

**THE INFRARED AND RAMAN SPECTRA OF
TETRACHLOROPHOSPHONIUM (V)
OXOTETRACHLOROVANADATE (V), $\text{PCl}_4\text{VOCl}_4$.
AN EXPERIMENTAL AND THEORETICAL STUDY**

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Received February 1st, 2004. Accepted in Final Form March 15th, 2004

Dedicated to Professor Dr. P. J. Aymonino on occasion of his 75th Anniversary

Abstract

Infrared and Raman spectra were obtained for tetrachlorophosphonium (V) oxotetrachlorovanadate (V), $\text{PCl}_4\text{VOCl}_4$, and a complementary quantum chemistry theoretical study was made for both ions. The molecular structures of the PCl_4^+ and VOCl_4^- ions were optimised by means of ab-initio and Density Functional Theory, using different basis sets. Such structures present the expected T_d symmetry for PCl_4^+ and C_{4v} symmetry for VOCl_4^- . The wavenumbers corresponding to the normal modes of vibration were calculated and used to confirm the spectral band assignments. The harmonic force constants given by theory were scaled to reproduce adequately the experimental wavenumbers.

Resumen

Se obtuvieron los espectros de infrarrojo y Raman del oxotetraclorovanadato (V) de tetraclorofosfonio (V), $\text{PCl}_4\text{VOCl}_4$, y se realizó un estudio teórico complementario utilizando técnicas de la química cuántica. Las estructuras moleculares de los iones PCl_4^+ y VOCl_4^- fueron optimizadas por medio de los métodos de la Teoría de los Funcionales de Densidad, utilizando distintas bases. Esas estructuras presentan la simetría T_d esperada para el PCl_4^+ y la simetría C_{4v} para el VOCl_4^- . Se calcularon los números de onda correspondientes a los modos normales de vibración, que fueron utilizados para confirmar la asignación de bandas realizada. Las constantes de fuerza armónicas suministradas por los cálculos teóricos fueron escaladas con el fin de reproducir adecuadamente los datos experimentales.

Introduction

As part of our studies about the structural and vibrational properties of vanadium oxohalides, which comprised the VO_2X_2^- anions [1] and the VOX_3 molecules [2], we considered the oxotetrachlorovanadate (V) ion as the tetrachlorophosphonium (V) salt. As neither structural data nor a vibrational study of this substance were found in the literature, a study was undertaken which include measurement of its infrared and Raman spectra and calculations of the molecular structure and vibrational properties using quantum chemistry procedures. The VOCl_4^- anion was first prepared in the form of salts of different organic cations by Nicholls and Wilkinson [3], who reported only the corresponding VO stretching wavenumber, besides the electronic spectra. Later, Griffiths et al. prepared the $\text{PCl}_4\text{VOCl}_4$ salt and proposed an assignment for the infrared spectra [4].

We present now a more detailed study of the vibrational spectra for this compound and use the revised assignment to define a force field for each ion.

Experimental

$\text{PCl}_4\text{VOCl}_4$ was prepared by reaction between a 1,2-dichloroethane solution of phosphorus pentachloride and vanadium (V) oxide trichloride in a Schlenk apparatus under dry nitrogen [4]. The red-brown precipitate was filtered off and dried in vacuum, after washing with 1,2-dichloroethane. The product appeared as an almost black solid with a green tinge.

The infrared spectra of the pure substance between AgCl or polyethylene windows at room temperature were run on a Bruker IFS 113v FTIR spectrophotometer with a resolution of 2.0 cm^{-1} (LANAIS-EFO, Universidad Nacional de La Plata, Argentina). The obtained infrared spectrum is reproduced in Fig. 1, showing bands which are practically coincident with those reported previously by Griffiths et al. [4]. The Raman spectrum were obtained for the solid contained in a glass vessel by means of a Bruker FT Raman RF100S instrument, which used 1.064 nm radiation from a Nd/YAG laser for excitation with a maximum power of 1.5 W and 2.0 cm^{-1} of resolution (Servicios Técnicos de Investigación, Universidad de Jaén, Spain). Excitation in the near infrared resulted in an excellent Raman spectrum, reproduced in Fig. 2, which could not be obtained by previous workers using visible light [4].

