

VIBRATIONAL SPECTRA, ASSIGNMENTS AND NORMAL COORDINATE ANALYSES FOR CRYSTALLINE ZIRCONIUM TETRACHLORIDE AND TETRABROMIDE

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Abstract—Raman and far-IR spectra have been obtained of crystalline $ZrCl_4$ and $ZrBr_4$. The observed frequencies have been interpreted on the basis of the C_{2h} symmetry of the Bravais unit cell and have been subjected to a normal coordinate analysis. The interpretation and results are satisfactorily in accord with the X-ray structure.

INTRODUCTION

The structure of solid zirconium tetrachloride is known from X-ray studies[1] to consist of extended chains of distorted octahedra with two bridging chlorine atoms between adjacent zirconium atoms. Although the unit cell possesses a center of symmetry, the two pairs of bridging chlorine atoms attached to a given zirconium atom are not trans to each other. The factor group symmetry thus is C_{2h} with two zirconium atoms per unit cell. The X-ray structure of zirconium tetrabromide has not been reported but Krebs in his report on the chloride[1] states that the bromide is isostructural with the chloride.

The zirconium halides have been subjected to a limited amount of spectroscopic study. In the vapor phase the work of Clark *et al.*[2] indicates that the tetrachloride, tetrabromide and tetraiodide all have the expected tetrahedral form. No complete studies of the liquid phase have been reported although a number of authors[3-6] have examined spectra of the octahedral hexahalide anion ZrX_6^{2-} in different solvents. Prior to the present work only the tetrachloride had been studied in the solid state[7,8]. In their IR and Raman study of $ZrCl_4$, Weidlein, Mueller and Dehnicke[7] suggested that a polymeric model with bridging chlorines and an octahedral structure around the zirconium was the most reasonable. However, since their work was prior to the X-ray work of Krebs[1] they assumed a D_{2h} symmetry model and made their assignments accordingly. Quite recently, Brockner and Demiray[8] analyzed and compared the spectra of solid and liquid $(ZrCl_4)_n$. The authors based their frequency assignments on a dimeric model with C_i symmetry.

In the present work the Raman and IR spectra of solid zirconium tetrachloride and tetrabromide are reported. Examination of the structure reported by

Krebs[1] indicated that the use of C_{2h} symmetry rather than the D_{2h} symmetry utilized previously provided a more realistic model. Assignments were made with the help of a normal coordinate analysis based on the factor group symmetry.

EXPERIMENTAL

Zirconium tetrachloride obtained from commercial sources was purified by repeated vacuum sublimation. The tetrabromide was prepared by direct combination of the elements and likewise purified by vacuum sublimation.

IR spectra in the range of 80-500 cm^{-1} were obtained with a Digilab FTS-20 Fourier transform spectrometer. Samples were in the form of mulls prepared in the dry box and contained between Mylar plates. Raman spectra were obtained from polycrystalline samples using a SPEX Ramalog 4 spectrometer equipped with a Spectra Physics 164 argon ion laser. Excitation utilized the 4880 Angstrom line with power levels of the order of 100 mw. Estimated uncertainties in peak positions are approximately 1 cm^{-1} for well defined peaks.

RESULTS

The observed IR and Raman fundamentals together with symmetry assignments are listed in Table 1 for the chloride and Table 2 for the bromide. Raman spectra are shown in Fig. 1 and far-IR spectra in Fig. 2. A factor group analysis based on two $ZrCl_4$ units per Bravais cell and C_{2h} symmetry predicts the following vibrational structure: $7A_g + 8B_g + 6A_u + 6B_u$. All g vibrations are Raman active and all u are infrared active. One lattice mode is included in the A_g class and two in the B_g leaving six internal modes in each class, three associated primarily with bond stretchings and three with deformations. Stretching frequencies may be expected in the range between 450 and 250 cm^{-1} when $X = Cl$ and between 300 and 150 cm^{-1} when $X = Br$.

