

Electronic structures of organometallic complexes of *f* elements LXXIV: First Raman spectroscopic polarization measurements on uniformly oriented sandwich complex molecules: Bis(η^5 -pentamethylcyclopentadienyl)ruthenium[☆]

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ABSTRACT

The polarized Raman spectra of oriented single crystals as well as far and mid infrared spectra of pellets of RuCp₂^{*} (Cp^{*} = η^5 -C₅Me₅) (**1**) were recorded. Assuming local C_{5v} symmetry for the intra-ligand vibrations, pairs of Raman and IR bands of nearly equal energy result for the symmetric and antisymmetric modes, respectively, for the irreducible representations (irreps) a₁, e₁, and partly (the IR part is symmetry forbidden, in principle, but sometimes observed) of e₂ symmetry. By this means, intra-ligand and skeletal vibrations (where no pairs of Raman and IR bands are expected) could be separated, and the Raman active modes were assigned to irreps on the basis of the observed polarizations. The still questionable type of vibration of some intra-ligand modes could be elucidated by the comparison of the vibrational spectra of **1** with the already assigned ones of NaCp^{*}. Transferring the results of **1** to the Raman and IR spectra of OsCp₂^{*} (**2**) and FeCp₂^{*} (**3**), a number of previous assignments have to be revised.

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1. Introduction

Typical synthetic chemists in organometallic chemistry use infrared and sometimes also Raman spectroscopy beside other methods in order to characterize their new products. Scientists who are somewhat more interested in vibrational spectroscopy additionally report about the polarizations of the Raman spectra of solutions or melts of these compounds in order to separate totally symmetric (polarized) from the remaining (depolarized) vibrations. Solid state physicists, however, perform Raman spectroscopic polarization measurements of oriented single crystals in order to get additional information about the Raman scattering tensor components which allow the assignment of symmetries to vibrations [2–5].

Recently, we tried to extend this method to the skeletal vibrations of pseudo trigonal planar SmCp₃^{*} [6] (Cp^{*} = η^5 -C₅Me₅) which crystallizes in the space group P6₃/m with two molecules in the unit cell. Indeed, distinct polarization effects with nearly negligible polarization leaks were observed [6]. However, the intra-ligand vibrations of the types β (CCH₃) (in plane) and γ (CCH₃) (out of

plane) have partly energies similar to those of the searched skeletal (inter-ligand) vibrations [6–9]. In order to separate both types of vibrations we need additional information from the spectroscopic properties of other Cp^{*} complexes.

Up to now, normal coordinate analyses (NCAs) of the vibrational spectra of only MCp^{*} (M = Li, Na, K) [8], Cp^{*}M(CO)₃ (M = Mn, Re) [9] and Cp^{*}ReO₃ [9] have been performed. Besides, the unassigned far infrared (FIR) and Raman spectra (in the range below 520 cm⁻¹) of both powdered and dissolved material of RuCp₂^{*} (**1**), OsCp₂^{*} (**2**) and FeCp₂^{*} (**3**) were reported [7]. Additionally, in the frame of the latter paper, the mid infrared (MIR) and Raman spectra (in the range above 520 cm⁻¹) of powdered and dissolved **2** were tentatively assigned to intra-ligand vibrations [7]. Last but not least, FeCp₂^{*} [10–12], [FeCp₂^{*}][PF₆] [10,12] and [FeCp₂^{*}][CCl₃COO]·2CCl₃COOH [10] were the target of vibrational studies, where vastly different assignments were made in spite of nearly identical frequency values.

The above-mentioned NCA calculations led partly to very different (by a factor of up to 2.5) energies of the β (CCH₃) and γ (CCH₃) vibrations [6, Table 5], thus not allowing a first glance separation of skeletal and intra-ligand vibrations of LnCp₃^{*} in the low energy range.

In order to get deeper insight into the vibrational spectra of Cp^{*} compounds, Raman spectroscopic polarization measurements of oriented monoclinic RuCp₂^{*} single crystals (space group P2₁/m, two molecules per unit cell [13–15]) and FIR/MIR measurements of

[☆] For part LXXIII, see Ref. [1].

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pellets were performed. This compound was chosen because the fivefold molecular axes of the two molecules per unit cell are parallel to each other (like in the case of **2** [14], but in contrast to **3** [16,17]), and the relations between molecular crystallographic and morphological axes are known [14].

