Vibrational Spectra and Molecular Association of Titanium Tetraisopropoxide

Paul D. Moran, Graham A. Bowmaker,* and Ralph P. Cooney

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand

Kim S. Finnie, John R. Bartlett, and James L. Woolfrey

Materials Division, Australian Nuclear Science and Technology Organisation, Private Mail Bag 1,
Menai, NSW 2234, Australia

Received July 31, 1997

The Fourier transform-infrared (FT-IR) and polarized FT-Raman spectra of titanium tetraisopropoxide (tetraisopropoxytitanium, TPT), in pure and diluted forms, and of 2-propanol have been investigated in conjunction with previous assignments for related compounds to obtain a comprehensive assignment of the vibrational spectra. Evidence was obtained for the presence of both monomeric and associated species of TPT. The latter are formed by coordination expansion through bridging isopropoxy ligands. For both monomeric and associated TPT species, vibrational modes of isopropoxy ligands with ν(C−O) mode character were coupled to ν_s(Ti−O) and ν_{as}(Ti−O) modes (interligand coupling). The symmetrically coupled ligand modes gave rise to intense, strongly polarized bands in the Raman spectrum. The antisymmetrically coupled ligand modes gave rise to strong bands in the IR spectrum at lower wavenumbers than the corresponding Raman bands. Molecular association of TPT produced negligible shifts in the ligand modes coupled to the ν_s(Ti−O) mode in the Raman spectrum. In contrast, the degeneracy of the strong ligand modes coupled to the ν_{as}(Ti−O) mode was lifted upon molecular association, yielding band shifts and splittings in the IR spectrum of neat TPT.

Introduction

The solution-based sol−gel method has been employed extensively in the production of oxide ceramics. In comparison to other synthetic techniques, it has the advantages of lower processing temperatures, the ability to form a range of products from powders to fibers, and control over the synthetic process from precursor to product.[1] An understanding of the sol−gel method involves an understanding of the reactions and processes occurring at the molecular level. This is lacking particularly for the transition metal oxides, whose chemistry is less studied than that of silica.[2]

Vibrational spectroscopy is an excellent method for structural analysis and for the determination of molecular interactions in the liquid or solid state. Of the transition metal oxide precursors used in the production of ceramics, titanium tetraisopropoxide $Ti(O^iPr)_4$ (tetraisopropoxytitanium, TPT) is one of the most widely used. However, the vibrational spectrum has not been thoroughly studied. Only tentative assignments of Ti−O[3−5] and C−O[3,5,6] stretching modes have been made, and there is a lack of agreement between these.

Titanium alkoxides are known to form dimeric, trimeric, and higher molecularity species,[7] which is a response to the electron-deficient nature of the transition metal in these tetracoordinated compounds.[1] This is achieved through the formation of alkoxide bridges, where the degree of association or "molecular complexity" (e.g., 1.4 for TPT based on ebullioscopic measurements)[7] is dependent on the steric constraints of the ligand.

To investigate reaction pathways in the sol−gel process, many recent studies have involved the complexes formed upon reaction of TPT with various coordinating species (acetic acid,[8−11] methacrylic acid,[12] acetylacetone[13,14]), focusing on structure determination of the oxo alkoxide formed. Complexes derived from TPT also find catalytic applications in organic chemistry,[15] and related structures are of current interest in inorganic chemistry.[16,17] However, nuclear magnetic resonance spectroscopy and X-ray crystallographic structure determination have been the chief investigative techniques in the absence of a sound understanding of the vibrational spectrum of TPT.