In the Raman Spectrum of the chloride, five bands are observed between 220 and 415 cm^{-1} . We conclude either the missing frequency has a very low intensity or one of the observed bands is an accidentally degenerate pair. The latter possibility seems a reasonable likelihood and the assumption appears borne out by the fact that the

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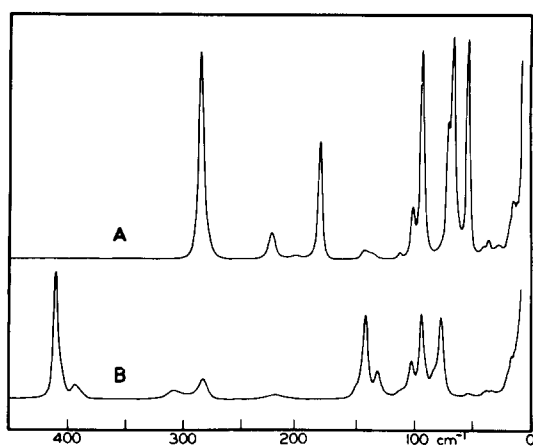
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Table 1. Observed and calculated fundamental frequencies, symmetry assignments and potential energy distributions for crystalline zirconium tetrachloride

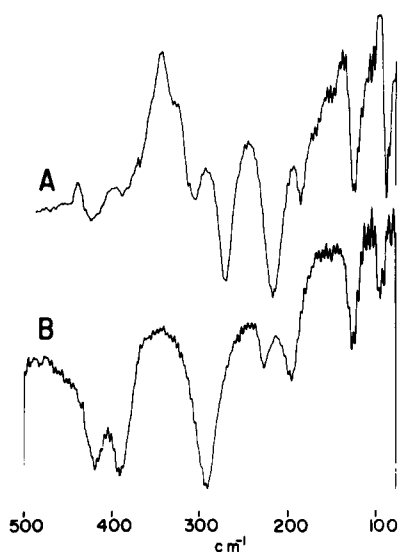
Symmetry Species	Freq. No.	Observed Frequency*	Calculated Frequency	Potential Energy Distribution**
A_g	1	411 cm^{-1}	411 cm^{-1}	96S1
	2	283	284	86S1, 12S6
	3	220	220	82S3
	4	142	142	89S4, 10S6
	5	95	96	75S6
	6	78	73	75S5, 10S6
B_g	7	394	394	93S7
	8	309	309	94S8
	9	220	220	86S9
	10	132	133	72S10, 17S12
	11	102	105	53S11, 44S12
	12	82	75	15S10, 42S11, 36S12
A_u	13	420	420	95S13
	14	293	293	100S14
	15	227	226	92S15
	16	126	125	46S16, 21S17, 33S18
	17	-	80	35S16, 64S17
	18	-	54	20S16, 13S17, 66S18
B_u	19	390	390	94S19
	20	293	293	92S20
	21	198	198	92S21
	22	98	98	88S22
	23	-	47	94S23
	24	-	25	89S24

* Gerade frequencies observed in Raman effect, ungerade in infrared

** Contributions less than 10 percent omitted

Fig. 1. IR spectra of crystalline ZrBr_4 (A) and ZrCl_4 (B) in the form of Nujol Mulls (resolution 2 cm^{-1}).

weak band at 143 cm^{-1} in the bromide spectrum, which corresponds to the band at 220 cm^{-1} in the chloride, shows a distinct shoulder at 135 cm^{-1} . We thus infer that the 220 cm^{-1} band is the degenerate pair, the two frequencies separating slightly when the heavier bromine mass is present. With this identification of the accidentally degenerate band, assignments were completed with the assumptions that the A_g modes would be somewhat more intense than the B_g , and that the stretching of short

Fig. 2. Raman spectra of crystalline ZrBr_4 (A) and ZrCl_4 (B) (resolution 0.5 cm^{-1}).

