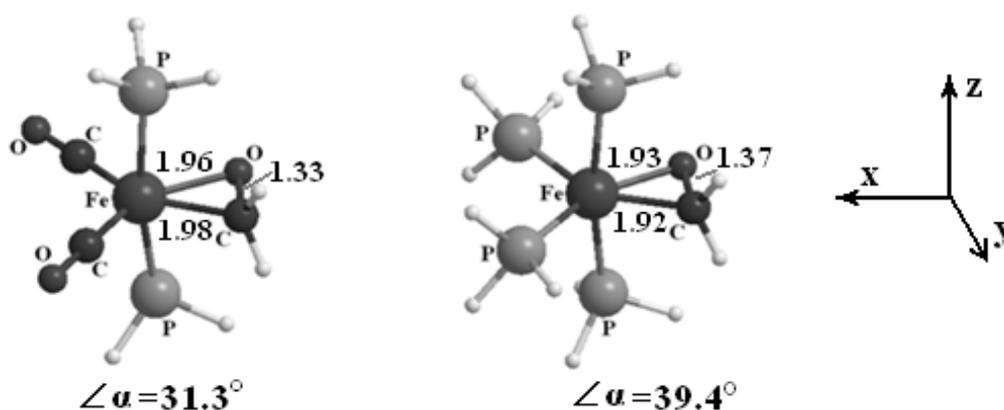


Fig. 1 – Optimized structures of $\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\eta^2\text{-CH}_2\text{O})$ **I** and $\text{Fe}(\text{PH}_3)_4(\eta^2\text{-CH}_2\text{O})$ **II**. $\angle\alpha$ is the distortion angle between the CH_2 plane and the C-O bond.

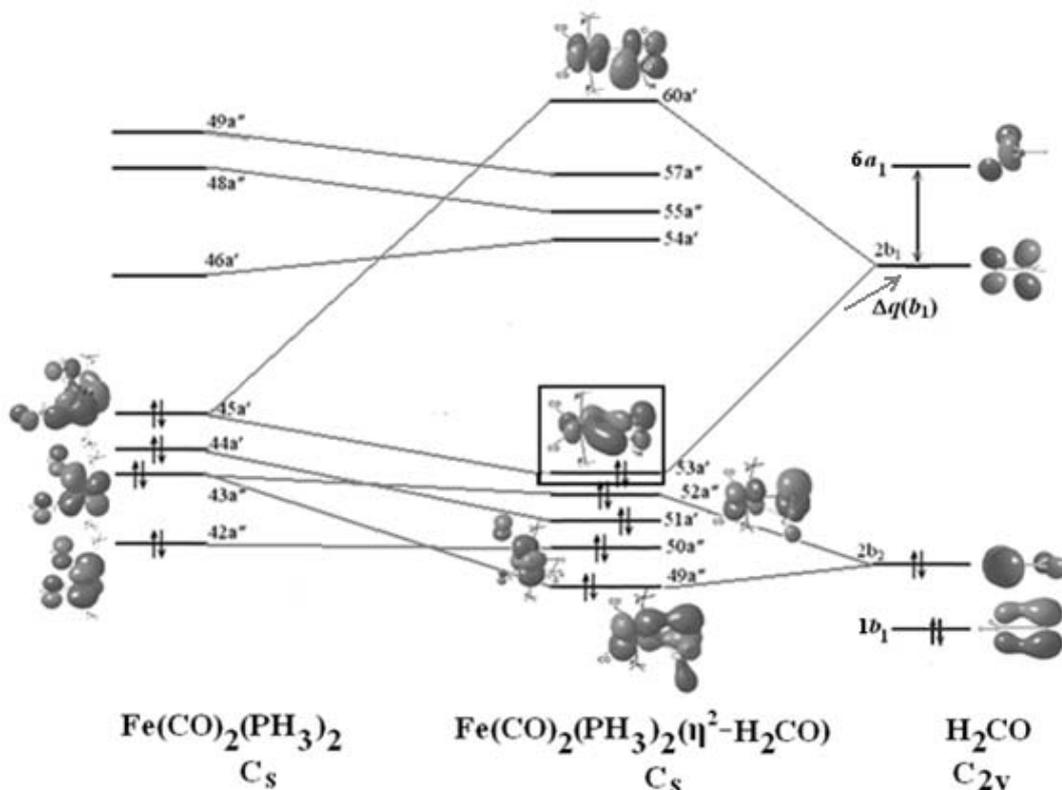


Fig. 2 – MO energy-level scheme for bonding between H_2CO and $\text{Fe}(\text{CO})_2(\text{PH}_3)_2$. For the sake of simplicity, only the main correlations are shown.

