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ARTICLE in CHEMICAL PHYSICS LETTERS · JANUARY 2006

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A multi state-CASPT2 vs. TD-DFT study of the electronic excited states of $\text{RCo}(\text{CO})_4$ ($\text{R} = \text{H}, \text{CH}_3$) organometallic complexes

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Received 18 August 2005; in final form 10 October 2005

Available online 8 November 2005

Abstract

The electronic spectroscopy of $\text{RCo}(\text{CO})_4$ ($\text{R} = \text{H}, \text{CH}_3$) has been investigated by means of MS-CASPT2/CASSCF and TD-DFT calculations. The UV energy domain of the absorption spectrum is dominated by a series of low-lying ^1E metal-to-sigma-bond-charge-transfer (MSBCT) and ^1E and $^1\text{A}_1$ metal-to-ligand-charge-transfer (MLCT) allowed transitions corresponding to $3\text{d}_{\text{Co}} \rightarrow \sigma_{\text{Co-R}}^*$ and $3\text{d}_{\text{Co}} \rightarrow \pi_{\text{CO}}^*$ excitations, respectively, slightly red shifted (by ca. 1800 cm^{-1}) in the methyl substituted complex. TD-DFT underestimates the transition energies calculated by MS-CASPT2 by more than 0.5 eV and predicts some of the MLCT states to be intercalated between the two low-lying MSBCT states.

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1. Introduction

Irradiation of organometallics in the UV/vis energy domain is one method for obtaining unsaturated intermediates, which are used in subsequent catalytic processes. One of the most extensively studied of these processes involves the ultra-fast dissociation of a carbonyl ligand. This primary reaction may compete with the homolysis of a metal–metal bond ($\text{Mn}_2(\text{CO})_{10}$) [1], metal–alkyl bond ($\text{RMn}(\text{CO})_3(\alpha\text{-diimine})$, $\text{R} = \text{methyl, ethyl, benzyl}$) [2], metal–methyl bond ($\text{MeMn}(\text{CO})_5$) [3] $\text{MeCo}(\text{CO})_4$ [4] or metal–hydrogen bond ($\text{HCo}(\text{CO})_4$, $\text{HMn}(\text{CO})_5$) [5]. Despite the number of experimental and theoretical studies dedicated to this class of compounds a detailed knowledge of their electronic spectroscopy and photoreactivity is still scarce. The ground state properties and reactivity of $\text{RCo}(\text{CO})_4$ and $\text{RMn}(\text{CO})_5$ ($\text{R} = \text{H}, \text{CH}_3$) have been extensively studied by means of density functional theory (DFT) [6,7] while the electronic spectroscopy, photochemistry, and quantum dynamics of $\text{HCo}(\text{CO})_4$ and $\text{HMn}(\text{CO})_5$ have

been investigated by accurate ab initio methods supplemented by wave packet dynamics [8–10]. Until now, only the two-dimensional potential energy surfaces (PES) along the Co–H and Co–CO_{axial} bond elongations have been calculated for $\text{HCo}(\text{CO})_4$, including the ^1E state ($3\text{d}_{\text{Co}} \rightarrow \sigma_{\text{Co-H}}^*$) and the $^3\text{A}_1$ ($\sigma_{\text{Co-H}} \rightarrow \sigma_{\text{Co-H}}^*$) states in the wave packet simulations (the $\sigma_{\text{Co-H}}$ and $\sigma_{\text{Co-H}}^*$ orbitals correspond to the sigma bonding and anti-bonding combinations between the cobalt 3d_z^2 and the hydrogen s orbitals) [8,9]. This limitation was, on the one hand, due to the restrictions in the choice of the complete active space self consistent field [11] (CASSCF) characteristics, and on the other hand, due to the lack of alternative methods based on the configuration interaction (CI) which take into account additional electronic correlation effects. Based on this pioneering study [9], it was shown that the photolysis of the cobalt–hydrogen bond occurs after absorption to the ^1E state, which is the responsible for the partial ultra-fast dissociation of $\text{HCo}(\text{CO})_4$ into $\text{H}^\bullet + \text{Co}(\text{CO})_4^\bullet$ (35% within 20 fs), while the rest of the population is transferred via intersystem crossing within 50 ps to the $^3\text{A}_1$ state, from where it dissociates into the diradicals $\text{H}^\bullet + \text{Co}(\text{CO})_4^\bullet$. This was probably the most complete study on the photodissociation dynamics of organometallics. However, in contrast