---

(1) Livage, J.; Henry, M.; Sanchez, C. *Prog. Solid State Chem.* **1989**, *18*, 259−341.
(2) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979.
(3) Barraclough, C. G.; Bradley, D. C.; Lewis, J.; Thomas, I. M. *J. Chem. Soc.* **1961**, 2601−5.
(4) van Vlierberge-Torgerson, B. A.; Dunuwila, D.; Berglund, K. A. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 65−70.
(5) Poncelet, O.; Robert, J. C.; Guilment, J. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 249−55.
(6) Zeitler, V. A.; Brown, C. A. *J. Phys. Chem.* **1957**, *61*, 1174−7.
(7) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*, 5th ed.; Academic Press: London, 1978; p 63.
(8) Doeuff, S.; Dromzee, Y.; Taulelle, F.; Sanchez, C. *Inorg. Chem.* **1989**, *28*, 4439−45.
(9) Alam, T. M.; Boyle, T. J.; Buchheit, C. D.; Schwartz, R. W.; Ziller, J. W. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 35−40.
(10) Livage, J.; Sanchez, C. *J. Non-Cryst. Solids* **1992**, *145*, 11−9.
(11) Sanchez, C.; Livage, J. *New J. Chem.* **1990**, *14*, 513−21.
(12) Schubert, U.; Arpac, E.; Glaubitt, W.; Helmerich, A.; Chau, C. *Chem. Mater.* **1992**, *4*, 291−5.
(13) Léaustic, A.; Babonneau, F.; Livage, J. *Chem. Mater.* **1989**, *1*, 240−7.
(14) Léaustic, A.; Babonneau, F.; Livage, J. *Chem. Mater.* **1989**, *1*, 248−52.
(15) Finn, M. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 113−26.
(16) Eilerts, N. W.; Heppert, J. A.; Kennedy, M. L.; Takusagawa, F. *Inorg. Chem.* **1994**, *33*, 4813−4.
(17) Hampden-Smith, M. J.; Williams, D. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 4076−81.

S0020-1669(97)00943-9 CCC: $15.00

To assign the vibrational spectrum of TPT, this study investigates the FT-IR and polarized FT-Raman spectra of 2-propanol and of neat and diluted TPT. These spectra have been analyzed in conjunction with previous assignments of compounds containing the isopropyl group.[18-26] This assignment will be invaluable in the investigations of coordination and sol−gel chemistry involving this common chemical precursor.

Experimental Section

Materials. A commercial sample of TPT (Hüls Troisdorf) was used without further purification. Hydrolysis of the pale yellow TPT in excess water and subsequent calcination of the hydrolysate yielded 99.99% of the theoretical yield of TiO_2. AR grade carbon tetrachloride, cyclohexane, and 2-propanol were dried by azeotropic distillation (except CCl_4) and stored over activated molecular sieves.

Spectroscopy. The mid-IR spectra were obtained using a Digilab FTS-40 spectrometer, equipped with a Globar infrared source, a KBr beam splitter and a liquid-nitrogen-cooled MCT detector. Spectra were scanned in the range 400−4000 cm^{-1}, with an effective resolution of 4 cm^{-1}, co-adding 256 scans. All samples and solutions were prepared under nitrogen, placed in an air-sealed attenuated total reflectance (ATR) cell, equipped with a ZnSe (or KRS-5) element, and quickly transferred from the glovebag to the nitrogen-purged sample compartment of the spectrometer.

The far-IR spectra were obtained using a Digilab FTS-60 spectrometer, equipped with an FTS-60V vacuum bench, a 6.25 μm Mylar film beam splitter, a mercury lamp source, and a room-temperature pyroelectric triglycine sulfate detector. Spectra were scanned in the range 75−500 cm^{-1}, with an effective resolution of 4 cm^{-1}, co-adding 64 scans. The sample was prepared under nitrogen, as a thin film between 1 mm thick polyethylene windows of 32 mm diameter, and mounted in a press-lock cell.

FT-Raman spectra were acquired using a Digilab FT-Raman II spectrometer, equipped with a liquid-nitrogen-cooled Ge detector and a holographic notch filter. The 1064 nm exciting line of a near-IR Spectra-Physics Nd:YAG diode laser system was used in all cases, with 500 mW of power at the sample. Spectra were obtained in the range 100−3500 cm^{-1}, at an effective resolution of 4 cm^{-1}, co-adding 2048 scans. To improve the signal-to-noise ratios for the 0.5 mol dm^{-3} solution, 4096 scans were co-added. Depolarization ratios were measured from the peak intensities of parallel and perpendicularly polarized Raman spectra. The samples were contained in sealed 20 cm^3 glass vials during spectral acquisition.

Spectra were manipulated by using the Spectracalc software package (Galactic Industries).