The bands observed for $\text{PCl}_4\text{VOCl}_4$ in the infrared and Raman spectra are collected in Table 1 and assigned to the normal modes of each ion, in accordance with the previous proposal [4] and the present calculations.

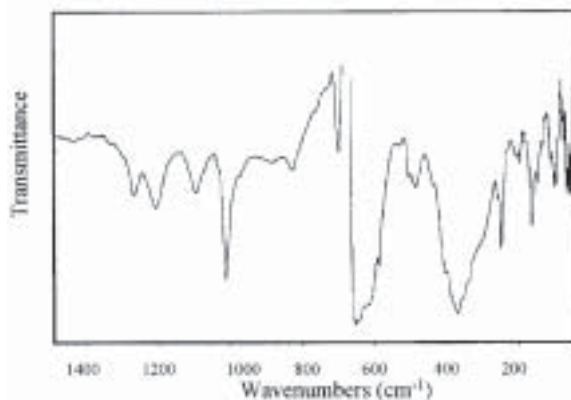


Figure 1. - The infrared spectrum of $\text{PCl}_4\text{VOCl}_4$.

Calculations

The molecular geometries of the PCl_4^+ and VOCl_4^- ions were optimised by means of Hartree-Fock procedures and also with Density Functional Theory (DFT) techniques, using in this last case the Becke's three-parameters exchange functional [5] in combination with the Lee-Yang-Parr correlation functional [6], i.e. B3LYP, with several basis sets. The wavenumbers corresponding to the normal modes of vibration were subsequently calculated with the same methods and basis sets. All the calculations were performed with the Gaussian 98 set of programs [7] considering the chemical species *in vacuo*, that is, with no interaction with the surroundings.

The harmonic force field in cartesian coordinates which resulted from the calculations were transformed to symmetry coordinates through the corresponding B matrix [8], obtained with a standard program. The resulting force field was subsequently scaled using the scheme of Pulay et al. [9], in which the diagonal force constants are multiplied by scaling factors f_i , f_j and the corresponding interaction constants are multiplied by $(f_i \cdot f_j)^{1/2}$, adjusting these factors by means of an iterative least squares procedure 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.

The force field transformation, scaling and P.E.D. calculation were performed with the program FCARTP [10]. The atomic displacements given by the Gaussian 98 programs for each vibrational mode were used to understand qualitatively the nature of the molecular vibrations; for that purpose, the corresponding data were represented graphically by means of the program GaussView [11].

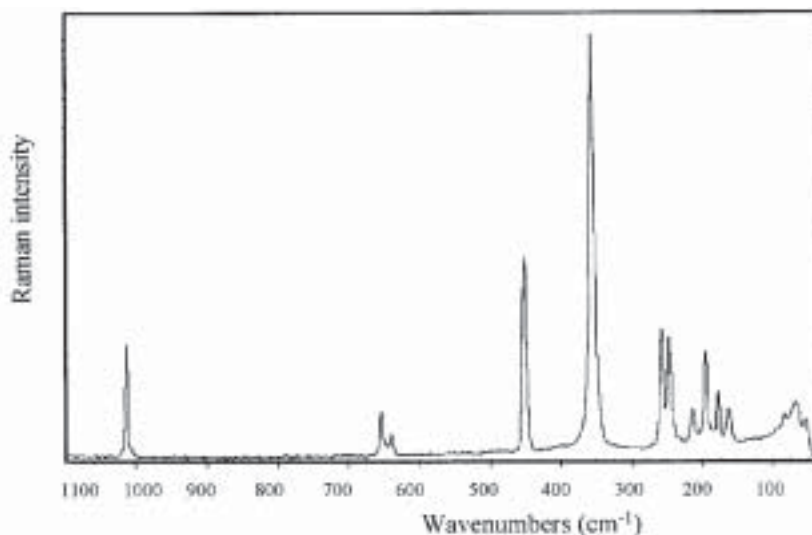


Figure. 2.- The Raman spectrum of $\text{PCl}_4\text{VOCl}_4$

The Wiberg bond indexes [12] in the studied species were calculated by means of the Natural Bond Orbitals (NBO) approach [13] as implemented in the Gaussian 98 package, using the B3LYP/6-31+G combination.

