Experimental and Theoretical Vibrational Study of the Oxotetrachlorochromate(V) Anion in [AsPh₄][CrOCl₄]

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Abstract. Infrared and Raman spectra were obtained for tetraphenylarsonium oxotetrachlorochromate(V), $[AsPh_4][CrOCl_4]$. Equilibrium geometry and vibrational frequencies for the anion, $CrOCl_4^-$, were studied employing Density Functional Theory (DFT) methods. A comparative theoretical study was performed in order to determine the best level of theory and basis set to reproduce the experimental structure parameters and vibrational frequencies. Such frequencies served as a basis for the calculation of the scaled quantum mechanical (SQM) force field for the anion. The obtained results were compared with those obtained previously for the $VOCl_4^-$ anion.

Keywords: Oxotetrachlorochromate (V); Vibrational spectra; DFT calculations; Force field

Introduction

The [CrOCl₄]⁻ anion was studied in the form of its tetraphenylarsonium salt as part of a series of vibrational studies on inorganic molecules or anions containing transition metals as central atoms. Such previous studies included the following chemical species: $CrO_2(NO_3)_2$ [1], $VO(NO_3)_3$ [2], $VO_2X_2^-$ (X = halogen) [3], VOX_3 (X = halogen) [4], $VOCl_4^-$ (and PCl_4^+) [5].

The crystalline structure of $[AsPh_4][CrOCl_4]$ was determined by X-ray diffraction [6] but no detailed study is known about its vibrational properties. It should be mentioned that the oxotetrahalochromates are very difficult to synthesize and study because of their sensitivity to light, moisture and heat. Besides, these substances are often impurified with Cr^{III} and Cr^{VI} compounds, which difficult a proper understanding of the infrared and Raman spectra.

Experimental Section

[AsPh₄][CrOCl₄] was prepared by the method reported by *Seddon* and *Thomas* [7]. In this procedure, a solution of CrO₃ in glacial acetic acid previously saturated with hydrogen chloride is mixed with a similar solution of AsPh₄Cl; the yellowish brown powder formed is filtered off, washed with glacial acetic acid and dried in vacuo. The solid is then recrystallized in CH₂Cl₂. All the synthesis was carried out in a dry box under nitrogen atmosphere.

The infrared spectrum of the substance was obtained in a pellet of KBr, prepared under dry nitrogen atmosphere, using a Perkin Elmer Model 1600 FTIR spectrophotometer. The Raman spectrum of the solid was registered in an FT–Raman Bruker RFS 100 spectrophotometer, with light of a Nd–YAG (1064 nm) laser for excitation and a Ge detector cooled to the liquid nitrogen temperature, with a resolution of 2 cm⁻¹.

The experimental Raman spectrum is shown in Figure 1. Only one band due to the studied anion, located at 1021 cm^{-1} , is observed in the measured range ($4000-400 \text{ cm}^{-1}$) of the infrared spectrum, which is not presented here. The frequencies, relative intensities and assignment of the observed bands in the infrared and Raman spectrum are given as Supplementary material.

Calculations

All the calculations were performed with the Gaussian 03 set of programs [8]. The equilibrium geometry was calculated using gradient standard techniques and the convergence criteria implemented by defect in Gaussian. For geometry optimization the molecule was modelled with the program GaussView [9] as a square pyramidal structure to generate the input for an explorative series of calculations using different methods and basis sets. These calculations served to determine the best theoretical approximation to predict the structure and the vibrational frequencies. The employed DFT functionals were mainly B3LYP [10, 11] and B3PW91 [10, 12], to-



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Figure 1 Calculated (upper) and experimental (lower) Raman spectrum of [AsPh₄][CrOCl₄]. The anion bands are indicated with arrows.

gether with several basis sets as implemented in Gaussian. The obtained results are added as Supplementary material (Table S2).

The harmonic force field in cartesian coordinates furnished by the calculations was transformed to symmetry coordinates. The resulting force field in these coordinates was subsequently scaled using the scheme of *Pulay* et al. [13], in which the main force constants are multiplied by scale factors f_i , f_j ,... and the corresponding interaction constants are multiplied by (f_i f_j)^{1/2}, adjusting the scale factors to reproduce as well as possible the experimental wavenumbers. The potential energy distribution was subsequently calculated with the resulting scaled quantum mechanics (SQM) force field. That force field was also used to calculate the force constants expressed in terms of simple valence internal coordinates.

