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SINDO1 study of electronic structure and carbonyl fluxionality in $Fe_3(CO)_{12}$

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Abstract

The electronic structure and carbonyl fluxionality of $Fe_3(CO)_{12}$ have been investigated by the semiempirical MO method SINDO1. Based on the calculated bond valence indices, it is pointed out that the electronic structure, due to the different σ/π bonding capacities of bridging and terminal carbonyls and the number of direct M–M bonds, is quite important besides the steric effects for the determination of the ligand geometry in $M_3(CO)_{12}$ type cluster compounds. The calculated energy profiles for three possible terminal–bridging carbonyl exchange mechanisms show that Cotton's mechanism is most probable for carbonyl exchange in solution and Johnson's mechanism is reasonable for solid state. The bond valence indices along these profiles have been studied as well.

Introduction

Binary transition metal carbonyl clusters are a very important type of cluster compounds for the modeling of metal surfaces in chemisorption and heterogeneous catalysis [1–3]. To understand the bonding patterns in such cluster compounds, several empirical rules, based on cluster topology and electron counting, are well established [4–7]. These rules are very useful for the correlation of the metal core geometries and the ligand stochiometries. However, they are limited in providing the finer details of ligand arrangement. Well-known examples are the different ligand geometries in $Os_3(CO)_{12}$ and $Fe_3(CO)_{12}$, in which the former has twelve terminal carbonyl ligands whereas the latter possesses two carbonyls bridging one edge of the metal triangle, although the two molecules are isoelectronic. To rationalize such geometric differences of the ligands Johnson and Benfield noticed the fit of the core metal cluster M_n within the $(CO)_n$ polyhedron as a key factor for the determination of the carbonyl ligands arrangement [8]. According to Johnson's model, the twelve COs of $Fe_3(CO)_{12}$ build up an icosahedron shell, whereas a cuboctahedron is found in $Os_3(CO)_{12}$. The Fe_3 core fits better into the smaller space of an icosahedron than the bigger Os_3 core, which is better accommodated in a cuboctahedral volume. Johnson's model is successful in explaining ligand shell structure in many cluster compounds. But it takes into account only the ligand packing effects and the ligand–ligand interactions. Although such steric effects are very important in cluster compounds [9–11], it was also argued that the difference in ligand shell structure may be at least in part electronic in origin [12].

The fluxionality of carbonyl ligands over the surfaces of core metal clusters is another interesting feature in binary carbonyl clusters. IR and NMR spectra in solution and solid state have confirmed that the terminal and bridging CO ligands in some cluster compounds, such as in $Fe_3(CO)_{12}$, undergo a fast exchange [13]. To explain such ligand exchange or ligand fluxional processes, three mechanisms have been proposed during the last 30 years. Cotton and Troup proposed that such fluxionality in $Fe_3(CO)_{12}$ occurs by a concerted bridge opening–closing process involving a D_{3h} intermediate whose ligand arrangement is similar to that in $Os_3(CO)_{12}$ [14]. Based on the polyhedron ligand shell model, Johnson argued that a libration of the Fe_3 core about the two-fold axis within the CO icosahedron will also result in the exchange of bridging–terminal carbonyl ligands [15, 16]. To rationalize the magical angle spin (MAS) ^{13}C NMR spectrum in solid state, Hanson suggested an alternative picture which involves a rotation of the Fe_3 core about the pseudo three-fold axis by 60° [17]. From the viewpoint of geometric equivalence, all of these mechanisms are reasonable and appealing. However, it is not so easy to distinguish by experiment

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one of the three as the most probable mechanism in solution and in the crystal phase [18].

In very recent work Johnson and co-workers [19, 20] point out that not only will libration of the Fe_3 triangle occur, but also flexing and eventually polyhedral conversion of the CO cage. This conversion corresponds to an icosahedral–cuboctahedral rearrangement in one of its modes with Cotton's mechanism. In this sense Cotton's approach would be a component of the more comprehensive view of Johnson.