Zr-Cl bonds would occur at higher frequencies than those of longer bonds. Assignments of the Zr-Br stretching modes paralleled those of the chloride. However, for this substance the normal coordinate calculations gave physically unreasonable results unless it

Table 2. Observed and calculated fundamental frequencies, symmetry assignments and potential energy distributions for crystalline zirconium tetrabromide

Symmetry Species	Freq. No.	Observed Frequency*	Calculated Frequency	Potential Energy Distribution**
A _g	1	285 cm ⁻¹	285 cm ⁻¹	86S1, 13S3
	2	183	183	93S2
	3	143	143	11S1, 80S3
	4	92	92	87S4, 11S6
	5	66	65	11S4, 74S6
	6	53	45	81S5, 10S6
B _g	7	285	285	83S7, 12S9
	8	223	223	80S8, 19S12
	9	135	135	14S7, 74S9
	10	100	98	16S8, 17S11, 58S12
	11	70	73	41S10, 53S11
	12	53	52	51S10, 22S11, 16S12
A _u	13	305	305	82S13, 16S15
	14	188	188	100S14
	15	155	155	17S13, 81S15
	16	90	90	56S16, 36S18
	17	-	51	39S16, 36S17, 24S18
	18	-	38	55S17, 37S18
B _u	19	270	270	86S19, 11S21
	20	218	218	92S20
	21	125	125	13S19, 83S21
	22	-	58	90S22
	23	-	28	93S23
	24	-	10	95S24

* Gerade frequencies observed in Raman effect, ungerade in infrared

** Contributions less than 10 percent omitted

was assumed that the band at 285 cm⁻¹ consisted of an accidentally degenerate pair of frequencies.

In the low frequency (60–150 cm⁻¹) Raman region, a group of six bands is present in the chloride spectrum, one a shoulder on the high side of the band at 78 cm⁻¹. We assign these to the six gerade deformation modes, the three most intense bands again arbitrarily being attributed to the A_g modes. In the bromide spectrum, only five bands could be identified, the presumption being that another accidentally degenerate pair is present. The most likely choice appears to be the 53 cm⁻¹ band of the bromide since the shoulder on the corresponding band in the chloride spectrum has disappeared. Three very low frequencies, below about 50 cm⁻¹, were observed in each spectrum and are assigned to the Raman active lattice modes.

Interpretation of the infrared spectrum was complicated by the fact that the lower limit of the spectrometer prevented observations below 80 cm⁻¹ where most of the deformation modes were located. Also, the very striking resemblance between the chloride and bromide spectra found in the Raman case is not as pronounced in the IR further hindering assignments. As in the Raman spectrum of the chloride, only five bands were observed in the range 200–420 cm⁻¹ in the infrared spectrum. We assumed the broad intense band at 293 cm⁻¹ to consist of an accidentally degenerate pair of frequencies, and were thus able to identify six Zr–Cl stretching frequencies. This assumption appears

reasonable since the band in question is replaced by two bands of lower intensity in the bromide spectrum. Unfortunately, single crystal spectra were not available and the respective symmetry assignments of the two sets of paired frequencies at 420 and 390 cm⁻¹, and 227 and 198 cm⁻¹ therefore has to be made arbitrarily in the absence of any significant guidance from the normal coordinate analysis. In the case of the bromide, six bands were identified in the Zr–Br stretching region, although the one at 155 cm⁻¹ was quite weak. Symmetry assignments again were made arbitrarily but matched with those for the chloride. Only two deformation bands were observed in the IR spectrum of the chloride and one in that of the bromide.

