



Insights into the coordination chemistry of alkanes to metal carbonyls from quantum chemical calculations



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This theoretical work is dedicated in memory of Professor A.E. Shilov for his important contributions to the fundamental aspects of the coordination chemistry and C–H bond activation of alkanes

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ABSTRACT

In this work DFT and CCSD(T) calculations were carried out to study the structure, energetic of the interactions, IR, UV/Vis spectra and the nature of the interactions related to Metal–fluoroalkane complexes of the type $M(\text{CO})_5(\text{CH}_3\text{F})$ [$M = \text{Cr}, \text{Mo}$ and W]. All possible coordination modes of the CH_3F molecule to the metallic fragments were attempted, however, only the η^1 mode through the hydrogen or fluorine atoms is obtained. The computed DFT vibrational frequencies showed that upon coordination the $\nu(\text{C}-\text{H})_{\text{asym}}$ and $\nu(\text{C}-\text{F})_{\text{asym}}$ modes have pronounced red shifts compared with the free fluoroalkane, and thus may be an important way to characterize and follow the alkane/fluoroalkane coordination to the metallic fragment. TD-DFT calculations of the electronic transitions show that, compared with the free metallic fragments, CH_3F coordination affects drastically the MLCT band, showing a maximum blue shift of 201 nm for the $[\text{W}(\text{CO})_5(\text{CH}_3\text{F})]-\eta^1\text{F}$ complex. Comparison with CCSD(T) energies shows that the B3LYP-D2 and BP86-D2 methods provide an accurate description of the energetic involved in metal–fluoroalkane complexes investigated.

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Introduction

The C–H activation and selective functionalization of saturated hydrocarbons by transition metal compounds at mild conditions is presently an exciting and challenging topic of research in chemistry, mainly due to the industrial importance and potential of this chemical process when alkane molecules are involved [1–3]. However, despite the considerable progress made in this research field, some fundamental questions are still open. One of the most fundamental questions regarding the C–H bond activation chemistry by transition metal complexes is related to the understanding of how alkanes molecules can coordinate to metallic centers [4,5]. From the basic inorganic chemistry point of view, the existence of the so-called metal–alkane σ -complexes is an intriguing fact because alkanes do not have any of the properties associated with

“good ligands” [5,6]. As example of good ligands we can cite carbon monoxide and olefins, which have orbitals of appropriate symmetry and energy available to donate and accept electron density of a given metallic center. In the case of alkanes, the $\sigma(\text{C}-\text{H})$ bond is strong ($\sim 100 \text{ kcal mol}^{-1}$) and nonpolar. In addition, the energies of the frontier molecular orbitals do not favor the donation and acceptance of electron density.

Fig. 1 illustrates these trends, showing an energetic comparison between the frontier molecular orbitals of methane, ammonia and carbon monoxide. As can be seen in Fig. 1, the HOMO energy of methane is considerably lower than calculated for NH_3 that is a Lewis base, with its electron lone pair mainly localized in HOMO orbital. Hence, the great stability of HOMO orbital of CH_4 characterizes it as a weak σ donor. The main characteristic that makes CO a special ligand in organometallic chemistry is its ability to accept electron density in its π^* orbitals and, due to this feature, CO can interact with different metallic centers generating stable complexes. According to Fig. 1, the LUMO of CH_4 is located considerably higher in energy than the observed in the good π -acceptor ligand

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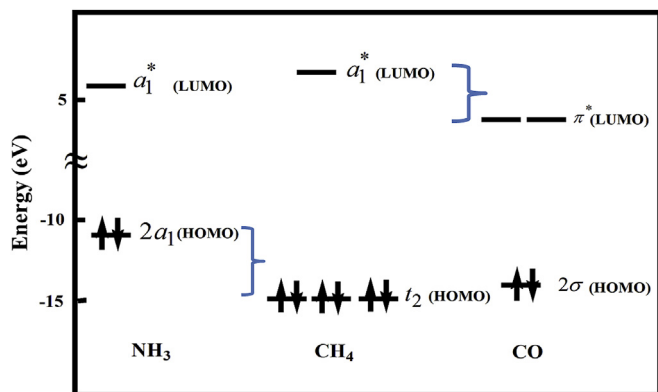


Fig. 1. Comparison of the energies involved in the frontier molecular orbitals of CH₄, CO and NH₃ molecules. The energies were computed at the MP2/6–31G(d,p) level of theory.

CO. Therefore, the direct coordination of an alkane molecule to a given transition metal complex would be unlikely. However, pioneering works of Shilov et al. [7] and also by Perutz and co-workers [8] showed, respectively that platinum tetrachloride in acidic solution and metal carbonyls of the type M(CO)₆ (M = Cr, Mo and W) in alkane matrix, can form σ -alkane complexes and thereafter catalyze the activation of C–H bond of alkanes. The work of Shilov and co-workers [7] represents a milestone in the organometallic chemistry related to the activation and functionalization of saturated hydrocarbons, and is still inspiring the development of more efficient catalytic systems for selective activation of alkanes [9–11].

