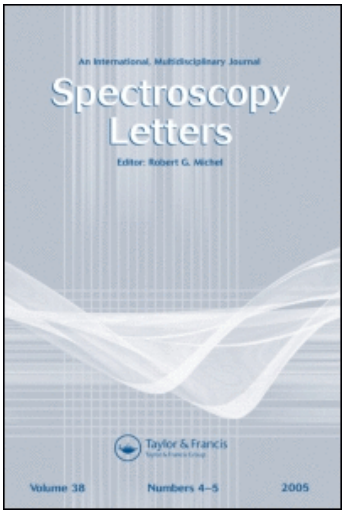

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Normal Coordinate Analysis of M-CH_3-Moieties in Transition Metal Complexes and Comparison to Results Obtained for Methylhalides

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NORMAL COORDINATE ANALYSIS OF M-CH_3-MOIETIES IN TRANSITION METAL COMPLEXES AND COMPARISON TO RESULTS OBTAINED FOR METHYLHALIDES

Keywords: Raman spectroscopy; Vibrational analysis; Normal coordinate analysis; Potential energy distribution; Methyl complexes.

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ABSTRACT

In order to examine the influence of the transition metal on the metal-methyl fragment M-CH_3 polarized Raman spectra of the complexes $Cp(CO)_2Fe$-CH_3 (1), $Cp(CO)_3W$-CH_3 (2), $Cp(CO)_2(PMe_3)W$-CH_3 (3) and O_3Re-CH_3 have been recorded. The spectral data were interpreted on the basis of a normal coordinate analysis of the M-CH_3-core and the derived force constants and potential energy distributions were compared to results obtained for analogous halogen derivatives in the series X-CH_3 [X = Br (5), I (6)].

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INTRODUCTION

The chemistry of M-EH_3-moieties (E = group IVA element) in transition metal complexes is well described in the literature with respect to carbon derivatives[1-2]. However, the vibrational behaviour of these groupings is not comprehensively reported. Vibrational studies are mainly concerned with the carbonyl ligands, mostly present at the transition metal. In the course of current work on the photochemistry of silyl-complexes it has become necessary to vibrationally characterize EH_3-groups bonded to transition metals by means of Raman spectroscopy and normal coordinate analyses. For the sake of completeness and for comparison purposes we first report spectra and force fields of the metal-methyl moieties of the complexes $Cp(CO)_2Fe\text{-}CH_3$ (1), $Cp(CO)_3W\text{-}CH_3$ (2), $Cp(CO)_2(PMe_3)W\text{-}CH_3$ (3), and $O_3Re\text{-}CH_3$ (4). Obtained force constants and potential energy distributions will be compared to the values of $X\text{-}CH_3$ molecules [X = Br (5), I (6)] in order to show differences resulting from the chemically different substituents. Valence force field calculations on silyl derivatives will be presented in a forthcoming paper.

EXPERIMENTAL

Raman spectra of 1 to 3 were excited with the 647 nm line of a krypton ion laser (Spectra Physics Model 2025). Spectra were recorded from benzene solutions filled in NMR-tubes. The scattered light was dispersed by means of a Spex model 1404 double monochromator and detected with a Photometrics-CCD-camera system (model RDS 2000)[3]. Force field calculations using modified versions of the program packages QCMP-067[4] and VIA[5] were used. Structural parameters of the complexes 1 - 4 were determined with the program package Autodesk HyperChem software (Version 3.0). Selected bond distances are: Fe-C, 1.94 Å; W-C (2), 2.07 Å; W-C (3), 2.075 Å; Br-C, 1.936 Å; I-C, 2.139 Å; C-H, 1.090-1.092 Å; selected bond angles: Fe-C-H, W-C-H, 1.09.47°; Br-C-H,

107.0°; I-C-H, 106.66°; H-C-H, average of all 109.5°. Data of the methyl halogenides 5 and 6 are taken from the literature[6-7]. The internal coordinates are defined in Fig. 1. Symbols s_1, s_2 denote stretching coordinates of C-M-, C-X-, and C-H-bonds, respectively, whereas α, β represent coordinates describing in-plane deformation motions. The methyl-complexes have been regarded as five-atomic species of ideally C_{3v}-symmetry.

Hence, nine normal modes of species 3 A_1 + 3 E are expected to arise, all Raman- and infrared-active. In order to sufficiently describe the vibrational dynamics of a M-CH_3 species *general-valence-force-fields* (GVFF) had to be created.