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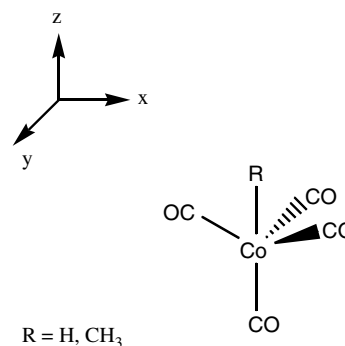
to what is observed in low-temperature matrix experiments [4] (CO loss and homolysis of the Co–H bond with an 8–1 branching ratio, respectively) no CO loss was confirmed by the dynamical simulations. This discrepancy may only be apparent due to matrices cage effects which may reverse the damage of homolysis. The main approximations made during the course of this theoretical study concerned the dimensionality of the problem which comprises two aspects: (i) the nuclear coordinates and (ii) the electronic coordinates. As far as the PES are concerned, only two nuclear coordinates were taken into account: the H– and CO–metal dissociation, as previously explained. More recently, the umbrella motion of the equatorial carbonyls [12] has also been included in the study, but it does not seem to modify significantly the main conclusions [13]. The other limitation is the small number of electronic states which were included in the simulation, namely: the 1A_1 ground state, together with the 1E and 3A_1 electronic excited states. Currently, CASSCF wave functions built on a large active space and supplemented by Multi State CAS Perturbation second-order (MS-CASPT2) [14] calculations, which also take into account dynamical electronic correlation effects, can be handled to obtain accurate transition energies and associated oscillator strengths for a dozen of electronic excited states. Moreover, new developments of DFT within the framework of the linear response theory, the so-called Time Dependent DFT (TD-DFT), have enabled for the calculation of several tens of states with a very small effort (a few hours) in comparison to the months of preliminary work necessary for accurate ab initio spectroscopy [15].

The aim of the present Letter is twofold: (i) to present a more extended investigation of the electronic spectrum of $HCo(CO)_4$ by means of TD-DFT and MS-CASPT2 approaches into the perspective of revisiting the quantum dynamics and (ii) to compare its electronic spectroscopy to that of the analog $CH_3Co(CO)_4$, which in principle could be a more suitable molecular model system for experimentalists working in the field of femtosecond laser control spectroscopy [16].

2. Computational details

The electronic calculations for the $RCo(CO)_4$ organometallic complexes have been performed in C_s under the C_{3v} symmetry constraint. For $HCo(CO)_4$ the experimental structure [17] was employed; for $CH_3Co(CO)_4$ there is no experimental information, thus the geometry was previously optimized within C_s symmetry at DFT (B3LYP) level of theory. The complexes show a distorted trigonal bipyramidal structure C_{3v} , where one CO and the H or CH_3 are in the axial locations and the other three carbonyls groups are at equatorial positions (see Scheme 1).

The electronic configuration of $RCo(CO)_4$ ($R = H, CH_3$) in its 1A_1 ground state is described by the following orbitals occupancies (σ_{Co-R})² ($3d_{\pi}$)⁴ ($3d_{\delta}$)⁴, the σ_{Co-R} bonding orbital being of a_1 symmetry and the $3d_{\pi}$ (d_{xz} , d_{yz}) and



Scheme 1. Idealized structure of $RCo(CO)_4$ ($R = H, CH_3$).

$d_{\delta}(d_{x^2-y^2}, d_{xy})$ of e symmetry with the C_{3v} axis taken as O_z according to Scheme 1. The low-lying vacant orbitals correspond to the σ_{Co-R}^* and π_{CO}^* anti-bonding orbitals. In order to describe the electronic spectroscopy the CASSCF active space has to include the 3d occupied orbitals of the Co, the σ and σ^* orbitals localized on the Co–R sigma bond and some of the low-lying π_{CO}^* . Additional orbitals assuring a good description of non-dynamical correlation effects have also to be included in the active space. For the hydride complex 16 active electrons have been correlated into 13 active orbitals whereas in the methyl substituted molecule 16 active electrons have been correlated into 14 orbitals. The following atomic natural orbitals (ANO-small) basis sets [18] have been used for both complexes: a (17s, 12p, 9d, 4f) contracted to [6s, 4p, 3d, 2f] for the cobalt atom, a (10s, 6p, 3d) contracted to [3s, 2p, 1d] for the C and O atoms and a (7s, 3p) contracted to [2s, 1p] for the hydrogen atom. The additional dynamical electronic correlation effects have been taken into account by means of MS-CASPT2 calculations with level shifts [19] (0.3–0.4) in order to avoid intruder states. The CASSCF/MS-CASPT2 calculations have been performed with the MOLCAS 6.0 package [20].