Table 1

One-electron states of valence zone of $\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\eta^2\text{-CH}_2\text{O})$		
MOs	Energy, a.u.	Composition*
$60 a'$	0.025	$0.47(3d_{xy}^{\text{Fe}}) + 0.40(2p_x^{\text{C}}) - 0.30(2p_x^{\text{O}})$
$53 a'$, HOMO	-0.198	$0.48(3d_{xy}^{\text{Fe}}) - 0.35(2p_x^{\text{C}}) + 0.39(2p_x^{\text{O}})$
$52 a''$, HOMO-1	-0.211	$0.49(3d_{xz}^{\text{Fe}}) - 0.61(2p_z^{\text{O}})$
$49 a''$	-0.264	$0.53(3d_{xz}^{\text{Fe}}) - 0.41(2p_z^{\text{O}})$

* For simplicity, only contributions of the AOs of Fe and MOs of CH_2O are presented

In order to reveal the main electronic redistribution details accompanying the formation of MOs of the complexes under investigation, consider the MO energy-level scheme of the active valence zone of the whole complex $\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\eta^2\text{-CH}_2\text{O})$ **I** and that of its fragments, $\text{Fe}(\text{CO})_2(\text{PH}_3)_2$ and CH_2O (Fig. 2). The orbital energies and the composition of the MOs of the complex **I** are presented in Table 1. The nomenclature of MOs in Table 1 is given in accordance with the coordinate system from Fig. 1.

The occupied $2b_2$ MO of CH_2O interacts with the occupied $3d_{xz}$ MO of Fe, giving rise to the two occupied π -type MOs of the $\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\eta^2\text{-CH}_2\text{O})$ complex: the bonding MO $49a''$ and the antibonding MO $52a''$ (Fig. 2). Because of the fact that both these MOs are double occupied by electrons, they compensate each other, and hence

their total contribution to the Fe- CH_2O bonding is very small²³. The results of the DFT calculations yield $\Delta q_\pi \cong 0$. This small value Δq_π characterizes the slightly asymmetrical charge distribution in the mutual compensating bonding ($49a''$) and antibonding ($52a''$) MOs.

The main contribution to the Fe- CH_2O bonding is provided by forming of the π -type bonding MO $53a'$ from the corresponding MOs of the above fragments, namely, from the filled MO $3d_{xy}$ of the $\text{Fe}(\text{CO})_2(\text{PH}_3)_2$ and the empty antibonding $2b_1(\pi^*)$ -MO of CH_2O . Due to forming of this ($53a'$) MO the electron density is transferred from the $3d_{xy}$ -AO of the atom of Fe to the π^* -MO of the formaldehyde molecule (the π -type back donation). The orbital charge transfer is quite significant in both considered complexes, $\Delta q_{\pi^*}(\mathbf{I}) = 0.52\bar{e}$ and $\Delta q_{\pi^*}(\mathbf{II}) = 0.63\bar{e}$. It is seen from Fig. 2 that only

this $53a'$ bonding MO of the complex is uncompensated by the antibonding orbital (the empty MO $60a'$ in our calculations). Therefore, one can conclude that Fe-formaldehyde bonding in the studied complex is provided by the π -back donation from the transition metal to the ligand.

Thus, as a result of coordination, the lower unoccupied MO $2b_1$ acquires the charge $\Delta q(2b_1)$. Since the distortion mode leading to the nonplanar configuration of formaldehyde molecule is also of the b_1 -symmetry, the OVCC mixing the partly occupied $2b_1$ with the unoccupied $6a_1$ states becomes nonzero:

$$f = f_{b_1}^{(2b_1,6a_1)} = \langle 2b_1 | (\partial H / \partial Q_{b_1})_0 | 6a_1 \rangle \neq 0. \quad (8)$$