Results of the geometry optimisations and wavenumber calculations using the different theory levels, as well as the SQM force constants matrices, are deposited as supplementary material (available on the Internet at www.quimica.unlp.edu.ar/cequinor/varetti/PCl4VOCl4.pdf).

Results

The mid-infrared spectra of $\text{PCl}_4\text{VOCl}_4$ are dominated mainly by the PCl_4^+ bands. In fact, with the exception of the 1017 cm^{-1} band, the VOCl_4^- bands appear below 370 cm^{-1} . The assignment of the PCl_4^+ bands was immediate, after comparison with the data of Griffiths et al. [4]. For the VOCl_4^- anion, however, the assignments rested heavily on the calculated wavenumbers.

The results for both ions can be summarized as follows:

The tetrachlorophosphonium (V) ion, PCl_4^+

The calculations confirm the expected T_d symmetry for this cation (Fig. 3). The molecular geometry optimized with the method mentioned below lead to a PCl distance of 1.98 \AA , coincident with that measured by X-ray diffraction in PCl_4ICl_2 [14]. The nine normal modes of vibration should belong to the following symmetry species: $A_1(\text{R}) + E(\text{R}) + 2F_2(\text{IR}, \text{R})$, where the infrared (IR) and Raman (R) activities are given in parentheses.

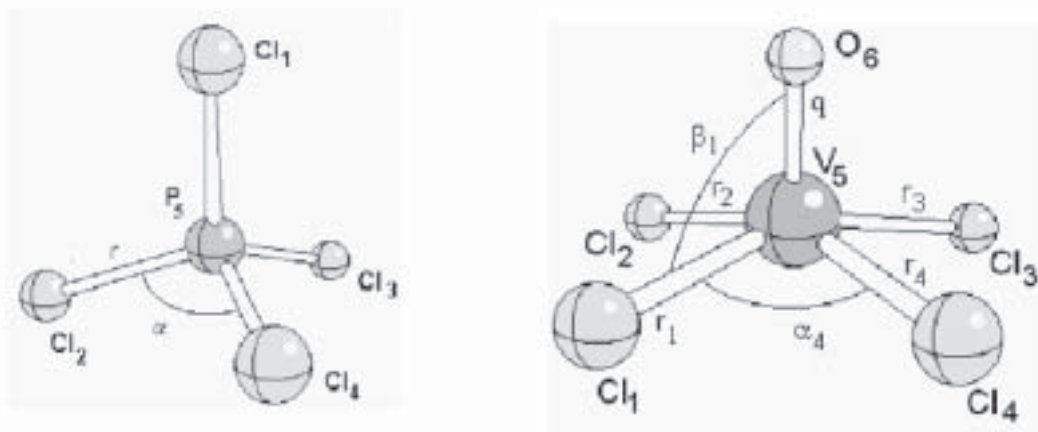


Figure 3. The calculated structures of the ions PCl_4^+ and VOCl_4^- .

Table 1.- Observed bands in the infrared and Raman spectra of PCl_4VOCl_4 .