2. Experimental

RuCp₂^{*} (**1**) was purchased from STREM and recrystallized from hot ethanol. According to Ref. [14], single crystals were grown by slow evaporation from diethylether solutions over a period of three weeks. The usually complicated orientation problem of monoclinic single crystals for polarization measurements [18] could be solved following Ref. [14]: The crystallographic *a* axis was identified by the finding that polarized light propagation along this axis shows no extinction under a stereomicroscope. Considering the monoclinic angle $\beta = 106^\circ$ and the fact that the Cp^{*} moieties lie parallel to the *bc* plane with an angle of 16° between the plane normal and the macroscopic *z* axis [14] allowed a rough orientation of the crystal. Preliminary Raman spectroscopic polarization measurements with the electric field vector of the laser radiation parallel (*pa*) and perpendicular (*pe*) to the quasi fivefold rotation axis of the individual molecules and analyzer positions *pa* and *pe*, respectively, showed nice polarization effects, but still noticeable leaks. A solution of **1** in CH₂Cl₂ exhibits a polarized Raman band at 387 cm^{-1} [7] which has to be correlated with a totally symmetric vibration of A₁' symmetry (assuming strict molecular D_{5h} symmetry). Vibrations of A₁' symmetry of an oriented single crystal of **1** are allowed for the combinations *pa/pa* and *pe/pe* of polarizer and analyzer, but forbidden in the case of *pa/pe* (= *pe/pa* in the case of axially symmetric molecules) combinations (see Table 1). In the frame of a trial and error procedure, the crystal was slightly reoriented in a way to maximize the intensity of the above-mentioned allowed vibration (adopting the *pa/pa* and *pe/pe* combinations, respectively) and to minimize the intensity of the corresponding polarization leak (using the *pa/pe* combination).

The Raman measurements were performed with the recently developed Senterra Raman instrument (with a 180° backscattering optic) from Bruker, equipped with a microscope and lasers with excitation lines at 785, 632.8 and 532 nm. The FIR/MIR spectra (polyethylene/KBr pellets) were recorded by means of the Fourier transform FIR/MIR spectrometer Vertex 70 from Bruker. Several preliminary efforts to organize polarized FIR/MIR spectra in cooperation with other groups were not successful.

3. Symmetry considerations and selection rules

Complex **1** crystallizes in the monoclinic space group P2₁/m with two molecules in the unit cell [13–15]. The molecules have crystallographic mirror symmetry with an eclipsed conformation of Cp^{*} ligands and the fivefold rotation axes of two molecules are (anti-)parallel, thus allowing spectroscopic polarization measurements. However, in a more recent study it was shown that the RuCp₂^{*} molecules actually adopt a conformation that differs somewhat from an ideal eclipsed structure by the torsion of one ligand through an angle of $\pm 6^\circ$ from the mirror plane passing through the atoms C(1), C(4), C(7) and C(10) (see Fig. 1), whereas the other ligand exhibits typical

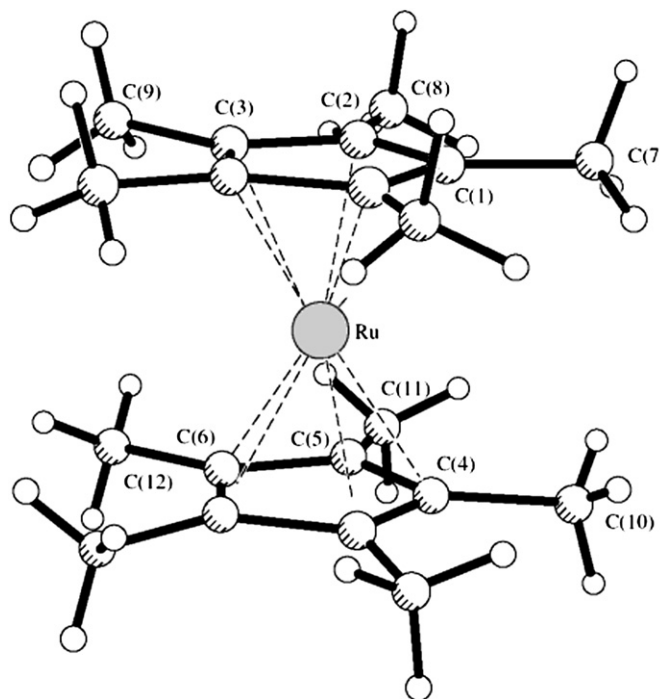


Fig. 1. Molecular structure of RuCp₂^{*} in the crystal (from Ref. [15]).

dynamic temperature behavior [15]. This finding suggests that the molecular D_{5h} symmetry of **1** is slightly distorted which may cause polarization leaks which are not due to a misorientation of the single crystal.

Neglecting any interactions of the two molecules of **1** in the unit cell (see below) as well as the H atoms of the methyl groups, thus considering only the Ru[C₅C₅]₂ moiety, $3N - 6 = 57$ (with number of atoms $N = 21$) normal vibrations are expected. These may be divided into nine skeletal ($A_1' + A_1'' + A_2' + 2E_1' + E_1''$) [19] and 48 intra-ligand vibrations ($3a_1' + a_1'' + a_2' + 3a_2'' + 4e_1' + 4e_1'' + 6e_2' + 6e_2''$) [20]. For a better discrimination the irreps of the skeletal vibrations are written in uppercase, but the intra-ligand ones in lowercase.