In this paper, we have carried out a theoretical study on the cluster compound $Fe_3(CO)_{12}$. The purpose of this investigation is two-fold. First, we analyze the chemical bonding in the molecule by calculated Fe–Fe and Fe–CO bond valence indices and we relate such indices to the different arrangement of carbonyl ligands. Second, we shall provide approximate energy profiles to the above-mentioned carbonyl exchange mechanisms and accordingly, the ranking of the mechanisms in terms of their energetic feasibility will be discussed.

Method of calculation

The calculations were performed with the semiempirical MO method SINDO1 which was recently extended to first row transition metal compounds [21, 22]. The parameters and the details of the method have been described elsewhere [21]. Atomic and bond valence indices, which are defined in terms of appropriate combinations of first-order density matrix elements of the molecules [23–25], have proved to be a powerful tool for the study of chemical bonding in molecules [22]. The experimental geometry of $Fe_3(CO)_{12}$ in the crystal phase [14] is used as the starting point of SINDO1 geometry optimization. In order to reduce the optimization of coordinates, all of the metal–terminal carbonyl bond lengths are averaged, without distinction of $M–C_{ax}$ and $M–C_{eq}$, and C_{2v} symmetry is adopted. The optimized M–Fe bond lengths for terminal and bridging carbonyls are 1.90 and 2.15 Å, respectively, which is comparable to the experimental data of 1.82 and 2.05 Å. The molecular structure with D_{3h} symmetry is optimized as well. The calculated energy difference indicates that the C_{2v} structure is about 12.9 kcal/mol more stable than the D_{3h} structure, which is in agreement with the experimental estimate of the activation energy of the bridging–terminal carbonyl exchange process.

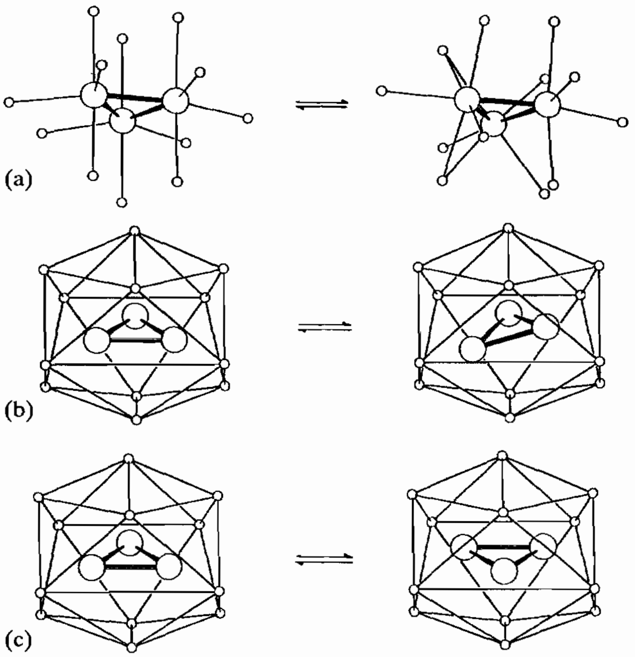


Fig. 1. Three possible mechanisms for the carbonyl exchange process in $Fe_3(CO)_{12}$: (a) Cotton, (b) Johnson, (c) Hanson.

Figure 1 shows three schemes (a)–(c) corresponding to the carbonyl exchange mechanisms in $Fe_3(CO)_{12}$ proposed by Cotton, Johnson and Hanson, respectively, where CO groups are represented as small circles for the sake of clarity. For Cotton's mechanism (a), we use a linear interpolation between C_{2v} and D_{3h} geometries to create an approximate reaction path, and the energies along this path are calculated. Because Johnson's mechanism can be used to account for the carbonyl exchange procedure in solid state, in which the shell of oxygen atoms is kept fixed due to the large packing effect, we shall consider such factor in the calculation. In (b) the slightly distorted icosahedron of the oxygen atoms is regarded as fixed and only the libration of the Fe_3 triangle about the two-fold axis from 0 to 20° is taken as reaction coordinate. However, due to the flexibility of M–C–O angles, the relaxation of the carbon shell within the oxygen icosahedron is not neglected. Therefore, in every point along this reaction pathway, coordinates pertinent to the carbon atoms will be optimized, which decreases the energy barrier for this pathway to a rather large extent. In order to discuss the validity of the model in solution and solid state in Hanson's mechanism (c), the oxygen shell will be treated both as rigid and non-rigid. As a model in solid state, we keep at first the oxygen shell fixed and relax the carbon atoms during the rotation of the Fe_3 ring about the pseudo three-fold axis by 60°. As a solution model, breathing of the oxygen shell accompanied by the rotation of the Fe_3 ring is considered. This means, the oxygen atoms are allowed to stretch in some special directions.

