

Normal Coordinate Analysis of complexes of the type $XReO_3$ (with $X = F, Cl, Br$ and CH_3)

R. PIKL AND W. KIEFER*

*Institut für Physikalische Chemie der Universität Würzburg
Marcusstr. 9-11, D-97070 Würzburg, Federal Republic of Germany.*

A normal coordinate analysis of several $XReO_3$ -complexes with $X = F, Cl, Br$ and CH_3 is performed and discussed. A comparison of the methyl group as point mass with the halogens has been examined and discussed. The calculations have also been expanded to include the whole methyl group.

1 Introduction

Complexes of transition metals containing oxygen double bonds are of interest in catalytical processes¹. Metal-oxygen bonds can be used to characterize the complexes, because their stretching vibration modes do not couple with other vibrations. By means of normal coordinate analysis of simple complexes we can achieve a better understanding of the vibrational behaviour of these systems. Thus, in the past vibrational analysis of simple five atomic rhenium-trioxo-complexes have been performed^{2,3} and expanded recently to alkyl derivatives⁴. Our present goal has been the calculation of halogen derivatives of rhenium bonded to three oxygens including the isotopes of bromine. The exchange of halogen against methyl was carried out first with the methyl as point mass in the centre of the carbon and compared with the whole ligands. This force field was then expanded to the whole complex, methyl-trioxorhenium (see Figure 1).

2 Experimental

Raman spectra were recorded with the 647 nm line of a krypton ion laser (Spectra Physics model 2025). The spectra of methyltrioxorhenium were record-

* Author to whom correspondence should be addressed

ed in the crystalline state as well as in methylene chloride (CH_2Cl_2) solutions. 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). Infrared spectra of Nujol mulls were recorded using a Perkin Elmer Model 283 double beam spectrometer with a resolution of 4 cm^{-1} .

3 Normal coordinate analysis

Structural data for the complexes of the halogen derivatives have been taken from literature⁵⁻⁷. Bond distances are: Re-F, 1.859 Å; Re-Cl, 2.229 Å; Re-Br, 2.250 Å; Re-C, 2.060 Å; Re-O, 1.692 - 1.709 Å; C-H, 1.105 Å; bond angles: O-Re-F, O-Re-Cl, O-Re-Br, 109.5° in the average; O-Re-C, 106.0° , Re-C-H, 112.0° in the average. Five-atomic molecules like the halogen-trioxorhenium complexes have C_{3v} -symmetry with three A_1 - and three E-modes, all Raman- and infrared active. In case of these complexes we used vibrational assignments based on the literature⁸⁻¹⁰. Methyltrioxorhenium possesses with its eight atoms also C_{3v} -symmetry and thus, six A_1 - and six E-modes. The assignments for it are based on reference 7. The internal coordinates are defined in Fig. 1.

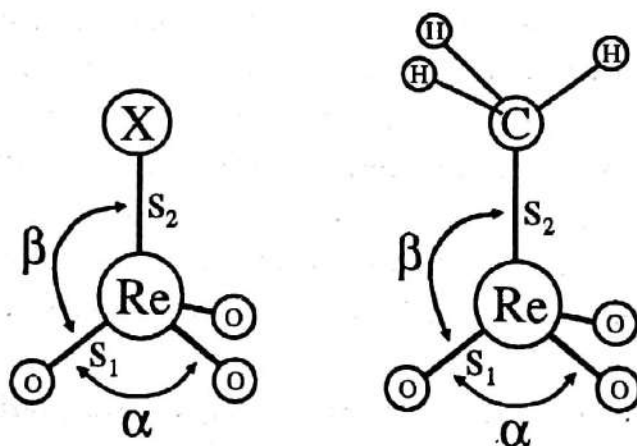


Fig. 1. Internal coordinates of XReO_3 (left) and CH_3ReO_3 (right): s_1 - rhenium-oxygen stretch coordinate, s_2 - rhenium-halogen and rhenium-carbon stretch coordinate, s_3 - carbon-hydrogen stretch coordinate, α - oxygen-rhenium-oxygen in-plane bend coordinate, β - oxygen-rhenium-halogen and -carbon in-plane bend coordinate, γ - rhenium-carbon-hydrogen in-plane bend coordinate, δ - hydrogen-carbon-hydrogen in-plane bend coordinate.

The force field calculations were carried out on personal computers with a modified version of QCMP¹¹ and VIA¹² on the basis of the GF-matrix method of Wilson¹³. The force fields of XReO₃ with methyl as point mass and as whole ligand are listed in Table 1.