The frequencies of a symmetric mode (Raman) and of the corresponding antisymmetric mode (infrared) of the internal vibrations of the two rings of MCp₂ complexes are nearly identical ($a_1' \approx a_2''$, $a_2' \approx a_1''$, $e_1' \approx e_1''$, $e_2' \approx e_2''$) [21] confirming that the coupling between the two rings is essentially negligible, and suggesting that the principle of local symmetry may be applied to **1** [21]. Assuming local C_{5v} symmetry for the Cp^{*} ligand, and making use of correlation Table 1, the number of intra-ligand vibrations is reduced to 24 ($3a_1 + a_2 + 4e_1 + 6e_2$) [8].

The selection rules for IR (pellet) and polarized Raman spectra (oriented single crystal) for skeletal and intra-ligand vibrations (assuming molecular D_{5h} and local C_{5v} symmetry, respectively) of the Ru[C₅C₅]₂ moiety are given in Table 2.

Essentially, three different numberings (ν_i) of intra-ligand vibrations of (C₅H₅)⁻ (and thus also [C₅C₅]⁻) exist [7,8,19,21]. As the previously assigned vibrations for NaCp^{*} [8] and complex **2** [7] were used here for comparison purposes, we adopt the numbering used there. Going from intra-ligand D_{5h} to local C_{5v} symmetry, the original irrep a_2'' (ν_4) transforms as a_1 (ν_3) [7,8]. In Refs. [7,8] the changed numbering is not always consequently considered. For this reason, we cite here in some cases ν_i s which differ from those of the original publications.

Table 1
Correlation table for descent in symmetry going from D_{5h} to C_{5v}.

D _{5h}	A ₁ '	A ₂ '	E ₁ '	E ₂ '	A ₁ ''	A ₂ ''	E ₁ ''	E ₂ ''
C _{5v}	A ₁	A ₂	E ₁	E ₂	A ₂	A ₁	E ₁	E ₂

Table 2

Selection rules for IR (pellet) as well as polarized Raman spectra (oriented single crystal) assuming molecular D_{5h} and local C_{5v} symmetry, respectively, of eclipsed sandwich complexes.

		IR	Raman		
		Pellet	pa/pa	pa/pe = pe/pa	pe/pe
n^a	D_{5h}				
1	A_1'	–	+	–	+
1	A_1''	–	–	–	–
1	A_2''	+	–	–	–
2	E_1'	+	–	–	–
1	E_1''	–	–	+	–
n^b	C_{5v}				
3	a_1	+	+	–	+
1	a_2	–	–	–	–
4	e_1	+	–	+	–
6	e_2	–	–	–	+

^a Numbers of irreps of skeletal vibrations.

^b Numbers of irreps of intra-ligand vibrations.

4. Results and discussion

4.1. General remarks

The unpolarized Raman spectrum of an unoriented single crystal as well as the FIR spectrum of a polyethylene pellet of **1** have the same appearance as those given in Ref. [7, Figures 1b, 2b] for powdered and dissolved material, respectively, and the corresponding wavenumbers of the observed signals are identical to ours within experimental error. Unfortunately, only the unassigned bands with wavenumbers lower than 450 cm^{-1} are explicitly mentioned for complex **1** in Ref. [7, Table 3]. However, in Ref. [7, Table 1], additionally the vibrational energies of **2** are given in the range $540\text{--}2970\text{ cm}^{-1}$, which are comparable to those we observed for complex **1** (see Table 3).

Intra-ligand and skeletal vibrations of sandwich complexes can be roughly separated by the fact that the Raman active symmetric intra-ligand modes usually have counterparts of comparable energy in the IR spectrum, whereas the skeletal vibrations have no

counterparts [21]. According to Table 2, the former rule holds for the skeletal vibrations of **1** and for the Raman bands of simultaneously pa/pa and pe/pe polarizations (a_1 modes), as well as of pa/pe polarization (e_1 modes), but not for pe/pe polarization (e_2 modes), as the latter are only Raman and not IR active, in principle, but can be observed with low intensities in some cases (vide infra). Surely, the above described rough separation of skeletal and intra-ligand vibrations only works if no accidental coincidences of Raman and IR bands of different irreps occur, and if at least in the case of Ra/IR pairs of a_1 and e_1 symmetry none of the components has accidentally vanishing intensity.

4.2. Intra-ligand vibrations

Applying the selection rules of Table 2 to the vibrational spectra of Figs. 2–4, a number of the here more interesting Ra/IR pairs of C–C type intra-ligand modes (the C–H bending and rocking modes are put in brackets) of a_1 , e_1 and e_2 (Ra/IR pairs with very weak IR signals or single Raman bands) symmetry could be identified: a_1 : 179/188, 586/590, (1034/1028), (1381/ \approx 1380), 1421/1425 and (1470/1474) cm^{-1} ; e_1 : 788/791, (1034/1028), 1367/1374, (1439/1447); e_2 : 279/283, 545/543, 623/635, 950/–, 1166/– and 1362/– cm^{-1} (see Figs. 2–4).