Results and discussion

Electronic structure of $Fe_3(CO)_{12}$

According to the electron counting method of organometallic compounds, $Fe_3(CO)_{12}$ should have the same electron assignment in both C_{2v} and D_{3h} structures, since the carbonyl ligand is regarded as a two-electron donating ligand in terminal and bridging situations. In order to obtain the 18-electron shell for the Fe atom, it is necessary to recognize the formal Fe–Fe bond between Fe atoms, even for those which are linked through bridging carbonyl ligands. However, it has been pointed out that in the case where metal atoms are bound via the bridging ligands, the occurrence of metal–metal bonds between such metal atoms is very questionable. From a charge density analysis of *ab initio* calculations it was concluded that there are no direct metal–metal bonds in $Fe_2(CO)_9$ and $Co_2(CO)_8$ [26, 27]. Our valence analysis [22] for these molecules arrived at the same conclusion. The bond valence for a pair of atoms is the exclusive contribution of all occupied molecular orbitals to the covalent bonding between these two atoms [25].

The calculated Fe–Fe and Fe–C bond valences both for C_{2v} and D_{3h} geometry $Fe_3(CO)_{12}$ are listed in Table 1. From this Table, it can be seen that the Fe–Fe bond valence in D_{3h} symmetry is 0.64, which confirms that there must be a direct Fe–Fe bond between each Fe atom pair. In C_{2v} geometry, the Fe–Fe bond valence between Fe atom pairs, which consists of the two edges of the Fe_3 triangle without bridging carbonyls, is 0.63, which indicates a normal Fe–Fe bond. But the Fe–Fe bond valence between the carbonyl bridged Fe atoms is much smaller, only 0.22. Accordingly, we may say that there is almost no direct Fe–Fe bond between these two Fe atoms although their distance is shorter than that of the other two Fe–Fe edges. Similar to the case in molecule $Co_2(CO)_9$ [27], the residual small Fe–Fe bond valence between these two Fe atoms may be attributed to the constructive interference of two Fe d_{yz} fragment orbitals which contribute very little to metal–metal bonding.

Comparison of Fe–C bond valence and its σ and π components for terminal and bridging carbonyl ligands reveals the different character of these two types of coordination although both of them donate two electrons to Fe atoms. For the bridging carbonyl ligands the Fe–C bond valence is 0.65 and the bond has almost pure σ character. However, for terminal carbonyl ligands, the Fe–C bond valence is 0.98 and its σ and π components are 0.72 and 0.26, respectively. This is in agreement with the prevalent σ-donor/π-acceptor picture of M–CO bonding in which the π interaction is rather important. Recently, Bauschlicher *et al.* have carried out a series of theoretical studies on the nature of M–CO bonding and they pointed out that the π donor contribution to such terminal carbonyl–metal bonding will play a more important, even dominant role if correlation is taken into account [28]. This means that the terminal M–CO bond has partially or dominantly π character.

TABLE 1. Bond valences of C_{2v} and D_{3h} structures of $Fe_3(CO)_{12}$

	V_{Fe-Fe}	V^{σ}_{Fe-Fe}	V^{π}_{Fe-Fe}	V^{δ}_{Fe-Fe}	V_{Fe-C}	V^{σ}_{Fe-C}	V^{π}_{Fe-Fe}
D_{3h}	0.64	0.58	0.04	0.00	0.98	0.72	0.26
C_{2v}	0.63[a]	0.57	0.04	0.00	0.98(t)	0.72	0.26
	0.22[b]	0.17	0.04	0.00	0.65(b)	0.57	0.07

[a] Bond valence between Fe atom pairs which consist of the two edges of Fe_3 triangle without bridging carbonyls. [b] Bond valence between Fe atoms which are linked via bridging carbonyls.