The TD-DFT calculations have been performed with GAUSSIAN 03 software [21] and the B3LYP functional [22] and the 6-31G(d) basis sets [23]. In order to validate the use of the DFT optimized geometry of $CH_3Co(CO)_4$, for which we have no experimental structure, the TD-DFT calculations have been performed either on the DFT optimized geometry or on the experimental structure of $HCo(CO)_4$.

The oscillator strengths f have been calculated using the CAS wavefunctions and the MS-CASPT2 energy. Because we are working in C_s symmetry – a subgroup of C_{3v} – degenerate states from $^1A'$ and $^1A''$ symmetry compose the 1E states, which have been paired averaging excitation energies and oscillator strengths. For both complexes a set of eight roots averaged for the A' symmetry and nine averaged states for the A'' symmetry have been used in the CASSCF and MS-CASPT2 calculations.

3. Results

The most important geometrical parameters of the two complexes optimized with DFT together with the available

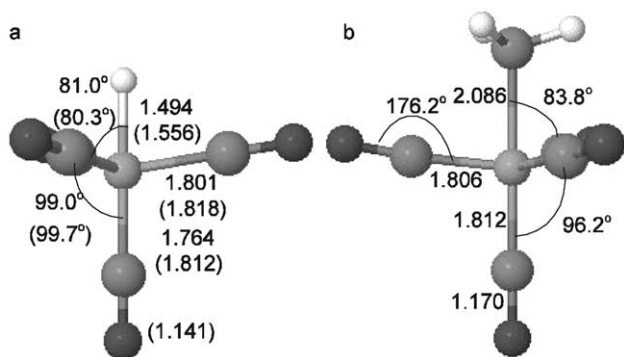


Fig. 1. Most relevant geometrical parameters of the complexes: (a) HCo(CO)₄ and (b) CH₃Co(CO)₄ optimized at B3LYP level of theory. The values in parenthesis correspond to the experimental structure [17]. The distances are in Å and angles in °.

experimental values are shown in Fig. 1. The comparison between the experimental and the DFT optimized structures of HCo(CO)₄ (cf. Fig. 1a) gives a reasonable agreement for the Co–H bond distance (1.556 vs. 1.494 Å) and the bond angles HCoC_{eq} (80.3° vs. 81°) and C_{ax}CoC_{eq} (99.7° vs. 99.0°). As expected, the observed difference between the Co–C_{eq} and Co–C_{ax} bond lengths is not well reproduced as it has been found in a number of transition metal carbonyls [6]. The optimized values of 1.812 Å for the Co–C_{ax} bond and of 1.801 Å for the Co–C_{eq} bond show an overestimate of the Co–CO axial bond (1.764 Å) and an underestimate of the Co–CO equatorial bond (1.818 Å). The O–C–Co angle has been considered 180° for all carbonyls. For the methyl substituted complex (cf. Fig. 1b) the metal–carbonyl bonds have been calculated at 1.806 Å (Co–C_{eq}) and 1.812 Å (Co–C_{ax}). These results agree rather well with those published by Ziegler et al. [6] using DFT (LDA) calculations. The Co–CH₃ bond distance has been optimized to 2.086 Å in agreement with the calculated value of 2.080 Å by Ziegler et al. [6]. The Co–CH₃ calculated value differs from the Co–H by 0.592 Å. This differ-

ence is consistent with the difference found for RCo(CO)₄ (0.609 Å) and RMn(CO)₅ (0.611 Å) [6]. A value of 96.19° has been obtained for the C_{ax}CoC_{eq} bond angle in CH₃Co(CO)₄ as opposed to the calculated value of 94.4° of [6]. The angle of the pseudo-linear Co–CO fragment is calculated to be 176.2°, to be compared with the value of 178.7° computed by Ziegler et al. [6].