At the present stage, the three expected intra-ligand normal vibrations (of the $[C_5C_5]^-$ moiety) of a_1 , and the six of e_2 but only two of e_1 symmetry have been identified up to now. This means that two additional e_1 modes beside the Ra and IR forbidden one of a_2 symmetry (see Table 2) are missing.

In case of $NaCp^*$, the latter was associated with the signal at 542 cm^{-1} “in the solid spectra of $NaCp^{*+}$ ” [8] (see Table 2), but the distinct Raman band of the Ra/IR pair at $545/543\text{ cm}^{-1}$ of complex **1** is pe/pe polarized and thus of e_2 symmetry (vide supra). Only an accidental coincidence of the a_2 and e_2 modes would be compatible with the assignment of Ref. [8].

Likewise, the correlation of the weak Raman signal at 620 cm^{-1} of **2** with the a_2 mode [7, Table 1] cannot be accepted, as the Raman part of the Ra/IR pair at $623/635\text{ cm}^{-1}$ of complex **1** is pe/pe polarized and thus of e_2 (vide supra) and not of a_2 symmetry.

Table 3

Assignment of the observed intra-ligand vibrations of $Ru[C_5C_5]_2$ on the basis of FIR/MIR spectra and Raman spectroscopic polarization measurements to irreps (C_{5v} symmetry) and (by comparison with $NaCp^*$) to normal modes, as well as comparison with previous measurements and assignments for $RuCp_2^*$ and $OsCp_2^*$. All values in cm^{-1} .

$RuCp_2^*$		$NaCp^{*a}$			$RuCp_2^{*b}$, $OsCp_2^{*b,c}$					
FIR/MIR pellet	Ra pa/pa	Ra pa/pe	Ra pe/pe	Concl. irrep (C_{5v})	Exp.	Assignment	FIR/MIR Pellet	Ra Powder	Ra Solution	Assignment
a_1, e_1	a_1	e_1	a_1, e_2	(C_{5v})						
		160		e_1	187	$\nu_8(e_1), \gamma(CCH_3)$		163		–
188	179			a_1	174	$\nu_3(a_1), \gamma(CCH_3)$	189	179	164 p ^d	–
243				e_1	277	$\nu_7(e_1), \beta(CCH_3)$	244			–
					234	$\nu_{13}(e_2), \gamma(CCH_3)$				
283			279	e_2	270	$\nu_{11}(e_2), \beta(CCH_3)$			283 dp	–
543			545	e_2	551	$\nu_{12}(e_2)^e$		547	546 dp	$\nu_{12}(e_2)$
590	586		586	a_1	583	$\nu_2(a_1)$	582	590	588 p	$\nu_2(a_1)$
			623	e_2	640	$\nu_{14}(e_2)$		620		$\nu_4(a_2)$
791		788		e_1	794	$\nu_6(e_1)$	792	793		$\nu_{14}(e_2)$
							850			$\nu_6(e_1)$
			950	e_2				955	944 dp	$\nu_{10}(e_2)?$
			1166	e_2	1164	$\nu_{10}(e_2)$		1172		$\nu_{10}(e_2)?$
			1362	e_2	1395	$\nu_9(e_2)$		1364	1365 dp	$\nu_9(e_2)$
1374			1367	e_1			1375	1370	1370 dp	$\nu_5(e_1)$
1425	1421		1421	a_1	1423	$\nu_1(a_1)$	1421	1423	1422 p	$\nu_1(a_1)$
					1475	$\nu_5(e_1)$				

^a From Ref. [8, Table 8] where a more detailed description of the normal modes ν_i is given.

^b From Ref. [7].

^c Data of $RuCp_2^*$ below 500 cm^{-1} , $OsCp_2^*$ above.

^d p polarized, dp depolarized.

^e In Ref. [8, Table 8], $\nu_3(a_2)$, $\beta(CCH_3)$ was correlated with 542 cm^{-1} instead.

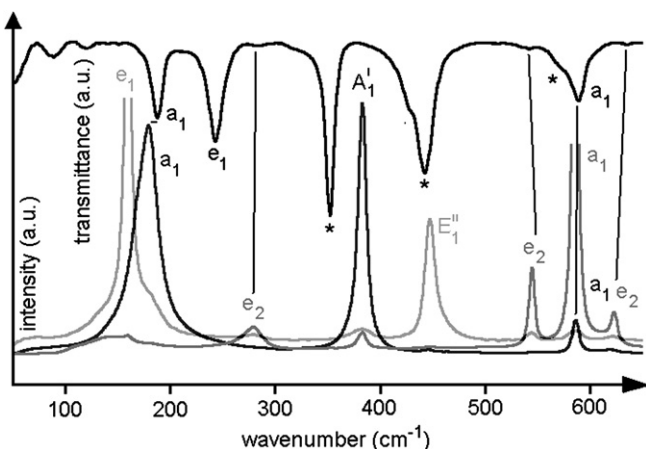


Fig. 2. Vibrational spectra of RuCp_2^* in the range $50\text{--}650\text{ cm}^{-1}$: black: FIR spectrum, polyethylene pellet; colored: Raman spectrum, oriented single crystal (red: combination pa/pa, blue: pa/pe, green: pe/pe). *: see text.