Nowadays, a considerable number of organometallic compounds are known to be capable of reacting with alkanes and activate the C–H bond [12–14]. However, independent of the kind of research conducted in the field of activation of alkanes by transition metal compounds it is of fundamental importance the understanding of how the coordination of the alkane molecule to the metallic center takes place. The detailed description of this interaction is crucial for a full understanding of the different mechanisms by which the metallic centers activate the C–H bond of alkanes. Fig. 2 illustrates the possible coordination modes of alkanes to metallic centers.

Studies using time-resolved infrared and nuclear magnetic resonance spectroscopies [15,16] have shown that the magnitude of the interaction energies in these organometallic complexes is in the range of 7–11 kcal mol⁻¹, which characterize it as a weak interaction. Mainly due to this low stability, the structural elucidation of these so-called σ -alkane metal complexes still represents an experimental challenge. An alternative approach to get insights into the coordination modes of alkanes to metallic complexes is to study this coordination using fluoroalkanes instead of alkanes [5]. The main idea is to perform spectroscopic (IR and UV/vis) measurements and to obtain energetic properties of the σ -fluoroalkane metal complex and compare the results with those obtained using alkanes. Due to the well-known vibrational behavior of CO ligand in

metal carbonyls of the type M(CO)₅ (M = Cr, Mo and W), these molecular systems are attractive to investigate the possible coordination modes of alkanes. Based on this fact, Rayner and co-workers [15] investigated the reaction between the W(CO)₅ fragment and a variety of fluoroalkanes, and concluded that the coordination of the substrates should occur only via a C–H σ -bond. However, experiments performed by Perutz and co-workers [5] showed that the fluorine atom can also interact directly with the metallic centers. As observed in studies with metal carbonyls and alkanes, Perutz and co-workers [5] showed that the complexes formed with fluoroalkanes exhibited low stability, but with well-defined spectroscopic features.

There are some computational studies reported in the literature about the interaction between alkanes/fluoroalkanes with metal carbonyls of Cr, Mo and W [17–19], however despite providing valuable information about the thermodynamics of these systems, little attention has been given for the elucidation of the spectroscopic properties measured for some of these complexes. Following a similar methodology used in a previous work, where the nature of the interaction between alkanes and metallic carbonyls of the type M(CO)₅ (M = Cr, Mo and W) was investigated [20], we decided to extend this study to the coordination chemistry of fluoroalkanes to metal carbonyls.

In this work, quantum chemical calculations were carried out to investigate the energetics, nature of the interactions and electronic and vibrational spectral characteristics involved in the coordination of fluoromethane to metallic carbonyls, forming complexes of the type M(CO)₅(CH₃F) (M = Cr, Mo and W). The traditional B3LYP [21,22] and BP86 [23–25] functionals with inclusion of dispersion effects were used to evaluate the capability of the DFT-D to describe the weak interactions in these complexes. The nature of Metal–Fluoroalkane interaction was explored using the EDA approach formulated by Su and Li [26]. The effects of the fluoroalkane coordination on the UV/vis and IR spectra of the metallic fragments were also evaluated.

We dedicate this theoretical work in memory of Professor A. E. Shilov for his important contributions to the fundamental aspects of the coordination chemistry and C–H bond activation of alkanes.

Computational details

Full unconstrained geometry optimizations and frequency calculations for the metallic fragments M(CO)₅ and the σ -complexes M(CO)₅CH₃F (M = Cr, Mo e W) were carried out using pure and hybrid exchange-correlation gradient corrected functionals. The pure functional uses the exchange functional of Becke [23], B, in conjunction with the correlation functional suggested by Perdew [24,25], P86. The hybrid functional uses the three parameters fit of the exchange-correlation potential suggested by Becke [22], B3, in conjunction with correlation functional of Lee, Yang and Parr [21], B3LYP. Dispersion effects were included through D2 correction proposed by Grimme [27]. The reason for using these two exchange-correlation functionals was based on previous experiences on treating metal–alkane complexes [20,28].

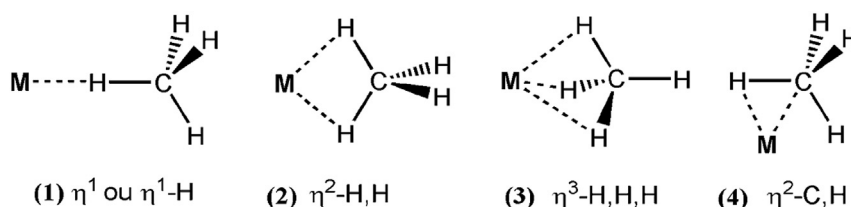


Fig. 2. Schematic representation of the possible coordination modes of an alkane to a metallic center M.

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