Based on the above discussions, we may conclude two different points about the bonding pattern and electronic structure of $Fe_3(CO)_{12}$ in C_{2v} and D_{3h} symmetries. First, there is one more direct Fe–Fe bond in D_{3h} symmetry than in C_{2v} symmetry. Second, the C_{2v} structure possesses two bridging M–CO bonds which have σ character and do not exist in D_{3h} geometry. We believe that such differences are electronic in origin and are the reason for the different structure of $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$. Recalling the different properties of 3d and 5d orbitals of Fe and Os atom, it can be said that the contracted 3d orbital of Fe atom is less favorable to M–M bonding overlap and π interactions, but is effective to accept the σ coordination of the bridging carbonyl ligand. Hence the C_{2v} symmetry with bridging carbonyls and less M–M bond is suitable for $Fe_3(CO)_{12}$. In contrast, the diffuse 5d orbitals in Os are preferable for direct M–M bonding and a π interaction with terminal carbonyl ligands. Therefore, $Os_3(CO)_{12}$ will adopt D_{3h} symmetry with more M–M bonding and terminal M–CO bonds. Evans noticed the same argument by a molecular fragment approach and isolobal analogy analysis [12].

TABLE 2. Relative energies (kcal/mol) of three carbonyl exchange schemes for $Fe_3(CO)_{12}$ along the reaction coordinate *RC*

(a)		(b)		(c)		
RC	ΔE	*RC* (°)	ΔE	*RC* (°)	ΔE[a]	ΔE[b]
1 (C_{2v})	0.0	0	0.0	0	0.0	0.0
2	−4.1	2	3.5	6	14.1	17.4
3	−14.6	4	8.6	12	40.0	47.8
4	−8.1	6	13.5	18	78.0	97.1
5	−4.2	8	22.7	24	103.1	134.0
6	−2.0	10	33.9	30	164.1	209.7
7	0.3	12	42.4	36	107.9	138.8
8	2.9	14	63.2	42	83.4	101.2
9	4.7	16	88.7	48	43.1	52.4
10	7.3	18	111.5	54	14.9	19.6
11 (D_{3h})	13.9	20	141.7	60	0.0	0.0

[a] Non-rigid oxygen shell. [b] Rigid oxygen shell.

Energy profiles of carbonyl fluxional processes

The calculated energies along the approximate reaction pathways for three possible CO exchange mechanisms are shown in Table 2 and Fig. 2. At first glance, it can be seen that (a) has the lowest energy barrier. The energy barrier for a $C_{2v} \rightarrow D_{3h} \rightarrow C_{2v}$ process is only about 14 kcal/mol, which is comparable to the experimentally estimated activation energy of about 10 kcal/mol for this carbonyl exchange process. For the energy curve of this process a minimum is not located at the C_{2v} structure, rather at a point during the transformation from C_{2v} symmetry to D_{3h} symmetry and near the C_{2v} side, which corresponds to an asymmetrical carbonyl bridging structure. Such an asymmetrical structure is about 15 kcal/mol more stable than the symmetric bridging structure. There should be a corresponding minimum in the back transformation from D_{3h} symmetry to C_{2v} symmetry, which results in another asymmetrical bridging structure. This result is in agreement with the molecular structure of $Fe_3(CO)_{12}$ determined by Wei and Dahl [29] and refined by Cotton and Troup [14], which demonstrated the presence of an inversion center within the unit cell, relating two crystallographic 'half molecules' with two orientations. If we take the energy difference between such an asymmetrical bridging structure and a D_{3h} structure as the energy barrier of carbonyl exchange, it seems that the energy barrier is overestimated. However, the relative comparison to other pathways suggests that Cotton's mechanism (a) is the most probable one in solution, but not so preferential in solid state because the scrambling of carbonyls from C_{2v} symmetry to D_{3h} symmetry will cause a dramatic change in the oxygen shell and will result in a large steric packing effect.