The conversion of the force constants in cartesian coordinates to symmetry coordinates, the adjustment of the scale factors and the calculation of the potential energy distribution was carried out with the program FCARTP [14].

Results and Discussion

Structural parameters

The performance of the different theoretical approximations in the prediction of the structural parameters was evaluated by comparison with the experimental data, obtained with X-ray diffraction techniques [6]. Such comparison is included in the Supplementary material as Table

Table 1 Geometric parameters calculated with the $6-31G^*$ basis set and different DFT functionals for $[CrOCl_4]^-$

Functionals	CrO ^{a)}	CrCl ^{a)}	ClCrCl b)	OCrCl ^{b)}
BLYP	1.558	2.298	86.3	104.7
BP86	1.549	2.274	86.3	104.7
PBEPBE	1.547	2.272	86.3	104.7
B3LYP	1.529	2.274	86.4	104.6
B3P86	1.520	2.252	86.4	104.6
PBE1PBE	1.515	2.251	86.4	104.5
B3PW91	1.521	2.258	86.4	104.5
Experimental values [6]	1.519	2.240	86.4	104.5

^{a)} Distances in Å; ^{b)} Angles in degrees

S2. In all cases the calculations predicted a structure with the expected C_{4v} symmetry (Fig. 2), in accordance with experiment. The CrO and specially the CrCl bond distances were systematically overestimated by the calculations. At least part of the discrepancies may be attributed to intermolecular forces in the crystal since the calculations were carried out in vacuo. It was found that the inclusion of polarization functions in the basis sets significantly improved the theoretical results and the lowest deviation with respect to the experimental data was obtained for the 6–31G* and 6–311G* basis sets and the B3PW91 functional. The lowest differences between experimental and calculated values were 0.003 Å for CrO and 0.018 Å for CrCl bond distances, and 0.1° for ClCrCl and 0.3° for OCrCl angles.

Additional calculations were made using different functionals with the 6–31G* basis set and the results are shown in Table 1. It can be seen that the BP86, PBEPBE and BLYP functionals yield CrO and CrCl bond distances values which are too large. Bond angles, however, were well predicted in all the calculations. The best results were obtained with the B3P86/6–31G* combination. This level of theory was used therefore to calculate the structural parameters of the [VOCl₄][–] anion, which has a predicted C_{4v} symmetry like [CrOCl₄][–] but which structure was not experimentally measured. The bond distances and angles predicted by this calculation were d(VO) = 1.541 Å, d(VCl) = 2.275 Å, α (CIVCl) = 86.9°, β (OVCl) =103.5°.

Vibrational frequencies

The 12 normal modes of vibration expected for the $[CrOCl_4]^-$ anion, of C_{4V} symmetry, are classified as $3 A_1 + 2 B_1 + B_2 + 3 E$, being the $3 A_1$ and 3 E modes active in infrared and all modes active inRaman. Exploratory calculations using the B3LYP and B3PW91 functionals and different basis sets were also performed to determine the level of theory which allowed a good agreement between theoretical and experimental frequencies, measured by the root mean standard deviation (RMSD). In this case, the use of diffuse functions improves clearly the quality of the calculated frequencies whereas the introduction of polarization functions gives less satisfactory results, that is, a reverse behaviour of that observed in the calculation of geometrical

Table 2 Definition of symmetry coordinates for $[CrOCl_4]^-$ (atomnumbers appear in Fig. 2)