The main difference between the two substituted complexes RCo(CO)₄ with R = H and CH₃, is the metal–R bond distance which is much shorter in the hydride compound. Besides the smaller size of the hydrogen atom, the long bond is related to the weakening of metal–alkyl bonds by a two-orbital, four-electron repulsive interaction which can not occur in the hydride [24]. The consequence on the absorption spectrum will be the occurrence of electronic transitions corresponding to a $\sigma_{\text{Co-CH}_3} \rightarrow \pi_{\text{CO}}^*$ excitations in the far-UV domain of energy which are not present in the spectrum of HCo(CO)₄.

The MS-CASPT2 and TD-DFT transition energies for the low-lying MSBCT and MLCT states (¹A₁ and ¹E) of HCo(CO)₄ and CH₃Co(CO)₄ complexes are reported in Table 1 together with the associated oscillator strengths.

For HCo(CO)₄, TD-DFT transition energies and oscillator strengths are reported for the experimental structure as well as for the optimized DFT geometry, whereas the MS-CASPT2 transition energies are reported for the experimental structure only. For CH₃Co(CO)₄ the ab initio and TD-DFT excited states calculations have been performed on the DFT optimized geometry.

The experimental information on the electronic spectroscopy of this class of transition metal carbonyl is usually scarce. Both complexes absorb at 254 nm (or 39 370 cm^{−1}) [4,5], the band for HCo(CO)₄ starting at 34 000 cm^{−1}. The absorption spectrum of this hydrido complex is characterized by an intense band at 44 000 cm^{−1} [5]. The theoretical absorption spectra of the methyl and hydrido complexes are very similar with an absorption starting at about

Table 1

CASSCF/MS-CASPT2 and TD-DFT transition energies ΔE (in cm^{−1}) of the low-lying electronic states of RCo(CO)₄ (R = H, CH₃) and associated oscillator strengths f

State	Main configuration	MS-CASPT2		TD-DFT ^A		TD-DFT ^B	
		ΔE	f	ΔE	f	ΔE	f
<i>R = H</i>							
a ¹ A ₁ → a ¹ E	3d _δ → σ _{Co-R} [*]	35 740	0.0013	30 860	~0.0	30 560	~0.0
a ¹ A ₁ → b ¹ E	3d _π → σ _{Co-R} [*]	40 280	0.0013	37 580	0.0012	36 900	0.0016
a ¹ A ₁ → c ¹ E	3d _δ → π _{CO} [*]	41 320	0.04	35 150	0.0056	34 400	0.002
a ¹ A ₁ → b ¹ A ₁	3d _δ → π _{CO} [*]	42 040	0.08	36 410	0.0233	35 900	0.028
a ¹ A ₁ → d ¹ E	3d _δ → π _{CO} [*]	44 190	0.08	38 945	0.0360	38 100	0.0326
a ¹ A ₁ → e ¹ E	3d _π → π _{CO} [*]	49 900	0.04	43 280	0.0002		
<i>R = CH₃</i>							
a ¹ A ₁ → a ¹ E	3d _δ → σ _{Co-R} [*]	33 980	0.0024	29 345	0.0009		
a ¹ A ₁ → b ¹ E	3d _π → σ _{Co-R} [*]	38 390	0.0032	34 650	0.0008		
a ¹ A ₁ → c ¹ E	3d _δ → π _{CO} [*]	40 720	0.0178	33 120	0.0029		
a ¹ A ₁ → b ¹ A ₁	3d _δ → π _{CO} [*]	42 340	0.0140	34 740	0.0158		
a ¹ A ₁ → d ¹ E	3d _π → π _{CO} [*]	48 200	0.0364	37 790	0.024		
a ¹ A ₁ → e ¹ E	σ _{Co-Me} → π _{CO} [*]	52 290	0.0200	45 750	0.0676		

^A TD-DFT performed on the experimental structure of HCo(CO)₄.

^B TD-DFT performed on the DFT optimized geometry of HCo(CO)₄.