However, a shoulder at ca. 574 cm^{-1} on the low energetic side of the FIR band at 590 cm^{-1} might correspond to this normal mode, or alternatively, it is not observable as suggested by the selection rules.

Bencze et al. [8] correlated the vibrations at 187 , 277 and 1475 cm^{-1} of NaCp^* with intra-ligand normal modes of e_1 symmetry (see Table 2). The polarization measurements of **1** (see Fig. 2) demonstrated, however, that the Ra/IR pairs at $179/188$ and $279/283\text{ cm}^{-1}$ are of a_1 and e_2 symmetry, respectively (vide supra), and the observation of the assumed normal mode at 1475 cm^{-1} is hampered by strong bands of C–H (asymmetric bending) modes (vide supra).

One of the two missing intra-ligand modes of e_1 symmetry might be correlated with the extremely strong Raman band at 160 cm^{-1} with pa/pe polarization (see Fig. 2). As the corresponding IR active counterpart is missing, we originally considered it as a candidate for a skeletal and not an intra-ligand vibration. Assuming D_{5h} symmetry for the assignment of skeletal vibrations of **1**, the observed pa/pe polarization would suggest a skeletal mode of E_1'' symmetry (see Table 1). The only skeletal vibration of E_1'' symmetry is the symmetric tilt which has in the case of **3** [10–12]

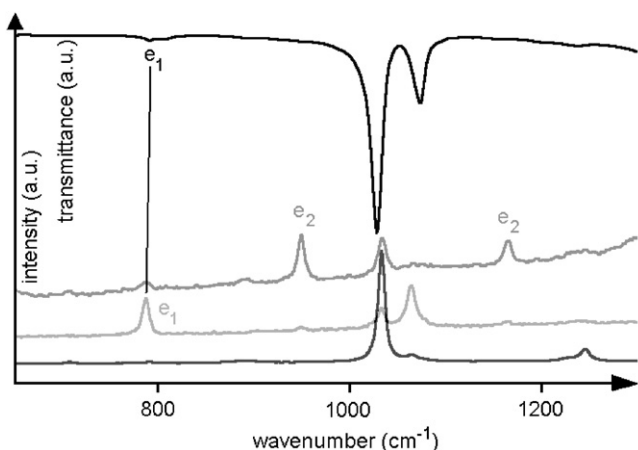


Fig. 3. Vibrational spectra of RuCp_2^* in the range $650\text{--}1250\text{ cm}^{-1}$: black: MIR spectrum, polyethylene pellet; colored: Raman spectrum, oriented single crystal (red: combination pa/pa, blue: pa/pe, green: pe/pe). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

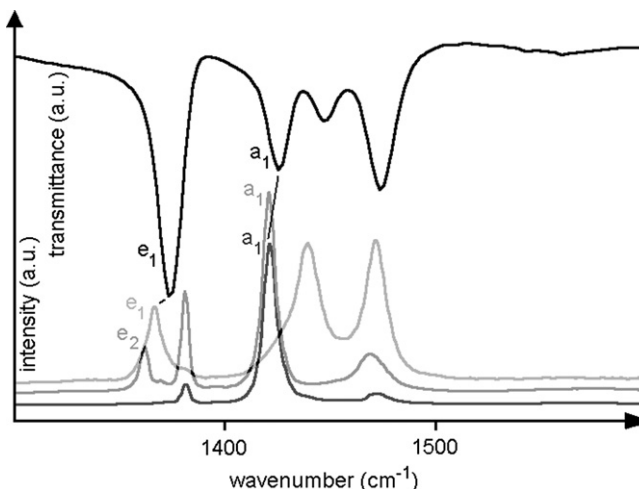


Fig. 4. Vibrational spectra of RuCp_2^* in the range $1300\text{--}1600\text{ cm}^{-1}$: black: MIR spectrum, polyethylene pellet; colored: Raman spectrum, oriented single crystal (red: combination pa/pa, blue: pa/pe, green: pe/pe). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

and MCp_2 ($M = \text{Fe, Ru, Os}$) [22, Table 1] much higher energies than 160 cm^{-1} (see Table 3). Hence, we conclude that the pa/pe polarized Raman band at 160 cm^{-1} corresponds to an intra-ligand vibration of e_1 symmetry (see Table 1), where the IR allowed counterpart is accidentally extremely weak.