Normal coordinate analysis

A diagram of the two ZrCl₄ units showing structure in the unit cell is displayed in Fig. 3. The atom numbers shown in the same figure serve to define the internal coordinates described in Table 3. Symmetry coordinates listed in Table 3 were assembled using the coordinates described by Cyvin[9] for Nb₂Cl₁₀ as a guide and are free of redundancies. A *g* matrix for the unit cell was constructed using the method outlined by Shimanouchi[10] and transformed into a symmetry coordinate basis using the definitions of the symmetry coordinates. Three types of Zr–Cl bonds are present in the ZrCl₄ structure based on the X-ray determination[1]: terminal bonds with lengths $d = 2.307$ Å, short bridging

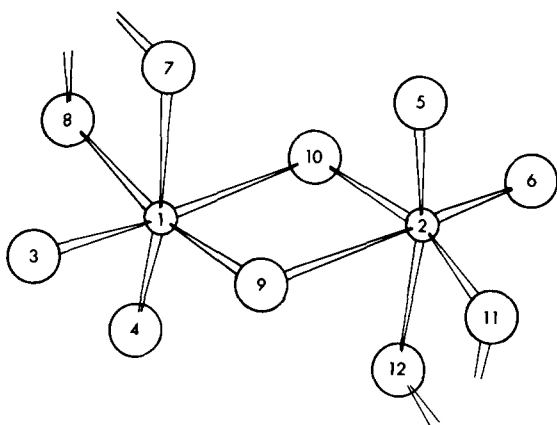


Fig. 3. Schematic diagram showing the atom numbering in the Bravais unit cell of $ZrCl_4$.

bonds with $r = 2.498$ Å, and long bridging bonds with $R = 2.655$ Å. In the crystal, the angles defined by the bonds to zirconium deviate by a few degrees from orthogonal. However, all angles were assumed to be ninety degrees for purposes of the present calculations. Since only two of the eight angles deviate by as much as ten degrees from a right angle, and most are appreciably less, the effect of this approximation was considered

minor. In the absence of structural parameters for the bromide, estimated Zr-Br bond lengths of $d = 2.45$ Å, $r = 2.64$ Å and $R = 2.80$ Å were used with the assumption that the chloride and bromide structures were closely similar. This appears quite reasonable in view of the very marked similarity of the two Raman spectra.

The observed vibrational frequencies for each species were fitted with symmetry force constants using a standard iterative least squares program carrying the laboratory designation JACO-3D[11]. Since no isotopic or other supplementary data were available, all off-diagonal constants were constrained to zero and the frequencies were weighted uniformly. In the A_u and B_u classes, estimated values for the missing deformation frequencies were included but with low weights. No difficulty was encountered in fitting the experimental frequency assignments with diagonal potential function.

Symmetry force constants for the chloride and bromide are shown in Table 4. Potential energy distributions for the two species are given along with the calculated frequencies in Tables 1 and 2. As can be seen from the potential energy distributions, the stretching frequencies are relatively unmixed but the low frequencies tend to be complex. The B_g class frequencies for the bromide particularly were strongly mixed and their description as a group had the poorest correspondence of all the classes to the corresponding class of the chloride. By

Table 3. Valence and symmetry coordinates for crystalline ZrX_4

<u>Valence Coordinate</u>	<u>Defined by atoms</u>	<u>Valence Coordinate</u>	<u>Defined by atoms</u>
d_1	1 - 3	ϕ_1	3 - 1 - 9
R_1	1 - 10	ϕ'_1	3 - 1 - 8
r_1	1 - 9	η_1	7 - 1 - 10
α_1	3 - 1 - 4	ω_1	7 - 1 - 9
β_1	3 - 1 - 7	τ_1	9 - 1 - 10 - 2
δ_1	7 - 1 - 8	τ'_1	10 - 1 - 9 - 2

No. 2 coordinates are related to No. 1 through inversion
 No. 3 coordinates are related to No. 1 through C_2 rotation

<u>A_g Symmetry Coordinates</u>	<u>Approximate description</u>
$S_1 = d_1 + d_2 + d_3 + d_4$	Sym. terminal Zr-X bond stretch
$S_2 = r_1 + r_2 + r_3 + r_4$	Short bridge bond stretch
$S_3 = R_1 + R_2 + R_3 + R_4$	Long bridge bond stretch
$S_4 = \alpha_1 + \alpha_2 + \eta_1 + \eta_2$ $- \beta_1 - \beta_2 - \beta_3 - \beta_4$	Terminal ZrX_2 deformation
$S_5 = \delta_1 + \delta_2 + \delta_3 + \delta_4$	Bridge ring deformation
$S_6 = \phi_1 + \phi_2 + \phi_3 + \phi_4$ $- \phi'_1 - \phi'_2 - \phi'_3 - \phi'_4$	ZrX_2 twist