| Experimental values (cm ⁻¹) | | Assignment |
|-----------------------------------------|--------------------|-------------------------------|
| Infrarrojo ^a | Raman ^a | |
| 1337.8 (vw) | - | $2\nu_3$ (PCl_4^+) |
| 1098.9 (m) | - | $\nu_1 + \nu_3$ (PCl_4^+) |
| 1015.6 (s) | 1017.0 (27) | ν_1 ($VOCl_4^-$) |
| 827.9 (m) | - | $\nu_2 + \nu_3$ (PCl_4^+) |
| 763.9 (vw) | - | ? |
| 699.8 (m) | - | $\nu_1 + \nu_4$ (PCl_4^+) |
| 657.0 (vs) | 656.0 (6) | ? |
| 640.0 (vs) | 641.0 (3) | ν_3 (PCl_4^+) |
| 588.9 (s) | - | $\nu_5 + \nu_6$ (VCl_5^-) |
| 505.7 (m) | - | $\nu_3 + \nu_4$ (VCl_5^-) |
| 488.6 (m) | 456.0 (sh) | ? |
| - | 454.0 (47) | ν_1 (PCl_4^+) |
| 435.3 (m) | - | ν_5 (VCl_5^-) |
| - | 359.0 (100) | ν_2 ($VOCl_4^-$) |
| 368.0 (vs) | - | ν_7 ($VOCl_4^-$) |
| 337.1 (s) | - | ν_2 ($VOCl_4^-$) |
| 256.0 (m) | 260.0 (30) | ν_8 ($VOCl_4^-$) |
| 246.0 (m) | 249.0 (28) | ν_4 (PCl_4^+) |
| - | 214.0 (12) | ν_4 ($VOCl_4^-$) |
| 195.0 (w) | 196.0 (24) | ν_6 ($VOCl_4^-$) |
| - | 178.0 (15) | ν_3 (PCl_4^+) |
| - | 163.0 (11) | ν_2 (PCl_4^+) |
| 161.0 (m) | - | ν_9 ($VOCl_4^-$) |
| 87.3 (w) | 86 (10) | b |
| 68.8 (w) | 69 (13) | b |
| - | 56 (8) | b |

^a Relative intensity in parentheses.^b Probably lattice modes.

The normal mode wavenumbers were calculated using several theory levels, as mentioned before. Comparison of the measured and theoretical wavenumbers showed that a very good reproduction of the experimental data is given by the B3LYP/6-31G* combination, with a Root Mean Square Deviation (RMSD) equal to 12.6 cm^{-1} . The calculations using different basis sets showed that the inclusion of polarization functions caused a remarkable improvement in the prediction of the vibrational wavenumbers for this ion. The calculated atomic displacement vectors did agree with the previously proposed assignment [4].

The force field in cartesian coordinates given by the calculations was transformed to a set of symmetry coordinates adequate for tetrahedral species [15]. The resulting force constants were subsequently scaled using the approach of Pulay et al. [9] already mentioned in the Calculations section, in order to reproduce as well as possible the experimental wavenumbers.

The observed and calculated wavenumbers and their RMSD values, theoretical infrared and Raman intensities and potential energy distribution appear in Table 2. The SQM force field was used to calculate the following internal force constants: $f(\text{PCI}) = 3.62$; $f(\text{PCI}/\text{PCI}) = 0.22$, in mdyn. \AA^{-1} and $f(\text{CIPCI}) = 0.83$; $f(\text{CIPCI}/\text{CIPCI}) = -0.33$, in $\text{mdyn. \AA} \cdot \text{rad}^{-2}$.

Table 2.- Experimental and calculated wavenumbers (cm^{-1}) and assignment for PCl_4^+ .

| Symmetry species | Mode | Observed | Calculated ^a | Calc. SQM ^b | IR intensities ^c | Raman activities ^d | PED ($\geq 10\%$) | Assignment |
|---------------------------|------|----------|-------------------------|------------------------|-----------------------------|-------------------------------|---------------------|------------------------|
| A_1 | 1 | 454.0 | 435.0 | 453.1 | 0.0 | 25.9 | 100 S_1 | $\nu_s(\text{PCl}_4)$ |
| E | 2 | 163.0 | 166.9 | 163.2 | 0.0 | 5.6 | 100 S_2 | $\delta(\text{CIPCI})$ |
| F_2 | 3 | 640.0 | 639.2 | 640.6 | 158.0 | 3.4 | 102 S_3 | $\nu_a(\text{PCl}_4)$ |
| F_2 | 4 | 246.0 | 245.7 | 245.5 | 6.5 | 7.2 | 88 S_4 | $\delta(\text{CIPCI})$ |
| RMSD (cm^{-1}) | | | 12.6 | 0.56 | | | | |

Key to table 2. ν , stretching; δ , deformation.