According to Ref. [7, Table 3], the above discussed Raman band of **1** was found at 163 cm^{-1} using solid material, but in the case of **1** dissolved in CH_2Cl_2 , a polarized signal appeared at 164 cm^{-1} . The obvious conclusion that the corresponding vibration is totally symmetric may be disregarded, as solvation effects shift the signal of the intra-ligand mode of a_1 symmetry from 179 cm^{-1} in the single crystal to 164 cm^{-1} in solution (see Table 3).

Obviously, not in all cases of e_1 modes, pairs of Ra/IR signals are observed. If this also holds for the Raman part of the IR band at 243 cm^{-1} , a correlation with an e_1 mode (ν_7 , 277 cm^{-1} in the case of NaCp^* , see Table 2) is suggested.

The thus concluded series of 14 intra-ligand normal modes of the $[\text{C}_5\text{C}_5]^-$ moiety is summarized in Table 3.

The assignments of the normal modes ν_1 (a_1), ν_2 (a_1), ν_9 (e_2) and ν_{12} (e_2) of NaCp^* and compound **2** not only agree with each other, but also with the irreps determined from Raman spectroscopic polarization measurements of complex **1**. In several cases, however, misassignments of the modes of NaCp^* and complex **2** occur. These can be recognized if their irreps differ from the experimental ones (at fixed comparable energy), or if the irreps are identical but the energies differ noticeably (see Table 3).

The entries of Table 3 represent an experimental criterion for previous assignments of Cp^* complexes which have to be revised in a number of cases.

For example, in Ref. [10], the Ra/IR pair at $590/595\text{ cm}^{-1}$ of compound **3** was assigned to the ring distortion (out of plane) which corresponds to ν_{14} (e_2) of Ref. [8, Fig. 1]. This correlation was repeated in Ref. [11], but in Ref. [12], the above-mentioned pair was assigned to the ring breathing mode ν_2 (a_1). The simultaneous pa/pa and pe/pe polarization of the Raman part of the Ra/IR pair at $586/590\text{ cm}^{-1}$ of complex **1** (see Fig. 2, Table 3) supports the latter assignment.

Additionally, it should be noted that in Ref. [11, Table 2] the symmetric bending CH_3 of **3** (1445 , 1471 cm^{-1}) has a higher energy than the asymmetric bending CH_3 (ca. 1370 cm^{-1}). This is in contrast to the assignments of all other Cp^* compounds [7–9,12].

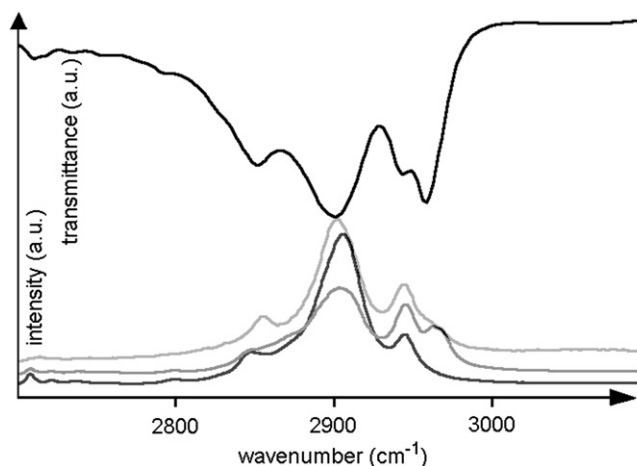


Fig. 5. Vibrational spectra of RuCp_2^* in the range 2700–3100 cm^{-1} : black: MIR spectrum, polyethylene pellet; colored: Raman spectrum, oriented single crystal (red: combination pa/pa, blue: pa/pe, green: pe/pe). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The range 2700–3000 cm^{-1} of Cp^* complexes is dominated by bands of the C–H stretching vibrations [7–12], but also weak overtones of the ν_9 (e_2) and ν_1 (a_1) normal modes as well as combination vibrations of both modes exist between 2700 and 2860 cm^{-1} [7, Table 1].

The above-mentioned C–H stretching vibrations (of MCp_2^* compounds) are usually roughly classified into ν_s at ca. 2900 cm^{-1} and ν_{as} at ca. 2945 cm^{-1} as well as ca. 2965 cm^{-1} [11,12]. In reality, numerous bands of Raman and IR active irreps are superimposed. This fact is clearly demonstrated by the polarized Raman spectra of an oriented single crystal of **1** (see Fig. 5): The C–H vibration of e_1 symmetry at 2900 cm^{-1} is by 3 cm^{-1} lower in energy than that of a_1 symmetry, and in case of the signals between 2950 and 2970 cm^{-1} , first of all the e_2 component of pe/pe polarization contributes to the intensity of the Raman band of powdered material.

4.3. Skeletal vibrations

As mentioned above, the signals of the two Raman (A_1' , E_1'') and the three IR active (A_2'' , $2E_1'$) skeletal vibrations are expected to have no counterparts apart from accidental coincidences.