Table 1-Force fields of XReO₃ with X = F, Cl, Br and CH₃

force constants ^a	F	Cl ^{35/37}	Br ^{79/81}	CH ₃ ^b	CH ₃
f (s ₁)	8.503	8.240	8.249	8.305	8.302
f (s ₂)	4.360	1.728/1.814	3.675/3.738	2.632	2.801
f (s ₃)					4.785
f (α)	1.116	0.200	0.302	0.436	0.456
f (β)	0.661	0.929	1.639	0.734	0.791
f (γ)					0.392
f (δ)					0.462
f (s ₁ s ₂)	0.016	0.006	-0.009	0.000	0.000
f (s ₁ s ₁)	0.404	0.458	0.428	0.456	0.457
f (s ₃ s ₃)					0.012
f (s ₁ α)	0.024	0.063	0.000	0.000	0.000
f (s ₁ α')	0.024	0.016	0.000	0.000	0.000
f (s ₂ α)	-	-0.122	-0.091	0.000	0.000
f (s ₂ β)	0.064	0.051	0.052	0.000	0.000
f (αα)	-	-1.075	-0.347	-	-
f (αβ)	-	-0.904	0.283	-	-
f (αβ')	-	-0.526	0.021	-	-
f (ββ)	0.274	0.158	0.500	0.000	-

a - values for stretches and their interactions are in mdyne(Å⁻¹), for bendings and all interactions thereof in mdyne(Å)(rad⁻²), and for interactions of stretchings with bendings in mdyne(rad⁻¹); b - methyl group as point mass in the centre of the carbon.

In Tables 2 and 3 we compile the potential energy distributions of XReO₃ and MeReO₃, respectively.

Table 2-Assignments and potential energy distribution for $X\text{ReO}_3$ derivatives

mode	FReO_3		ClReO_3		BrReO_3	
	calculated [cm^{-1}]	PED [%]	calculated [cm^{-1}]	PED [%]	calculated [cm^{-1}]	PED [%]
$\nu_s(\text{ReO})$	1009	100 s_1	1001	100 s_1	997	100 s_1
$\nu_{as}(\text{ReO})$	980	100 s_1	960	100 s_1	963	100 s_1
$\delta_s(\text{OREO})$	321	31 β + 69 α	293	17 s_2 + 80 β	195	33 s_2 + 67 β
$\delta_{as}(\text{OREO})$	403	31 β + 69 α	344	100 β	332	99 β
$\nu(\text{ReX})$	666	100 s_2	435	80 s_2 + 17 β	350	86 s_2 + 14 β
$\rho(\text{ReO}_3)$	196	100 α	196	68 α + 31 β	168	78 α + 21 β

Table 3-Potential energy distribution of Methyl-ReO₃

mode	measured [cm ⁻¹]	calculated [cm ⁻¹]	PED [%]
ν_s (CH)	2989	2989	100 s_3
ν_{as} (CH)	2900	2900	100 s_3
δ_{as} (CH ₃)	1371	1371	4 γ + 95 δ
δ_s (CH ₃)	1204	1204	7 s_2 + 39 γ + 54 δ
ν_s (ReO)	999	999	100 s_1
ν_{as} (ReO)	966	966	100 s_1
ρ (CH ₃)	740	740	1 β + 95 γ + 4 δ
ν (ReC)	568	568	91 s_2 + 3 γ + 5 δ
δ_s (ReO ₃)	324	324	2 s_2 + 22 α + 76 β
δ_{as} (ReO ₃)	252	252	25 α + 73 β + 1 γ
ρ (ReO ₃)	226	226	60 α + 40 β

5 Discussion

In case of the rhenium-oxygen bond we achieved for all molecules almost the same data for the force constants s_1 with values of about 8.3 +/- 0.2 mdyne/Å. This supports that the rhenium-oxygen bond lies between double and triple bond. The force fields for the halogen derivatives have no significant difference. Changes are remarkable for the values of the coordinates involving the X-Re bond. Thus, the force constant s_2 of this bond has higher values with increasing mass and smaller bond length of the halogen metal bond and has its minimum in the chlorine derivative. The methyl group fits well in this row. The first approximation as point mass shows for the used force constants nearly the same values as for the calculation including the hydrogen atoms. This effect is supported by the potential energy distribution of methyltrioxorhenium. For both calculations we have the same distribution of the internal coordinates to the vibrations. There are almost no coupling effects between stretch and deformation modes. Only the methyl-rhenium stretching vibration has part of deformation character with 8 percent.

The potential energy distribution of the halogen derivatives are different to that of the methyl group. The fluorine derivative shows only coupling effects of the deformation modes. In case of the chlorine and bromine derivatives we observe strong coupling between stretching and deformation modes. For example, the stretching vibration of the chlorine-rhenium bond has 20 percent deformation character and vice versa, the symmetrical rhenium-oxygen deformation vibration has 17 percent stretching character. This is a good example for the mixing of some vibrational modes in a molecule.

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