35 000 cm^{-1} ($\text{HCo}(\text{CO})_4$) and 34 000 cm^{-1} ($\text{CH}_3\text{Co}(\text{CO})_4$). Four low-lying states calculated between 35 740 and 42 040 cm^{-1} ($\text{HCo}(\text{CO})_4$) and 33 980 and 42 340 cm^{-1} ($\text{CH}_3\text{Co}(\text{CO})_4$) contribute to the first band with a maximum observed at about 40 000 cm^{-1} , namely the $a^1\text{E}$, $b^1\text{E}$ states corresponding to Metal-to-Sigma-Bond-Charge-Transfer (MSBCT) excitations ($3d_{\text{Co}} \rightarrow \sigma_{\text{Co-R}}^*$) and the $b^1\text{A}_1$ and $c^1\text{E}$ states corresponding to Metal-to-Ligand-Charge-Transfer (MLCT) excitations ($3d_{\text{Co}} \rightarrow \pi_{\text{CO}}^*$). According to the calculated oscillator strengths the major contribution originates from the MLCT states. The far-UV domain of the spectrum is characterized by strong absorption which corresponds to two ^1E MLCT states ($d^1\text{E}$ and $e^1\text{E}$). The $d^1\text{E}$ of $\text{HCo}(\text{CO})_4$ with an oscillator strength of 0.08 should be responsible for the intense band observed at 44 000 cm^{-1} [5]. This band is shifted to higher energies in the methyl derivative at 48 000 cm^{-1} . At around 50 000 cm^{-1} the $\text{CH}_3\text{Co}(\text{CO})_4$ compound shows a peak of intermediate strength corresponding to a Sigma-Bond-to-Ligand-Charge-Transfer (SBLCT) state ($\sigma_{\text{Co-Me}} \rightarrow \pi_{\text{CO}}^*$), while in its hydride counterpart it is replaced by a MLCT state appearing at lower energies (48 000 cm^{-1}).

The TD-DFT excitation energies and oscillator strengths obtained for the experimental geometry of $\text{HCo}(\text{CO})_4$ and for the one optimized with DFT agree reasonably, validating the use of the DFT in the obtention of geometries for these complexes. The assignment of the states in the TD-DFT spectrum of both complexes, however, differs significantly from the *ab initio* one. The relative positions of the $b^1\text{E}$ and $c^1\text{E}/b^1\text{A}_1$ MLCT states are modified. As seen in Table 1, TD-DFT predicts two and one MLCT states intercalated between the lowest MSBCT states of the $\text{HCo}(\text{CO})_4$ and $\text{CH}_3\text{Co}(\text{CO})_4$ spectra, respectively. Moreover the transition energies are underestimated by more than 0.5 eV. This discrepancy could be due to the use of a standard B3LYP functional which could treat differently the MLCT states and the MSBCT states. Additionally, the B3LYP functional is also limited due to its incorrect asymptotic behavior, which is known to underestimate transition energies in atoms and clusters [25]. The underestimation of TD-DFT transition energies has been also observed in a number of transition metal complexes as illustrated by the examples reported in [15].

4. Conclusion

The electronic absorption spectra of $\text{HCo}(\text{CO})_4$ and $\text{CH}_3\text{Co}(\text{CO})_4$ have been investigated by means of CASSCF/MS-CASPT2 and TD-DFT calculations. Both complexes absorb in the UV (at ca. 35 000 cm^{-1}) with a strong band centered at 40 000 cm^{-1} . The *ab initio* calculations agree with the main experimental features showing three low-lying ^1E states (SBLCT and MLCT) and one $^1\text{A}_1$ state (MLCT) contributing to these bands. According to the calculated oscillator strengths the third ^1E state and the $b^1\text{A}_1$ state, both MLCT, contribute mainly to the absorption. The two low-lying ^1E SBLCT states should

be responsible for the photoreactivity of these two complexes. The photoreactivity of $\text{CH}_3\text{Co}(\text{CO})_4$ should not differ drastically from the one observed for the hydride analog. In order to study the ultra-fast photodissociation of these molecules PES have been calculated at the CASSCF level as a function of the Co–R bonds elongation and of the umbrella angle [13]. The preliminary simulation of the ^1E excited states dynamics seems to indicate an ultra-fast dissociation of the axial carbonyl ligand.

Acknowledgements

The PROCOPE bi-lateral Program No. 07579RB and the SFB 450 ‘Analysis and control of ultra-fast photoinduced reactions’ are gratefully acknowledged. The calculations have been performed either on the HP workstations of the Theoretische Chemie group at FU-Berlin, on the workstations of the LCQS (Strasbourg) or at the IDRIS national computer center (Orsay).

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