This ideally holds for the Raman band at 383 cm^{-1} , which is dominantly pa/pa polarized (see Fig. 2) and thus of A_1' symmetry (see Table 2), corresponding to $\nu_s(\text{Ru–Cp}^*)$. The Raman band of pa/pe polarization at 447 cm^{-1} unfortunately has an IR counterpart at

443 cm^{-1} (see Fig. 2), nevertheless, both the concluded E_1'' symmetry (see Table 1) as well as the frequency of this Raman band agree well with the expected properties of the symmetric tilt $\text{Cp}^*-\text{Ru}-\text{Cp}^*$ (see Table 4).

In case of powdered **3**, the symmetric tilt of E_1'' symmetry was correlated with Ra/IR bands between 375 and 381 cm^{-1} [10–12] (see Table 4), which lie suspiciously close to ν_s of complex **1** (383 cm^{-1}). Dissolved **1**, **2** and **3** show polarized Raman bands at 387, 404 and 377 cm^{-1} , respectively [7, Table 3], suggesting a totally symmetric vibration of A_1' and not one of E_1'' symmetry. This is even better demonstrated by the polarization measurements of an oriented single crystal of **1** (see Fig. 2). The last assignment was additionally suggested in Ref. [10, Table V, assignment 2] (see Table 4) but was considered as less probable.

Energetically isolated FIR signals of **1** without Raman counterparts which can possibly be correlated with the expected skeletal vibrations of E_1' ($\text{Cp}^*-\text{Ru}-\text{Cp}^*$ def.), A_2'' ($\nu_{as}(\text{Ru}-\text{Cp}^*)$) and E_1' (antisymmetric tilt $\text{Cp}^*-\text{Ru}-\text{Cp}^*$) appear at 89/112 and 352 cm^{-1} , beside the above-mentioned Ra/IR coincidence at 447/443 cm^{-1} . Surely, only polarized IR (and not polarized Raman spectra recorded here) present new arguments for their assignments. However, previous assignments of the skeletal vibrations of complex **3** [10–12] (see Table 4) and further Cp^* compounds [7–9] can be checked by means of the intra-ligand and the as yet assigned Raman active skeletal modes (see Tables 3 and 4), and perhaps some assignments unexcluded by these assignments remain that might be transferred to complex **1**.

IR active but Raman inactive ν_{as} modes (of A_2'' symmetry) of powdered **3** have values at ca. 453 cm^{-1} [10,12] or 511 cm^{-1} [11], and the antisymmetric tilt mode (of E_1' symmetry) was correlated with Ra/IR pairs at 550/515 cm^{-1} [10] or 511/515 cm^{-1} [12] or with the IR band at 454 cm^{-1} [11] (see Table 4).

Going from **3** to complexes **1** and **2**, the strong band at ca. 453 cm^{-1} is shifted to 443 and 446 cm^{-1} [7, Table 3], respectively, and that at 511 cm^{-1} can not be detected (in the range 470–530 cm^{-1}) neither in the IR nor in the Raman spectrum of **1** or **2** [7]. (Perhaps the latter signal corresponds to an overtone of the intra-ligand vibration at 256 cm^{-1} of **3** [11,12].) If the correlation of ν_{as} of **3** with the band at 453 cm^{-1} [10,12] is correct, ν_{as} of **1** and **2** would have values of 443 and 446 cm^{-1} , respectively. The values of ν_{as} of MCp_2 ($M = \text{Fe}, \text{Ru}, \text{Os}$) sandwich complexes are strongly dependent on the mass of the central ion, whereas those of tilt_{as} are much less influenced (see Table 3). If one transfers these findings to MCp_2^* ($M = \text{Fe}, \text{Ru}, \text{Os}$), the above concluded nearly constant values of ν_{as} better have to be correlated with tilt_{as} . The triple of FIR signals at ca. 375 (**3**), 352 (**1**) and 332 (**2**) cm^{-1} [7, Table 3] of MCp_2^* complexes shows a much stronger dependence on the mass of the central ion, thus suggesting that these signals correspond to ν_{as} modes (see Table 4).

Table 4

Comparison of the observed skeletal vibrations of RuCp_2^* with those of selected sandwich complexes. All values in cm^{-1} .

Concl. irrep ^a	Mode	RuCp_2^*		FeCp_2^{*b}		FeCp_2^{*c}		FeCp_2^{*d}		FeCp_2^{*e}		FeCp_2^{*f}		RuCp_2^g		OsCp_2^g	
		Ra	IR	Ra	IR	Ra	IR	IR	Ra	IR	Ra	IR	Ra	Exp.	Exp.	Exp.	
A_1'	ν_s	383	–	179	–	378	375	169	162, 172, 178	–	–	303	329	356			
A_2''	ν_{as}	–	352	451	455	451	455	511	453	453	–	478	385	353			
E_1''	tilt_s	447	–	378	375	–	–	–	376	381	–	388	402	415			
E_1'	tilt_{as}	–	443	550	515	550	515	454	511	515	–	492	446	428			
E_1'	ring-M-ring def.	–	s. text	–	–	–	–	–	–	–	140	170	162/172	160/166			

^a The irreps correspond to D_{5h} symmetry.