Then the curvature of the adiabatic potential of coordinated formaldehyde molecule with respect to the bending mode can be estimated from the Eq. (9):

$$K^{coord} = K^{free} - \frac{\Delta q(f^2)}{\Delta_{2b_1,6a_1}}. \quad (9)$$

To obtain the value of $f_{b_1}^{(2b_1,6a_1)}$ considered more in detail free CH_2O molecule. The formaldehyde molecule is well studied. It is known that unlike the ground state, the lowest excited 1A_2 and 3A_2 electronic states have a nonplanar nuclear configuration with an elongated C-O bond.^{28,29} Both these excited states are formed by the one-electron excitation $|2b_2\rangle \rightarrow |2b_1\rangle$ (Fig. 2). Earlier we have shown³⁰ that the instability of the planar configuration of CH_2O molecule in the excited A_2 states with respect to the bending coordinate of the b_1 symmetry is due to the PJT coupling of these states with the higher in energy excited B_2 states formed by the one-electron excitation $|2b_2\rangle \rightarrow |6a_1\rangle$ (Fig. 2). The vibronic coupling constant mixing these states, $F_{Q_{b_1}}^{(A_2, B_2)} = \langle A_2 | (\partial H / \partial Q_{b_1})_0 | B_2 \rangle$, is calculated to be 3.03 eV/\AA . In the one-electron approximation this value is just equal to the required OVCC from Eq. (8). Calculated value of the curvature of the AP of free formaldehyde molecule with respect to the bending is equal to $K_{b_1}^{free}(\text{CH}_2\text{O}) = 0.56 \text{ eV/\AA}^2$, and the value of the energy gap is equal to $\Delta_{2b_1,6a_1} = 6.18 \text{ eV}$.

With these numerical data we get the following resulting values for the curvature of the AP of CH_2O molecule with respect to the bending mode: $K(\mathbf{I}) = -0.21 \text{ eV/\AA}^2$ and $K(\mathbf{II}) = -0.37 \text{ eV/\AA}^2$. It is seen that in the coordinated state the curvature of the AP of the CH_2O molecule in the b_1 direction

becomes negative in both complexes. This explains the origin of the geometry of coordination of this molecule and provides for numerical estimates of the strength of the distortion.

In the same approximation, by applying the above equations to the formaldehyde molecule with respect to the totally symmetric displacements of A_1 symmetry corresponding to the C-O stretching mode, we can explain also the elongation of its C-O bond by coordination (1.33 \AA and 1.33 \AA for \mathbf{I} and \mathbf{II} respectively versus 1.22 \AA for free molecule). In the ground state equilibrium configuration of free CH_2O molecule the distorting force F_{A_1} with respect to the A_1 displacement equals zero. After the charge transfer $\Delta q(2b_1) > 0$ this force changes by the value $\Delta F_{A_1} = \Delta q(2b_1) f_{A_1}^{2b_1}$. Since the $2b_1$ MO is the antibonding one (with respect to C-O bonding), then $f_{A_1}^{2b_1} > 0$ and therefore $F_{A_1} > 0$.²³ Thus the OCT induce a JTE distorting force which pushes away the carbon and oxygen nuclei and thereby increases the C-O bond length, the distorting force being dependent on the OCT values.

Simultaneous JT and PJT interactions in coordinated allene molecule

Consider now the case when the structural distortion of coordinated molecule is caused by the simultaneous JT and PJT interactions induced by the orbital charge transfer by coordination. As an example we analyze the changes in allene molecule (C_3H_4) geometry by its coordination in the $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_4$ complex (Fig. 3a).

In the ground 1A_1 electronic state allene has the nuclear configuration of D_{2d} symmetry (Fig. 3e). In this configuration it possesses doubly degenerate electronic states and vibrational degrees of freedom. It is seen from Fig. 3 and Table 2 that coordinated C_3H_4 molecule undergoes significant structural changes in comparison with the free allene. They are: the antisymmetric C-C-C stretching, the C-C-C bending, the out-of-plane $\text{C}_1\text{H}_1\text{H}_2$ wagging, and the not very strong antisymmetric CH_2 scissoring. Two of these distortions, the antisymmetric C-C-C stretch and the antisymmetric CH_2 scissoring, transform according to the b_2 irreducible representation of the D_{2d} symmetry point group. The C-C-C bending and the out-of-plane $\text{C}_1\text{H}_1\text{H}_2$ wagging represent the e_x -components of doubly degenerate e -modes (in the coordinate system of Fig. 3).