As for the ligand exchange process in solid state, the calculated energy barrier suggests that Johnson's mechanism (b) is very likely. From Fig. 2, it can be seen that the energy change is very small with small angle librations of a few degrees. From the optimized Fe–C distances, we can estimate that it is sufficient to change bridging carbonyl ligands to terminal carbonyl ligands and the energy barrier is about 43 kcal/mol, when the Fe_3 ring librates from its equilibrium position about 12°. If the Fe_3 ring undergoes a further libration, the energy will rise dramatically due to the large repulsion of carbonyl ligands. Although we believe that our energy barrier is somewhat overestimated, it seems that such a process is possible in solid state. In this process, the oxygen shell is completely kept fixed, which does not add any steric packing effect in the process. The experimental support to this mechanism came from the thermal ellipsoids for Fe atoms in crystallographic structure studies of this molecule.

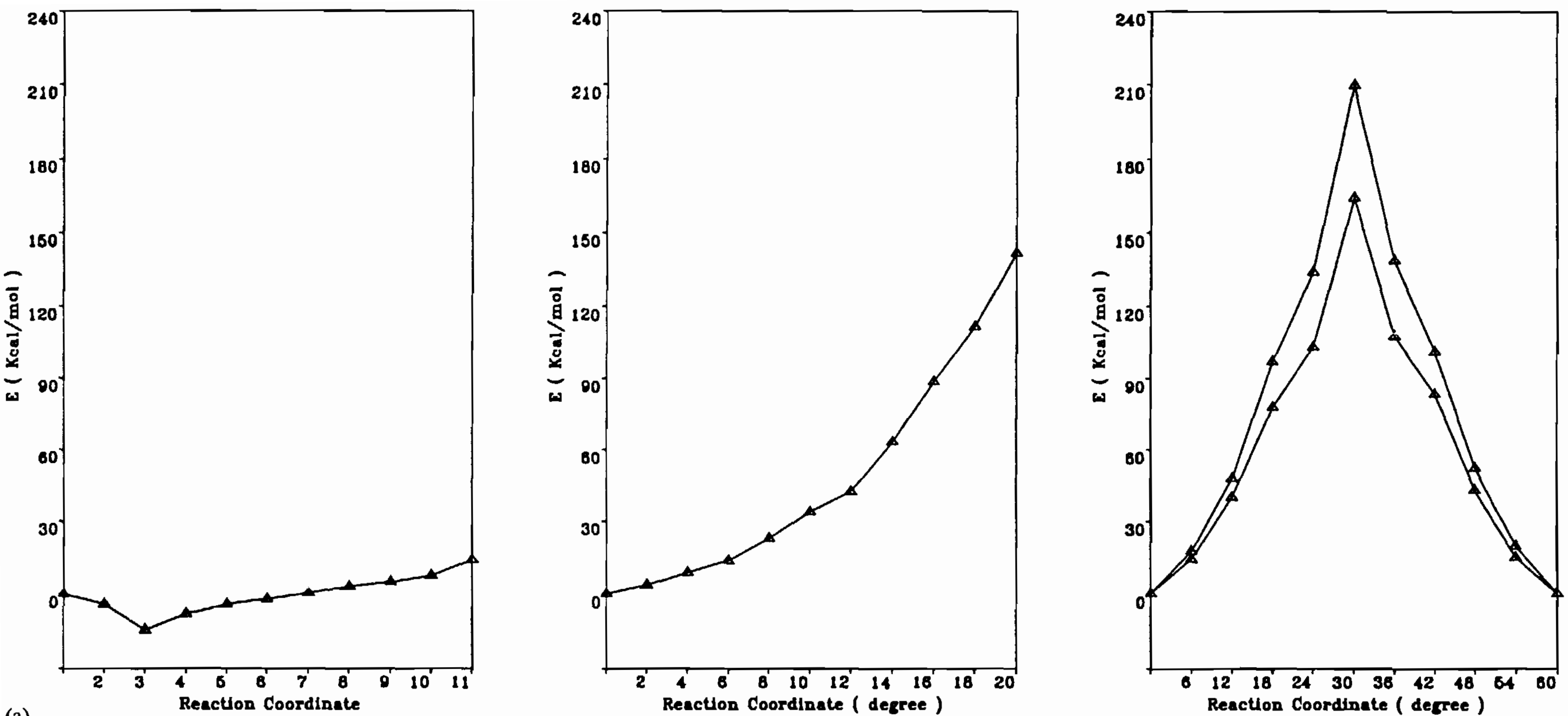
The calculated energies show that Hanson's mechanism (c) has a high energy barrier. Both for a rigid and non-rigid oxygen shell, the energy barrier for rotation of the Fe_3 ring by 60° within the oxygen shell is higher than 150 kcal/mol. The maxima of energy curves are located at the half-rotated configuration, i.e. for a rotation of the Fe_3 ring by 30° about the pseudo three-fold axis. At this point, some Fe–C distances are dramatically shortened and some are lengthened although the relaxation of carbonyl orientation has been taken into account. The shortest Fe–C distance is about 1.4 Å and the longest above 2.1 Å, which is not a small change compared to the equilibrium bond length of 1.82 Å. It has been estimated that an expansion of the M–C bond by 0.03 Å requires 1.8 kcal/mol energy [7]. Therefore, such dramatic changes of the M–C bond length in this process are energetically not favorable. Otherwise, it seems that a 60° rotation of a rigid Fe_3 ring within the $(CO)_{12}$ distorted icosahedron shell is too much for a thermal atomic motion in molecular systems. In addition, the $(CO)_{12}$ shell is not an ideal icosahedron, the breathing of the CO shell accompanied by the rotation of the Fe_3 ring will add the extra packing effect in the carbonyl exchange process.