^b From Ref. [10, Table V, assignment 1].

^c From Ref. [10, Table V, assignment 2].

^d From Ref. [11, Table 3].

^e From Ref. [12, Table 2].

^f From Ref. [23, Table 1].

^g From Ref. [22, Table 1].

The transmission spectrum of crystalline **3** recorded by means of a recently developed GaP Raman THz spectrometer shows a weak signal at 4.2 THz (140 cm^{-1}) which was tentatively correlated with the IR allowed and Raman forbidden $\text{Cp}^*-\text{Fe}-\text{Cp}^*$ deformation vibration [23]. In case of complex **1**, we could not observe a signal in this range neither in the Raman nor in the IR spectrum, but low energetic FIR bands at 89 and 117 cm^{-1} appeared (see Fig. 2), one of which might be correlated with the $\text{Cp}^*-\text{Ru}-\text{Cp}^*$ deformation and the other to a lattice vibration.

4.4. Consequences for the vibrational spectra of LnCp_3^* complexes

Going from **1** to SmCp_3^* [6], the energies of the intra-ligand modes greater than 500 cm^{-1} remain essentially unchanged. If this also holds for the low energetic ones, the observation of the polarized Raman spectra of the skeletal vibrations of SmCp_3^* ($\approx 95, 145, 210, 270, \approx 286, \approx 330, 362, \approx 378\text{ cm}^{-1}$) [6] is only hampered by the intra-ligand vibration of e_2 symmetry at 279 cm^{-1} . Close to this energy, two signals at 270 and 286 cm^{-1} appear using the pe/pe combination of polarizer and analyzer, and one at 270 cm^{-1} applying the pa/pa combination [6]. As the interfering intra-ligand mode is of e_2 symmetry, only the pe/pe polarization is involved (see Ref. [6, Table 4]). As the band at 270 cm^{-1} appears in both the pe/pe and pa/pa combinations it does not correspond to an intra-ligand but to a skeletal vibration of A_1' symmetry (see Ref. [6, Table 4]). The pe/pe polarized Raman signal at 286 cm^{-1} has a strong counterpart in the FIR spectrum [6], where intra-ligand vibrations of e_2 symmetry are forbidden (see Ref. [6, Table 4]). Applying the selection rules (see Ref. [6, Table 4]) to the above described Ra/IR coincidence, the corresponding skeletal vibration is of E' symmetry. Obviously, the polarized Raman spectra of SmCp_3^* (in the range below 500 cm^{-1}) only show signals of skeletal vibrations.

5. Conclusions

Raman spectroscopic polarization measurements of sandwich complex solutions allow only the separation of totally symmetric from the remaining irreps, whereas those of oriented single crystals with uniformly oriented sandwich complex molecules permit the assignment of all Raman allowed modes to their irreps.

In addition, bands of the solvent do not obscure signals of the compound under consideration, and the solvation which may shift Raman bands by some cm^{-1} (as compared to the solid) and thus may cause misinterpretation is avoided (*vide supra*).

The polarized Raman spectra of an oriented single crystal of complex **1** provide unequivocal assignment of the intra-ligand, and Raman allowed skeletal vibrations which suggest the revision of a number of previous assignments of compounds **2** and **3**. In order to proceed in the same way with the exclusively IR allowed skeletal vibrations, and to clarify some still open questions, FIR/MIR polarization measurements and model calculations considering the actual molecular D_{5h} symmetry of **1** [24] are urgently needed.

However, if one assumes that the frequencies of ν_s and ν_{as} modes of compounds **1**, **2** and **3** much stronger depend on the mass of the central ion than those of tilt_s and tilt_{as} modes, the energies of

these skeletal vibrations of **1**, **2** and **3** could be derived on the basis of the actual assignments and previously recorded spectra. Obviously, for MCp_2^* , like in the case of MCp_2 ($M = \text{Fe, Ru, Os}$), ν_s increases going from Fe via Ru to Os, whereas ν_{as} shows the opposite trend.

Nevertheless, in order to check the preliminary assignments of complexes **2** and **3**, we plan to perform polarized Raman, and if possible, polarized FIR/MIR measurements of oriented single crystals. Surely, only compound **2** will exhibit well polarized spectra, whereas **3** will only show (because of its less favorable crystal structure) polarization trends which hopefully will allow unequivocal assignments.

The polarized Raman spectra of SmCp_3^* show in the range below 500 cm^{-1} only skeletal vibrations and the observed polarizations of intra-ligand vibrations of LnCp_3^* complexes can be assigned on the basis of the results obtained for complex **1**.

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