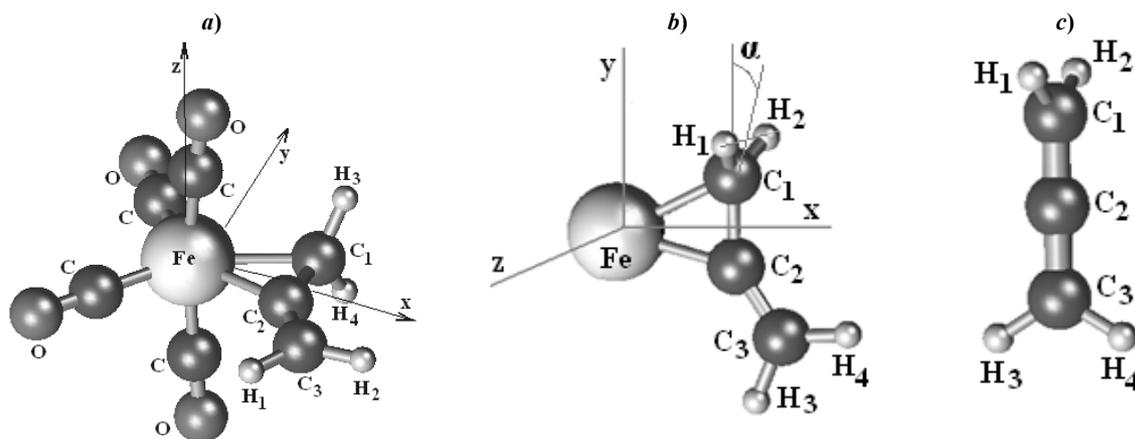


Fig. 3 – (a) Structure of the $\text{Fe}(\text{CO})_4\text{C}_3\text{H}_4$ complex in the *ab initio* optimized geometry; (b) The $\text{Fe}-\text{C}_3\text{H}_4$ fragment of the complex in comparison with free allene molecule (c).

Table 2

Geometrical parameters (distances in Å, angles in degrees) of the free and coordinated C_3H_4 molecule

	C_1-C_2	C_2-C_3	$\angle \text{C}_1-\text{C}_2-\text{C}_3$	$\angle \alpha$	$\angle \text{H}_1\text{C}_1\text{H}_2$	$\angle \text{H}_3\text{C}_3\text{H}_4$
C_3H_4 , free	1.31	1.31	180	0	117.4	117.4
C_3H_4 , coordinated	1.32	1.41	147.7	27.9	113.5	116.3

To reveal which orbital charge transfers lead to these distortions, it is useful to analyze the correlation between the MOs of the complex and those of the free C_3H_4 molecule (Fig. 4). The orbitals mainly involved in the iron-allene bonding are $47a'$, $48a''$, $50a''$, and $52a'$. Two of them, $48a''$ and $50a''$, are respectively the bonding and antibonding linear combinations of the bonding π_z -MO of allene (with respect to C_2-C_3) and appropriate $3d_{\pi^-}$ AO of the atom of iron. They compensate each other, and hence their total contribution to the $\text{Fe}-\text{CH}_2\text{O}$ bonding is small.²³ The σ -MO $47a'$ is composed from the bonding π_x -MO of coordinated C_1 and C_2 atoms of C_3H_4 molecule and $3d_{\sigma^-}$ AO of the metal. This bonding $47a'$ MO provides the transfer of electronic density from the ligand to the metal (σ -type donation). Corresponding antibonding MO $53a'$ is empty. The π -type bonding MO $52a'$, also uncompensated by the antibonding orbital (the empty MO $62a'$ in our calculations) is formed from the filled $3d_{\pi}$ AO of iron and the empty antibonding (with respect to C_1-C_2) π_x^* -MO of allene. The formation of this bonding π -MO $52a'$ leads to transfer of electronic density from the metal to the π^* -MO of the C_3H_4 molecule (the π back donation). One can conclude that the Fe -allene bonding in the studied complex is the diorbital one.