A ₁ :	
$S_1 = q (5-6)$	$v_1 (v CrO)$
$S_2 = r(1-5) + r(2-5) + r(3-5) + r(4-5)$	$\nu_2~(\nu_s~CrCl_4)$
$ \begin{split} S_3 &= \alpha \; (1{-}5{-}2) + \alpha \; (2{-}5{-}3) + \alpha \; (3{-}5{-}4) + \alpha \; (4{-}5{-}1) \\ &- \beta \; (1{-}5{-}6) - \beta \; (2{-}5{-}6) - \beta \; (3{-}5{-}6) - \beta \; (4{-}5{-}6) \end{split} $	v_3 (π CrOCl ₄)
B ₁ :	
$S_4 = r (1-5) - r (2-5) + r (3-5) - r(4-5)$	$\nu_4 \; (\nu_a \; CrCl_4)$
$S_5 = \beta (1-5-6) - \beta (2-5-6) + \beta (3-5-6) - \beta (4-5-6)$	$\nu_5~(\delta_a~CrCl_4)$
B ₂ .	
$S_6 = \alpha (1-5-2) - \alpha (2-5-3) + \alpha (3-5-4) - \alpha (4-5-1)$	$\nu_6~(\delta_s~CrCl_4)$
E.	
$S_7 = r (1-5) + r (2-5) - r (3-5) - r(4-5)$	$v_7 (v_d \operatorname{CrCl}_4)$
$S_{7'} = r (1-5) - r (2-5) - r (3-5) + r(4-5)$	
$\begin{array}{l} S_8 = \beta \left(1{-}5{-}6\right) + \beta \left(2{-}5{-}6\right) - \beta \left(3{-}5{-}6\right) - \beta \left(4{-}5{-}6\right) \\ S_{8'} = \beta \left(1{-}5{-}6\right) - \beta \left(2{-}5{-}6\right) - \beta \left(3{-}5{-}6\right) + \beta \left(4{-}5{-}6\right) \end{array}$	$v_8 \; (\pi_d \; CrCl_4)$
$S_9 = \alpha (1-5-2) - \alpha (3-5-4)$	$v_9 (\delta_d \ CrCl_4)$
$S_{9'} = \alpha (4 - 5 - 1) - \alpha (2 - 5 - 3)$	

v, stretching; δ , angular deformation; π , out of plane deformation

parameters. Such an influence of the additional diffuse functions had already been observed for other compounds containing transition metals [3, 4, 5]. The lowest RMSD value (21.7 cm^{-1}) was obtained with the combination B3LYP/6-31+G (Table S3, Supplementary material) and therefore such level of theory was used in subsequent calculations. Similar results were obtained in the study of the [VOCl₄]⁻ anion [5].

Additional calculations were also carried out with other functionals and the 6-31+G basis set. Calculated frequencies with the BP86 and PBEPBE functionals were almost as good as those obtained with B3LYP. The frequencies predicted with the other functionals showed less agreement with the experimental data (Table S4, Supplementary material).

 Table 3
 Scale factors for force field of [CrOCl₄]⁻

Coordinate	Scale factor
v (CrO)	0.936
v_s (CrCl ₄)	1.128
π (CrOCl ₄)	1.150
v_a (CrCl ₄)	1.150
δ_a (CrCl ₄)	1.015
δ_s (CrCl ₄)	1.150
v_d (CrCl ₄)	0.860
π_d (CrCl ₄)	1.150
δ_d (CrCl ₄)	1.150

v, stretching; δ , deformation; π , out of plane deformation

Assignment of the observed bands

The infrared spectrum of the $[CrOCl_4]^-$ anion as a $[PCl_4]^+$ salt was previously studied by *Seddon* and *Thomas* [15]. They assigned three of the six infrared active bands, which were the CrO stretching mode at 1017 cm⁻¹ and the symmetric and antysimmetric CrCl stretching modes at 401 cm⁻¹ and 348 cm⁻¹, respectively.

The infrared spectrum of [AsPh₄][CrOCl₄] show the CrO stretching as a strong sharp band located at 1021 cm^{-1} , with a strong counterpart Raman band at the same frequency. The experimental Raman spectrum is shown in Figure 1 and is compared with the theoretical Raman spectrum calculated at the B3LYP/6-31+G level of theory. The anion bands are indicated by arrows, being other bands due to the AsPh₄⁺ cation. Out of the nine Raman active modes, eight bands can be assigned to normal modes of vibration of the studied anion. The measured frequencies compare well with those observed for the $[VOCl_4]^-$ anion [5] and therefore the assignments were similar in both cases and are detailed in Table 4. The calculated Raman intensities are in general good agreement with relative intensities in the experimental spectrum, although in some cases the anion bands overlap partially with the bands of the cation.