^a B3LYP/ 6-31G* calculation. Observed and calculated values in cm^{-1} .

^b From scaled quantum mechanics force field. (see text).

^c Units are km.mol^{-1} .

^d Units are $\text{\AA}^4 (\text{amu})^{-1}$.

The oxotetrachlorovanadate (V) ion, VOCl_4^-

The optimized geometry obtained by the calculations for this anion using different theory levels predict in all cases a C_{4v} structure, as shown in Fig. 3. The twelve normal modes of vibration should be classified as $3A_1$ (IR, R) + $2B_1$ (R) + B_2 (R) + $3E$ (IR, R), where the infrared (IR) and Raman (R) activities are given in parentheses.

Here again, the wavenumbers corresponding to the normal modes of vibration were calculated using several theory levels. The best agreement with the experimental data was given by the B3LYP / 6-31+G calculation, with a RMSD value of 18.4 cm^{-1} . The corresponding

optimized geometrical parameters were: $d_{\text{VO}} = 1.584 \text{ \AA}$; $d_{\text{VCl}} = 2.322 \text{ \AA}$; $\alpha_{\text{ClVCl}} = 86.9^\circ$; $\beta_{\text{OVCl}} = 103.5^\circ$. It should be remarked that in this case, in contrast with the calculations made for PCl_4^+ , the introduction of polarization functions in the used basis sets degraded notably the agreement between calculated and experimental wavenumbers, whereas the introduction of diffuse functions gave better results. Such observation is coincident with those made in the study of the VO_2X_2^- [1] and VOX_3 [2] species and point to a notably different behavior of the theoretical calculations when the central atom is a metal or a non-metal element.

As in the case of the cation, the calculated force constants in cartesian coordinates were transformed to the symmetry coordinates given in the literature for chemical species having the same geometry [16] and subsequently adjusted with the method proposed by Pulay et al. [9], generating a SQM force field which reproduces the experimental data with a RMSD of 2.5 cm^{-1} . The observed and calculated wavenumbers, potential energy distribution and other calculated data appear in Table 3. The SQM force field served to calculate the internal force constants which follows: $f(\text{VO}) = 7.26$; $f(\text{VCl}) = 1.50$; $f(\text{VO/VCl}) = 0.14$; $f(\text{VCl/VCl}) = 0.33$, in mdyn. \AA^{-1} and $f(\text{VOCl}) = 0.52$; $f(\text{ClVCl}) = 1.00$, in $\text{mdyn. \AA} \cdot \text{rad}^{-2}$.

Table 3.- Experimental and calculated wavenumbers (cm^{-1}) and assignment for VOCl_4^- .

| Symmetry species | Mode | Observed | Calculated ^a | Calc. SQM ^b | IR intensities ^c | Raman activities ^d | PED ($\geq 10\%$) | Assignment |
|---------------------------|------|----------|-------------------------|------------------------|-----------------------------|-------------------------------|---------------------|--------------------------|
| A_1 | 1 | 1015.0 | 1067.9 | 1012.9 | 125.5 | 25.4 | 98 S_1 | $\nu(\text{VO})$ |
| | 2 | 359.0 | 332.1 | 352.3 | 4.8 | 39.3 | 98 S_2 | $\nu_s(\text{VCl}_4)$ |
| | 3 | 178.0 | 188.1 | 175.8 | 1.4 | 7.4 | 98 S_3 | $\pi(\text{VOCl}_4)$ |
| B_1 | 4 | 214.0 | 217.4 | 213.6 | 0.0 | 6.3 | 98 S_4 | $\nu_a(\text{VCl}_4)$ |
| | 5 | - | 37.2 | 38.9 | 0.0 | 2.7 | 119 $S_5 + 22 S_4$ | $\delta_a(\text{VCl}_4)$ |
| B_2 | 6 | 195.0 | 214.7 | 198.9 | 0.0 | 5.2 | 100 S_6 | $\delta_s(\text{VCl}_4)$ |
| E | 7 | 368.0 | 368.8 | 367.8 | 249.6 | 0.0 | 107 S_7 | $\nu_d(\text{VCl}_4)$ |
| | 8 | 256.0 | 256.2 | 255.6 | 1.3 | 3.3 | 76 S_8 | $\pi_d(\text{VCl}_4)$ |
| | 9 | 161.0 | 162.9 | 162.0 | 12.9 | 1.0 | 112 S_9 | $\delta_d(\text{VCl}_4)$ |
| RMSD (cm^{-1}) | | | 18.4 | 2.5 | | | | |