Valence changes along the carbonyl fluxional processes

The bond valence is an index which measures the magnitude and strength of chemical bond in a molecular system. Hence, the change of bond valence along a chemical process will reflect the features of bond-breaking and bond-forming in this process. We expect that a feasible chemical process should change the total bond valence as little as possible and move in the direction of increasing total bond valence. Figure 3 shows how the bond valence changes for the above-mentioned three carbonyl fluxional schemes. The $V_{\mathrm{Fe-Fe}}$ is an average over three Fe–Fe bond valences and $V_{\mathrm{Fe-C}}$ is the average over all Fe–C bonds. From Fig. 3, it can be seen that the valence change in (b) is the smallest while the change in scheme (c) is rather dramatic. In (a) and (b), the bonding character of the Fe–Fe and Fe–C bonds in $Fe_3(CO)_{12}$ is retained. This means, the Fe–Fe and Fe–C bonds do not change much. However, in (c) too many Fe–C bonds will be involved in bond-breaking and bond-forming and even the Fe–Fe bonds are weakened. This is another reason why (c) is a process with a high energy barrier and cannot be realized both in solid state and in solution.

Conclusions

By examining the relative energy barriers for the three schemes of the carbonyl exchange process in $Fe_3(CO)_{12}$, we were able to show that the carbonyl



(a)

(b)

(c)

Fig. 2. Energy profiles for the carbonyl exchange process in $Fe_3(CO)_{12}$.