Results and Discussion

The Raman and IR spectra of neat TPT are shown in Figure 1. Given the presence of four isopropoxy ligands per TPT molecule, the likelihood of extensive coupling of the C−O and C−C stretching modes of each isopropoxy ligand, and the possibility of molecular association, it is not surprising that the spectra are complex. This is most probably the main reason for the absence of a comprehensive vibrational assignment for this molecule to date. To assign the bands in the spectra, three steps were followed:

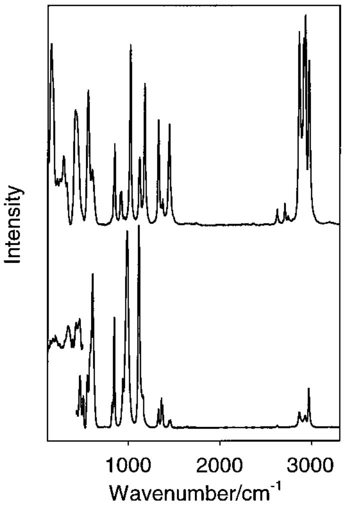

Figure 1. Vibrational spectra of TPT: (a) top, Raman; (b) bottom, mid- and far-IR (inset).

1. A direct comparison of the bands in the Raman and IR spectra of 2-propanol and TPT was made. This revealed significant differences in wavenumber and intensity of the skeletal isopropoxy modes between 2-propanol and TPT and a large degree of noncoincidence in the 900−1200 cm^{-1} region of the Raman and IR spectra of TPT.
2. Comparisons were made between the depolarization ratios of the bands in the TPT spectra and the band wavenumbers, intensities, and vibrational assignments given by other authors for tetracoordinated titanium species and compounds containing the isopropyl group.
3. IR and polarized Raman spectra of solutions of TPT in cyclohexane, carbon tetrachloride, and 2-propanol were compared with those of neat TPT.

The spectra of TPT solutions revealed that a number of bands in the Raman and IR spectra of neat TPT could be assigned to associated species. These species are responsible for the presence of extra bands in the spectra of neat TPT compared with 0.5 mol dm^{-3} TPT (see below). This study has led to an assignment of the vibrational modes of TPT, with the relative intensities and depolarization ratios given in Table 1. These assignments will be discussed with reference to the steps outlined above.

Comparison of the Raman and IR Spectra of TPT and 2-Propanol. It is useful to compare the vibrational spectra of alkoxides with those of the corresponding alcohol. Any differences between these can be correlated with structural differences between the molecules, to aid in the understanding of the vibrational spectrum of the alkoxide. In this case, there are significant band shifts and increases in the relative intensities of the skeletal vibrations between 800 and 1200 cm^{-1} (C−C and C−O stretching modes) in the spectra of TPT relative to corresponding bands in the spectra of 2-propanol (Table 1).

In the neat state, the concentrations of the isopropoxy species in TPT and 2-propanol are approximately the same ([TPT] = 3.4 mol dm^{-3}, or [O^iPr] = 13.6 mol dm^{-3}; [2-propanol] = 13.7 mol dm^{-3}). Bands assigned to the antisymmetric bending modes of methyl groups at 1450−1463 cm^{-1} in the Raman and IR spectra act as an internal reference, assuming that the intensities of these bands are approximately equal for these two compounds. Using this criterion, the bands at 1024, 1180, and 1330 cm^{-1} in the Raman spectrum (Figure 2) and at 849, 988, and

---

(18) McMurry, H. L.; Thornton, V. *J. Chem. Phys.* **1951**, *19*, 1014−8.
(19) Durig, J. R.; Guirgis, G. A.; Compton, D. A. C. *J. Phys. Chem.* **1980**, *84*, 3547−54.
(20) Sheppard, N. *Trans. Faraday Soc.* **1950**, 533−9.
(21) Durig, J. R.; Cox, A. W., Jr. *J. Phys. Chem.* **1976**, *80*, 2493−8.
(22) Durig, J. R.; Cheng, M. S.; Li, Y. S.; Groner, P.; Stanley, A. E. *J. Phys. Chem.* **1989**, *93*, 3492−503.
(23) Durig, J. R.; Guirgis, G. A.; Compton, D. A. C. *J. Phys. Chem.* **1979**, *83*, 1313−23.
(24) Durig, J. R.; Kanes, K. J.; Sullivan, J. F. *J. Mol. Struct.* **1983**, *99*, 61−76.
(25) Rosas, R. L.; Liefooghe, H. H.; Laane, J.; van der Veken, B. J. *J. Raman Spectrosc.* **1993**, *24*, 143−65.
(26) van der Veken, B. J.; Maas, R. *J. Mol. Struct.* **1989**, *200*, 413−41.