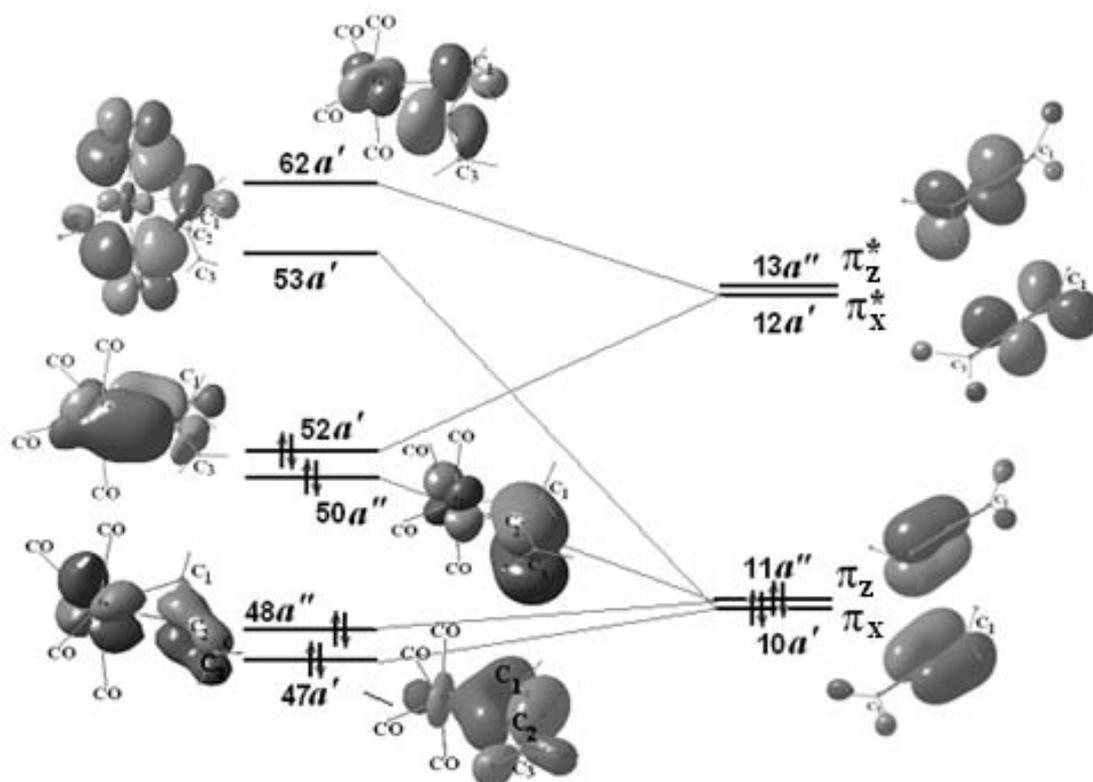
The net effect of the metal-ligand bonding on the allene molecule can be described by the formation of the allene electronic configuration $\{\dots(e_x)^{2-\Delta q\sigma}(e_z)^2(e_x^*)^{\Delta q\pi}\}$ with partially filled doubly degenerated molecular orbitals. The effect of populating (or depopulating) e -MOs is equivalent to the formation of a twofold degenerate charge distribution resulting in the JT interactions. Note, however, that the symmetric direct product of the E representation in the D_{2d} point group yields $[\text{E} \times \text{E}] = \text{A}_1 + \text{B}_1 + \text{B}_2$, that is, it does not contain the E irreducible representation. Therefore,

$$\langle e_x | (\partial H / \partial Q_{b2})_0 | e_x \rangle \neq 0 \text{ and}$$

$\langle e_x | (\partial H / \partial Q_{ex})_0 | e_x \rangle = 0$. It means that the JTE can activate only nondegenerate vibrational modes (the b_2 -type antisymmetric C-C-C stretch and the antisymmetric CH_2 scissoring), but not the e -modes. The e -type distortions (the C-C-C bending and the out-of-plane $\text{C}_1\text{H}_1\text{H}_2$ wagging) can be excited only by the PJT coupling of the partly occupied e_x^* MO (π_x^* in Fig. 4) with the higher lying empty a_1 MO of C_3H_4 molecule through the degenerate vibrational modes (the PJT coupling constant

$$f_{ex}^{ex^*,a1} \equiv \langle e_x^* | (\partial H / \partial Q_{ex})_0 | a_1 \rangle \neq 0$$

between these MOs is not equal to zero).

Fig. 4 – MO correlation diagram for Fe-C₃H₄ bonding.

CONCLUSIONS

In this study we have demonstrated that structural distortions of molecules caused by their coordination to transition metal complexes may be interpreted as the consequences of the JTE and PJTE induced by the orbital charge transfers. It is shown that the out-of-plane bending of coordinated formaldehyde molecule is due to the PJTE initiated by the π -type back donation to its empty antibonding $2b_1(\pi^*)$ -MO. The distortion of coordinated allene can be explained by the common action of the JT and the PJT effects induced by the orbital charge transfers from the occupied e_x MO and to the unoccupied e_x^* MO. The b_2 -type antisymmetric C-C-C stretching and the antisymmetric CH₂ scissoring are due to the JTE, while the C-C-C bending and the out-of-plane C₁H₁H₂ wagging are the results of the PJTE.

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