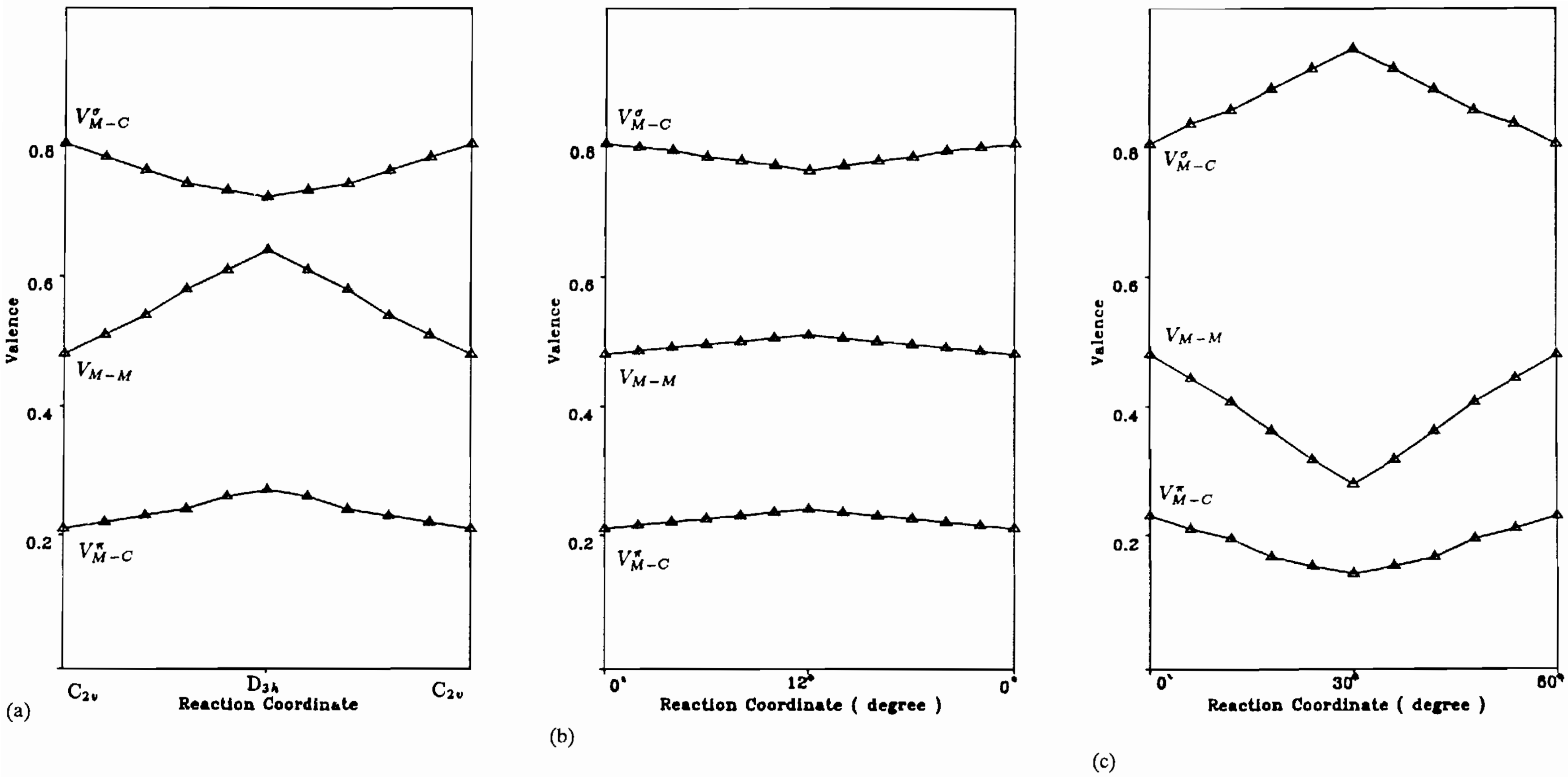


Fig. 3. Valence changes in the carbonyl exchange process.

bridge closing–opening mechanism is the lowest energy process. It seems that such a mechanism is suitable for the carbonyl exchange in solution. For solid state, the mechanism proposed by Johnson is most reasonable both for energetic and steric reasons. Hanson's mechanism involves too much bond-breaking and bond-forming and the structural changes are another limitation. The valence change along such a pathway provides a direct way of insight into the change of bonding character of the molecular system and may be used to rationalize the most probable mechanism. Fe–Fe and Fe–C bond valences and their σ and π components in C_{2v} and D_{3h} geometries of $Fe_3(CO)_{12}$ describe the different bonding character in these two isomers. The calculations reveal the electronic origin, as a supplement to the steric origin, of the two different ligand geometries in $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$.

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