<u>B_g Symmetry Coordinates</u>	<u>Approximate description</u>
$S_7 = d_1 + d_2 - d_3 - d_4$	Asym. terminal Zr-X stretch
$S_8 = r_1 + r_2 - r_3 - r_4$	OOP short bridge bond stretch
$S_9 = R_1 + R_2 - R_3 - R_4$	OOP long bridge bond stretch
$S_{10} = \beta_1 + \beta_2 - \beta_3 - \beta_4$	ZrX_2 rock
$S_{11} = \omega_1 + \omega_2 - \omega_3 - \omega_4$	Chain mode
$S_{12} = \phi_1 + \phi_2 - \phi_3 - \phi_4$ $- \phi'_1 - \phi'_2 + \phi'_3 + \phi'_4$	ZrX_2 flap

Table 3. (Contd)

<u>A_u</u>	<u>Symmetry Coordinates</u>	<u>Approximate description</u>
	$S_{13} = d_1 - d_2 + d_3 - d_4$	OOP sym. terminal Zr-X stretch
	$S_{14} = r_1 - r_2 + r_3 - r_4$	Asym. short bridge bond stretch
	$S_{15} = R_1 - R_2 + R_3 - R_4$	Asym. long bridge bond stretch
	$S_{16} = \alpha_1 - \alpha_2 + \eta_1 - \eta_2$ $- \beta_1 + \beta_2 - \beta_3 + \beta_4$	OOP ZrX ₂ deformation
	$S_{17} = \phi_1 - \phi_2 + \phi_3 - \phi_4$ $- \phi_1' + \phi_2' - \phi_3' + \phi_4'$	OOP ZrCl ₂ twist
	$S_{18} = \tau_1 + \tau_2 + \tau_3 + \tau_4$ $- \tau_1' - \tau_2' - \tau_3' - \tau_4'$	Ring torsion
<u>B_u</u>	<u>Symmetry Coordinates</u>	<u>Approximate description</u>
	$S_{19} = d_1 - d_2 - d_3 + d_4$	OOP asym. terminal Zr-X stretch
	$S_{20} = r_1 - r_2 - r_3 + r_4$	OOP asym. short bridge bond stretch
	$S_{21} = R_1 - R_2 - R_3 + R_4$	OOP asym. long bridge bond stretch
	$S_{22} = \beta_1 - \beta_2 - \beta_3 + \beta_4$	OOP ZrX ₂ rock
	$S_{23} = \phi_1 - \phi_2 - \phi_3 + \phi_4$ $- \phi_1' + \phi_2' + \phi_3' - \phi_4'$	OOP ZrX ₂ flap
	$S_{24} = \omega_1 - \omega_2 - \omega_3 + \omega_4$	chain flex

OOP = Out-of-phase, referring to the two ZrX₄ units in the Bravais cell.

Table 4. Symmetry force constants for crystalline ZrCl₄ and ZrBr₄

<u>Symmetry Species</u>	<u>Indices</u>	<u>ZrCl₄</u>	<u>ZrBr₄</u>
A _g	1, 1	2.420	1.803
	2, 2	1.481	1.485
	3, 3	.722	.683
	4, 4	.591	.567
	5, 5	1.009	.574
	6, 6	.455	.458
B _g	7, 7	2.180	1.740
	8, 8	1.058	.710
	9, 9	.765	.587
	10,10	.534	.494
	11,11	.416	.355
	12,12	.445	.647
A _u	13,13	2.507	2.011
	14,14	1.769	1.665
	15,15	.831	.853
	16,16	.309	.399
	17,17	(.350)†	(.234)
	18,18	(.100)	(.125)
B _u	19,19	2.161	1.608
	20,20	.916	.742
	21,21	.637	.533
	22,22	.400	(.302)
	23,23	(.350)	(.262)
	24,24	(.150)	(.050)