Table 4 Experimental and calculated wavenumbers and assignment for [CrOCl₄]⁻

Mode	Experimental	Calculated ^{a)}	SQM ^{b)}	IR Intensities ^{c)}	Raman Activities d)	PED (>10 %)	Assignment
A ₁							
v ₁	1021	1053	1021	92.8	45.0	98 % S ₁	v (Cr=O)
V ₂	346	328	346	4.0	37.0	95 % S ₂	v_{s} (CrCl ₄)
v ₃	208	187	200	0.8	8.0	95 % S ₃	π (CrOCl ₄)
B ₁							
V ₄	259	231	246	0.0	15.0	$98\% S_4 + 45\% S_5$	v_a (CrCl ₄)
v ₅	_	36	36	0.0	3.0	145 % S ₅	δ_a^{u} (CrCl ₄)
B ₂							
v ₆	238	214	228	0.0	9.0	100 % S ₆	$\delta_s \; (CrCl_4)$
Е							
V7	360	377	364	149.9	0.0	$78 \% S_7 + 40 \% S_8$	v_d (CrCl ₄)
V ₈	279	259	265	5.0	3.4	$48\% S_8 + 36\% S_7$	π_d (CrCl ₄)
V ₉	193	176	188	1.1	2.0	97 % S ₉	δ_d (CrCl ₄)
RMSD (cm ⁻¹)		21.7	8.3				

v, stretching; δ , deformation; π , out of plane deformation; ^{a)} B3LYP/6-31+G calculation (observed and calculated values in cm⁻¹); ^{b)} From scaled quantum mechanics force field (See text); ^{c)} Units in km.mol⁻¹; ^{d)} Units in Å⁴ (amu)⁻¹

The force constants

The symmetry coordinates used for the calculations are defined in Table 2 and follow the numbering of atoms shown in Figure 2.

CI2 CI2 CI2 CI3 CI4 Y

q = CrO; r = CrCl; α = ClCrCl; β = OCrCl

Figure 2 Structure and definition of internal coordinates for $[CrOCl_4]^-$.

The force constants were computed at the B3LYP/ 6-31+G level of theory and then scaled according to the process previously described in the Calculations section, leading to a final RMSD = 8.3 cm⁻¹. The computed scale factors are collected in Table 3. The SQM force field obtained in that way was used to calculate the potential energy distribution (PED), which gives the relative contribution of each symmetry coordinate to the normal modes of vibration. These values appear also in Table 4 and show that most of the modes are well described by single symmetry coordinates of Table 2, with the exception of the v₄ mode, showing a mixing of the S₄ and S₅ coordinates, and the v₇ and v₈ modes, which show a strong mixing of the S₇ and S₈ coordinates.

The scaled (SQM) force field is added as Table S5 to the Supplementary material and was used to calculate the internal or valence force constants which appear in Table 5.

Table 5 Internal force constants for [CrOCl₄]⁻

^{a)} Units are: mdyn Å⁻¹ for stretchings, stretching/stretching interactions and mdyn Å rad $^{-2}$ for deformations

Table 6 Comparison between [CrOCl₄]⁻ and [VOCl₄]⁻

	[CrOC	$[4]^{-a}$	[VOCl ₄] ^{- b)}		
	Experimental	Calculated	Experimental	Calculated	
v (MO) f (MO)	1021.0	1021.0 7.39	1017.0	1013.0 7.26	
d (MO) ^{c)}	1.519 ^d	1.520	-	1.541	
v (MCl ₄) f (MCl)	360.0, 346.0	364.0, 346.0 1.44	368.0, 359.0	368.0, 352.0 1.50	
d (MCl) ^{c)}	2.240 ^{d)}	2.252	-	2.275	

^{a)} Experimental frequencies, and calculated frequencies and force constants using the SQM force field [this work]; ^{b)} Experimental frequencies, and calculated frequencies and force constants using the SQM force field [5]; ^{c)} Bond distances calculated with B3P86/6-31G* (Table 1 and text); ^{d)} From Ref. [6]

A comparison between [CrOCl₄]⁻ and [VOCl₄]⁻

The stretching frequencies, calculated force constants and bond distances of $[CrOCl_4]^-$ are compared in Table 6 with those obtained for $[VOCl_4]^-$. It can be seen that the CrO bond is somewhat stronger than the VO bond, as evidenced by the greater stretching frequency and force constant, whereas an inverse behaviour is shown by the CrCl and VCl bonds. The bond distances are in accordance with the vibrational data in the case of the MO bonds (a smaller bond distance correspond to a stronger bond) but not for the MCl bonds. No clear explanation was found for such discrepancy.

Supplementary material. Observed vibrational bands, calculated geometry and frequencies and SQM force field matrix are provided as Supplementary material.

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