RESULTS

Experimental and calculated wavenumbers, together with the potential energy distribution for 1 to 3 and 4 to 6, are compiled in Tables 1 and 2, respectively. The corresponding force fields are listed in Table 3. The vibrational analysis of methyl groups bonded to transition metals is straightforward. The vibrational wavenumbers are observed in the expected regions, assuming the tendencies known for methylhalides to be valid, that are: strong mass dependence for ν_3 and the deformation modes ν_4 and ν_6, little mass dependence for ν_5, and only little variations for the C-H-stretches ν_1 and ν_4 (see Tables 1 and 2). The wavenumbers of ν_3, the metal-methyl stretching mode, are around 445 cm^{-1} for the tungsten complexes and at 466 cm^{-1} for the iron derivative, hence showing a relatively little mass effect compared to those observed for the halides. Despite the similar mass of rhenium and tungsten the metal-methyl stretching wavenumber is much higher in the oxorhenium complex. Force constants of the metal-methyl stretching modes (s_1) of 1 to 3 are calculated to be between 2.4 and 2.5 mdyn/Å and hence about 0.5 mdyn/Å lower than for bromo- and iodomethane. The oxocomplex of rhenium shows a higher value for s_1 (about 2.8 mdyn/Å) which is responsible for the higher wavenumber mentioned above. The PED in

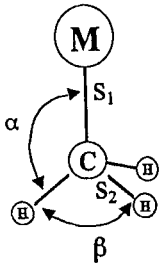

Figure 1 Structure and internal coordinates of a M-CH_3-moiety

Tables 1 and 2 point out a remarkable difference between the ν_3 mode in transition metal methyl compounds and methyl halides. This mode can satisfactorily be described by the coordinates s_1 (around 90 %) and s_2 (around 5 %) in the halides. Therefore X-C-stretching is only accompanied with little C-H-stretching in these cases. However, when substituted with a transition metal the methyl group vibrates in a more complicated way: only 50 to 60 % corresponds to stretching along s_1, around 20 % now corresponds to each of the *in-plane*-deformation motions represented by α and β. Thus, it can be stated that the designation of ν_3 as a pure ν(M-CH_3) mode is incorrect. Similar relations are generally assumed to be present for ν(M-CO) vibrations in transition metal complexes, where M-C-stretching is accompanied by large extents of M-C-O-deformation and C-O-stretching[8].

The bands of the C-H-stretching modes ν_1 and ν_4 of the metal compounds are observed at somewhat lower wavenumbers compared to those of the halides. Remarkably, the corresponding force constants show the reversed order, 4.8 mdyn/Å and 4.6 mdyn/Å in 1 to 4 and 5 to 6, respectively. An explanation for this behaviour can again be deduced from the PED in Table 2. It shows that, in the case of the halides, deformational coordinates (at least to the extent of a few percent) are necessary to fully describe the C-H-stretches. This is not the case in the metal complexes, where ν_1 and ν_4 are respresented by s_2 to 100 %.

TABLE 1 Assignments and Potential Energy Distribution of 1 to 3.

description	mode	observed [in cm^{-1}]	calculated [in cm^{-1}]	Potential energy distribution [%]			
				s_1	s_2	α	β
1 $Cp(CO)_2Fe\text{-}CH_3$							
ν_{as} (CH)	ν_4	2968	2968		100.0		
ν_s (CH)	ν_1	2895	2895		100.0		
δ_{as} (CH_3)	ν_5	1430	1430		3.5	3.5	93.0
δ_s (CH_3)	ν_2	1362	1362	7.0	3.0	39.0	51.0
δ (FeCH)	ν_6	920	920		13.0	80.0	7.0
ν (Fe-C)	ν_3	466	466	57.0	5.0	16.5	21.5
2 $Cp(CO)_3W\text{-}CH_3$							
ν_{as} (CH)	ν_4	2977	2977		100.0		
ν_s (CH)	ν_1	2907	2907		100.0		
δ_{as} (CH_3)	ν_5	1350	1350		8.5	4.5	87.0
δ_s (CH_3)	ν_2	1190	1190	7.5	12.0	40.5	40.0
δ (WCH)	ν_6	817	817		20.0	76.0	4.0
ν (W-C)	ν_3	445	445	50.5	11.5	19.0	19.0
3 $Cp(CO)_2(PMe_3)W\text{-}CH_3$							
ν_{as} (CH)	ν_4	2974	2974		100.0		
ν_s (CH)	ν_1	2913	2913		100.0		
δ_{as} (CH_3)	ν_5	1358	1358		9.5	3.0	87.5
δ_s (CH_3)	ν_2	1187	1187	7.5	15.5	38.0	39.0
δ (WCH)	ν_6	813	813		20.5	77.5	2.0
ν (W-C)	ν_3	444	444	50.0	13.0	18.0	19.0