Units: Stretching constants, md/Å; bending, md-Å²

† Numbers in parentheses correspond to unobserved frequencies; they were set initially and not adjusted.

means of the defining equations for the symmetry coordinates (Table 3), the symmetry force constants for the stretching motions can be decomposed into the corresponding valence force constants. This is not possible for the deformation modes due to redundancies. The values for $ZrCl_4$ derived from the A_g and B_g symmetry constants are: for the terminal $Zr-Cl$ bonds, $f_d = 2.30$ md/A; for the short $Zr-Cl$ bridge bonds, $f_r = 1.27$ md/A and for the long $Zr-Cl$ bridge bonds, $f_R = 0.74$ md/A. The stretch-stretch interaction constants are $f_{dd} = 0.12$, $f_{rr} = 0.21$, $f_{RR} = -0.02$, all in md/A. The corresponding constants for $ZrBr_4$ are (in md/A): $f_d = 1.77$, $f_r = 1.10$, $f_R = 0.64$, $f_{dd} = 0.03$, $f_{rr} = 0.39$ and $f_{RR} = 0.05$.

No previous calculations of force constants for solid ZrX_4 were found in the literature and hence there is no ready comparison for the values found in the present work. However, the constants for $ZrCl_4$ in Table 3 are quite similar in magnitude to the symmetry force constants given in Ref. [9] for Nb_2Cl_{10} which also has an octahedral configuration around Nb with bridging chlorine atoms. Brisdon, Ozin and Walton [6] have reported a value of 1.54 md/A for the $Zr-Cl$ bond in the anion species $ZrCl_6^{2-}$ and a value of 1.24 md/A for the $Zr-Br$ bond in $ZrBr_6^{2-}$. Again, the comparison is not simple but their values agree very well with those obtained in the present work. Moreover, the ratio of their zirconium-chloride stretching force constant to that of the bromide is essentially the same as that found here. One may conclude from the present study that the vibrational spectra of the two zirconium tetrahalides in the solid state are straightforwardly interpretable in terms of the X-ray structure. The principal uncertainties which exist

relate to relative symmetry assignments of neighboring bands, a problem which can be resolved only by single crystal work.

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REFERENCES

1. B. Krebs, *Angew. Chem. Int. Edn.* **8**, 146 (1969); B. Krebs, *Z. Anorg. Allgem. Chem.* **378**, 263 (1970).
2. R. J. H. Clark, B. K. Hunter and D. M. Rippon, *Chem. and Indian* **787** (1971); R. J. H. Clark, B. K. Hunter and D. M. Rippon *Inorg. Chem.* **11**, 56 (1972).
3. W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A.* 675 (1967).
4. D. M. Adams and D. C. Newton, *J. Chem. Soc. A.* 2262 (1968).
5. J. E. O. Davies and D. A. Long, *J. Chem. Soc. A.* 2560 (1968).
6. B. J. Brisdon, G. A. Ozin and R. A. Walton, *J. Chem. Soc. A.* 342 (1969).
7. J. Weidlein, U. Mueller and K. Dehnicke, *Spectrochim. Acta* **24A**, 253 (1968).
8. W. Brockner and A. F. Demiray, *J. Raman Spectros.* **7**, 329 (1978).
9. S. J. Cyvin, H. Hovdan and W. Brockner, *J. Inorg. Nucl. Chem.* **37**, 1905 (1975).
10. T. Shimanouchi, M. Tsuboi and T. Miyazawa, *J. Chem. Phys.* **35**, 1597 (1961).
11. L. H. Jones, R. C. Taylor and R. T. Paine, *J. Chem. Phys.* **70**, 749 (1979).