Table 1. Assignment of Bands in the Raman and IR Spectra of Neat TPT

2-propanol					TPT					
Raman			IR		Raman			IR		
cm^{-1}	ρ	int[a]	cm^{-1}	int[a]	cm^{-1}	ρ	int[a]	cm^{-1}	int[a]	assignment
					155	0.68	vs			δ(O−Ti−O)
					178	**0.62**	**vs sh**	177	vvw	**δ(O−Ti−O)**[b]
								208	vvw	
					227	**0.32**	**vvw**			**δ_s(CCO)**
					253	**0.22**	**vw sh**			**δ_s(CCO)**
486	0.13	vw			292	0.13	w	312	vvw sh	δ_s(CCO)
					329	dp[c]	w	343	vw b	δ(O−Ti−O)
					391		vvw sh	393	vvw	
370	0.53	vw			422	0.13	s b			δ_s(CCC)
426	0.61	vw b			434	p[c]	s sh	430	vw	δ_s(CCC)
								469	vw	
					486		vvw sh			δ(CCC)
								509	**vw**	**ν_{as}(Ti−O)**
								557	**s**	**ν_{as}(Ti−O)**
					561	0.06	s			ν_s(Ti−O)
								583	**s sh**	**ν_{as}(Ti−O)**
					608	**0.14**	**w**			**ν_s(Ti−O)**
								611[d]	vs	ν_{as}(Ti−O)
			630	vw vb						
								826	**w**	**ν_s(CCC), ν(Ti−O)**
					839	**0.34**	**vw sh**			**ν_s(CCC), ν(Ti−O)**
818	0.06	vvs	816	m						ν_s(CCC)
					851	0.32	m	849[d]	s	ν_s(CCC), ν(Ti−O)
918		vvw			916	0.80	vw			$\rho_r(CH_3)$[f,h]
934	0.73	vvw	935	vvw sh	926	0.79	vw			$\rho_r(CH_3)$[f,g]
951	0.79	vw	951	vvs						$\rho_r(CH_3)$[f,g]
								940	**m**	**ν(C−O), ν(Ti−O)**
					958		**vvw**			**ν(C−O), ν(Ti−O)**
								988[d]	vvs	ν(C−O), ν_{as}(Ti−O)
1130	0.52	vw	1128	m						ν(C−O)
					1024	0.05	vs			ν(C−O), ν_s(Ti−O)
								1115[d]	vvs	$\rho_r(CH_3)$[e], ν_{as}(Ti−O)
1109	0.66	vvw sh	1107	w	1125	0.76	w			ν_{as}(CCC)
1161	0.45	vvw	1160	w				1161	mw	$\rho_r(CH_3)$[e]
					1180	0.05	s			$\rho_r(CH_3)$[e], ν_s(Ti−O)
1306	0.69	vvw sh	1307	vw b						
1339	0.77	vw	1342	vw	1330	0.80	m	1331	vw	δ(C−H)
			1368	w	1360	0.81	vvw	1362	w	$\delta_s(CH_3)$[f]
1381		vvw sh	1379	w	1375	0.66	vvw	1376	vw	$\delta_s(CH_3)$[e]
1410	0.71	vw sh	1409	vw						
1450	0.81	w	1456	vvw sh	1446	0.86	m	1450	vw	$\delta_{as}(CH_3)$[f]
1462	0.77	vw sh	1466	vw	1461		vw sh	1463	vw	$\delta_{as}(CH_3)$[e]
					2623	0.41	vw	2625	vvw	
2654	0.48	vvw	2659	vvw						
2716	0.07	vvw	2718	vvw	2708	0.15	vw	2712	vvw	
2750	0.18	vvw			2743	0.22	vvw			
2880	0.10	w	2884	vvw b	2862	0.13	vvs	2866	w	$\nu_s(CH_3)$,[f] ν(C−H)
2918	0.11	w	2917	vvw sh	2911	0.10	vvs	2912	vvw sh	$\nu_s(CH_3)$[e]
2936	0.11	w	2933	vvw	2930	0.12	vvs	2930	vw	$\nu_{as}(CH_3)$[f]
2972	0.59	w	2970	mw	2967	0.66	vs	2968	m	$\nu_{as}(CH_3)$[e]
3260	0.45	vvw sh								
3350	0.47	vvw b	3338	mw vb						

[a] s = strong; m = medium; w = weak; b = broad; sh = shoulder. [b] The wavenumbers and assignments in bold refer specifically to modes of associated species. [c] p = polarized; dp = depolarized. In some cases it was not possible to measure an accurate depolarization ratio due to the overlapping of a band or bands belonging to other vibrations. The assignment of a polarized band at 434 cm^{-1} in the Raman spectrum of TPT was based upon inspection of parallel and perpendicularly polarized Raman spectra (Figure 6). [d] These wavenumbers in the IR spectrum display shifts upon dilution, indicating that the band contains a component due to an associated species. [e] In-phase. [f] Out-of-phase. [g] In-plane. [h] Out-of-plane.