TABLE 2 Assignments and Potential Energy Distribution of 4 to 6.

description	mode	observed	calculated	Potential energy distribution [%]			
		[cm^{-1}]	[cm^{-1}]	s_1	s_2	α	β
			4 O_3Re-CH_3				
ν_{as} (CH)	ν_4	2989	2989		100		
ν_s (CH)	ν_1	2900	2900		100		
δ_{as} (CH_3)	ν_5	1371	1371			4.5	95.0
δ_s (CH_3)	ν_2	1204	1204	7.0		39.0	54.0
δ (ReCH)	ν_6	740	740		1.0	95.0	4.0
ν (ReC)	ν_3	568	568	91.0	1.0	3.0	5.0
			5 Br-CH_3				
ν_{as} (CH)	ν_4	3060	3060		95.0		5.0
ν_s (CH)	ν_1	2972	2972		98.0	1.5	0.5
δ_{as} (CH_3)	ν_5	1449	1449		30.5	15.5	54.0
δ_s (CH_3)	ν_2	1306	1306	1.5	24.0	21.0	53.5
δ (CH_3)	ν_6	954	954		45.5	24.5	30.0
ν (BrC)	ν_3	610	610	91.5	8.0		0.5
			6 I-CH_3				
ν_{as} (CH)	ν_4	3062	3062		95.0		5.0
ν_s (CH)	ν_1	2970	2970		98.5	1.0	0.5
δ_{as} (CH_3)	ν_5	1439	1439		29.5	18.5	52.0
δ_s (CH_3	ν_2	1251	1251		20.5	18.0	61.5
δ (CH_3)	ν_6	881	881		45.0	20.5	20.5
ν (IC)	ν_3	533	533	86.0	3.5	1.5	9.0

TABLE 3 Force fields of 1 to 6.

internal coordinates	description	force constants[a]					
		1	2	3	4	5	6
diagonal							
s_1	M-C stretch	2.400	2.456	2.455	2.801	3.100	2.964
s_2	C-H stretch	4.815	4.808	4.799	4.785	4.601	4.614
α	M-C-H stretch	0.542	0.569	0.539	0.392	0.654	0.654
β	H-C-H stretch	0.702	0.559	0.552	0.462	0.649	0.649
stretch/stretch interaction							
s_1s_2	M-C / C-H	-0.159	-0.220	-0.201	-0.201	-0.623	-0.654
s_2s_2	C-H / C-H	0.010	0.000	0.003	0.012	0.085	0.100
stretch/bend interaction							
$s_1\alpha$	M-C / M-C-H	0.012	0.049	0.098		0.454	0.536
$s_1\beta$	M-C / H-C-H	-0.302	-0.147	-0.100		-0.047	-0.194
$s_2\alpha$	C-H / M-C-H bond unit	0.124	0.145	0.174		0.057	0.023
$s_2\beta'$	C-H / H-C-H adjacent	-0.366	-0.417	-0.384		-0.806	-0.833
bend/bend interaction							
$\alpha\alpha$	M-C-H / M-C-H	-0.100	-0.006	-0.022		-0.286	-0.267
$\alpha\beta$	M-C-H / H-C-H bond unit	0.093	0.090	-0.070		-0.214	-0.204

[a] values for stretches and their interactions are in mdyn/Å; bendings in mdynÅ/rad^2; other interaction values in mdyn/rad.

The interaction force fields determined for every species require only few further comments. In most cases, the interaction forces are stronger in the halides. For instance, stretch-stretch interaction s_1s_2 in 5 and 6 is three times as high as in the complexes 1 to 4. The vibrational behaviour of the oxocomplex 4 could be calculated by means of a very simplified force field, neglecting most stretching-bending and bending-bending interactions. For a more detailed description of this complex we refer to reference[9].

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