ν , stretching; δ , deformation; π , deformation out of plane.

^a B3LYP/6-31+G calculation. Observed and calculated values in cm^{-1} .

^b From scaled quantum mechanics force field (see text).

^c Units are km.mol^{-1} .

^d Units are $\text{\AA}^4 (\text{amu})^{-1}$.

Discussion

The internal force constants and other parameters obtained for VOCl_4^- and for the previously studied species VO_2Cl_2^- and VOCl_3 are compared in Table 4.

Table 4 - Comparison of internal force constants ^a and other parameters for VO_2Cl_2^- , VOCl_3 and VOCl_4^- .

| | VO_2Cl_2^- (C_{2v}) | VOCl_3 (C_{3v}) | VOCl_4^- (C_{4v}) |
|-----------------------|-----------------------------------------|------------------------------|--------------------------------|
| f(V-O) | 6.55 ^b | 7.73 ^c | 7.26 ^d |
| f(V-Cl) | 1.87 | 2.67 | 1.50 |
| f(VO/VCl) | 0.17 | 0.18 | 0.14 |
| f(VCl/VCl) | 0.12 | 0.14 | 0.33 |
| f(VOCl) | 0.50 | 0.58 | 0.52 |
| f(CIVCl) | 0.46 | 0.41 | 1.00 |
| d(VO) (Å) | 1.582 ^e | 1.570 ^f | 1.580 ^g |
| WI (VO) ^h | 1.838 | 2.065 | 2.027 |
| d(VCl) (Å) | 2.226 ^e | 2.142 ^f | 2.322 ^g |
| WI (VCl) ^h | 0.698 | 1.091 | 0.841 |
| α (CIVCl) | 110.8 ^e | 111.0 ^f | 86.9 ^g |

^a Units are $\text{mdyn } \text{Å}^{-1}$ for stretching and stretching/stretching interaction and $\text{mdyn } \text{Å rad}^{-2}$ for angle deformation.

^b Force constants from Ref. 1; ^c Force constants from Ref 2; ^d Force constants from this work; ^e Experimental value from Ref. 17; ^f Experimental value from Ref. 18; ^g Calculated with B3LYP/6-31+G; ^h Wiberg index calculated with B3LYP/6-31+G.

It is observed that the VO force constants and Wiberg indexes for the VO bond follow the same trend, with a maximum in VOCl_3 . The VO distances, however, are quite similar although the smaller value measured for VOCl_3 seem to correspond with the larger VO force constant. The comparison of the VCl force constants show again the larger value for VOCl_3 , correlated with a relatively large Wiberg index and smaller VCl bond distance.

The VOCl_4^- anion, with a very different geometry in comparison with the other two species, show notably high values for the CIVCl deformation and VCl/VCl interaction force constants. Such observation as well as the relatively large VCl bond distance could be explained by the small CIVCl angle, which causes a strong interaction between the bulky chlorine atoms.

The potential energy distributions obtained for both ions (Tables 2 and 3) shown that there is only a small degree of mixing between the modes of vibration defined by the used symmetry coordinates. This is shown by the participation of the diagonal force constants in each mode, which are $\geq 88\%$ for PCl_4^+ and $\geq 76\%$ for VOCl_4^- .

Acknowledgements

The research grants provided by CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina) and UNLP (Universidad Nacional de La Plata) are gratefully

acknowledged, as well as the financial help received from CIUNT (Consejo de Investigaciones de la Universidad Nacional de Tucumán).

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