1115 cm^{-1} in the IR spectrum (Figure 3) of TPT show intensities far greater than bands of approximately the same wavenumber in the corresponding spectrum of 2-propanol.

The Raman and IR spectra of TPT differ in the appearance of several strong Raman bands at 155, 422 (Figure 4), 561, 1024, and 1180 cm^{-1} (Figure 5) and their corresponding absence (or weakness in the case of the band at ca. 561 cm^{-1}) in the IR spectrum. The bands at 561 and 1180 cm^{-1} have been tentatively assigned previously to Ti−O and C−O stretching modes, respectively.[4,5] Similarly, the strong IR band at 988 cm^{-1} has no counterpart in the Raman spectrum.

A combined XANES and EXAFS study[27] obtained a single Ti−O bond length of 1.76 Å, with a near-tetrahedral environment for the TiO_4 framework of the TPT molecule in its pure liquid form. If the TiO_4 oscillator exhibited T_d symmetry, this

---

(27) Babonneau, F.; Doeuff, S.; Léaustic, A.; Sanchez, C.; Cartier, C.; Verdaguer, M. *Inorg. Chem.* **1988**, *27*, 3166−72.

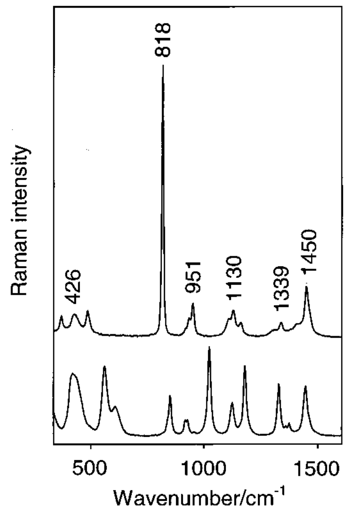

Figure 2. Comparison of Raman spectra in the 400−1500 cm^{-1} region: (a) top, 2-propanol; (b) bottom, TPT.

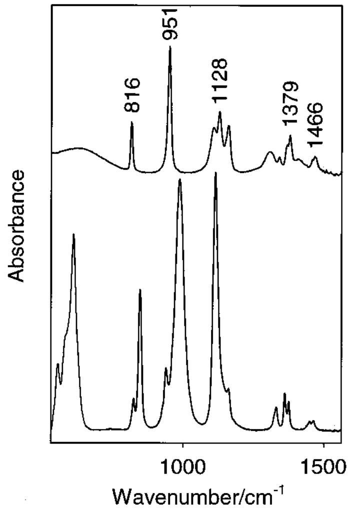

Figure 3. Comparison of IR spectra in the 500−1500 cm^{-1} region: (a) top, 2-propanol; (b) bottom, TPT.

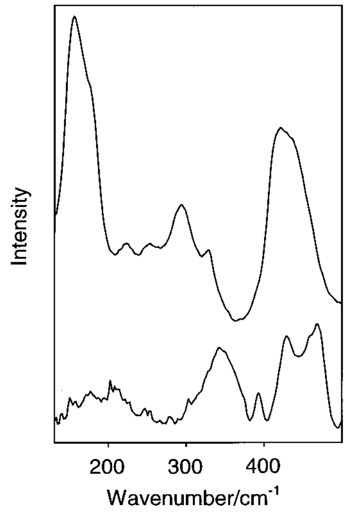

Figure 4. Vibrational spectra of TPT in the 100−500 cm^{-1} region: (a) top, Raman; (b) bottom, IR.

would yield $A_1 + E + 2T_2$ symmetry species for the normal modes of the TiO_4 framework, where all the modes would be Raman-active and only the triply degenerate T_2 modes would be IR-active.

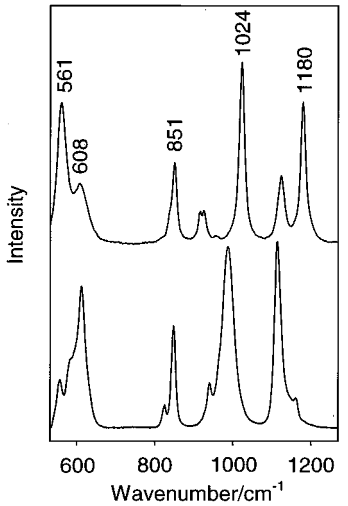

Figure 5. Vibrational spectra of TPT in the 500−1200 cm^{-1} region: (a) top, Raman; (b) bottom, IR.

In contrast, the local symmetry of the isopropoxy ligand is C_s so that all modes are Raman- and IR-active (Table 1; see the data for 2-propanol). The absence of a coincident IR band corresponding to the 1180 cm^{-1} Raman band suggests that this ligand mode may be coupled to IR-inactive modes of the TiO_4 oscillator. Hence, this ligand mode would be coupled to symmetric stretching (A_1) or doubly degenerate bending (E) modes of the TiO_4 unit.

Evidence for coupling between modes of the isopropoxy ligand and Ti−O bonds is also apparent from results of previous studies:

1. Complete deuteration of the isopropoxy ligands of TPT yielded a pronounced shift in a ν(Ti−O) mode of the IR spectrum from 619 to 563 cm^{-1}.[17] This value of $\Delta\nu$ (56 cm^{-1}) was somewhat lower than the value calculated on the basis of a diatomic model, treating the ligand as a point mass. This indicates that the Ti−O stretching mode has isopropoxy ligand mode character.

2. The bands at 1024 and 1180 cm^{-1} in the preresonance Raman spectrum of TPT under 363.8 nm excitation of the TiO_4 chromophore showed increased intensities, relative to the C−H bending modes, compared with the same bands under 514.5 nm excitation.[28] This shows that these modes contain a vibrational component of the TiO_4 oscillator.

These findings indicate that these intense ligand modes at 1024 and 1180 cm^{-1} in the Raman spectrum do have Ti−O character, and this results in the large differences in band wavenumber, intensity, and Raman- and IR-coincidence observed between the spectra of TPT and the spectra of 2-propanol.

Assignment of TPT Modes. To investigate coupling of the ligand modes to vibrations of the TiO_4 framework, the depolarization ratios of Ti−O bending and stretching modes below 700 cm^{-1} have been compared with those of the ligand modes (Table 1 and Figures 6 and 7). These band wavenumbers and intensities from the Raman and IR spectra and polarization from the former have been compared with those of related species (Tables 2 and 3) to obtain an assignment of the vibrational spectra of TPT.

The 100−700 cm^{-1} Region. The strong, polarized band at 561 cm^{-1} (Figure 5) is assigned to the ν_s(Ti−O) mode (ν_1, A_1 symmetry) on the basis of its Raman intensity, its depolarization ratio, and the absence of any bands in this region of the Raman

---

[28] Payne, M. J.; Berglund, K. A. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 627−31.

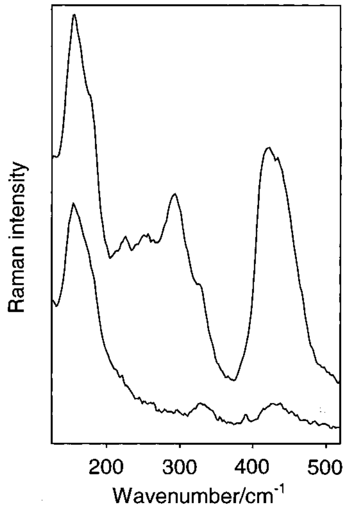

Figure 6. (a) Parallel (top) and (b) perpendicularly (bottom) polarized Raman spectra of TPT in the 100−500 cm^{-1} region.

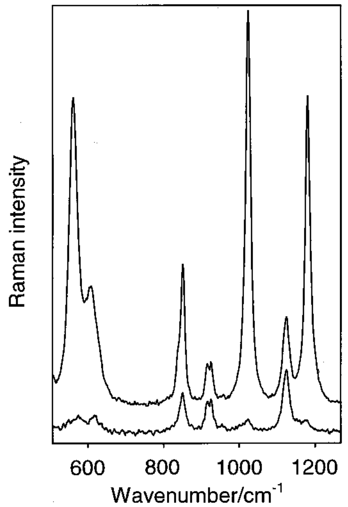

Figure 7. (a) Parallel (top) and (b) perpendicularly (bottom) polarized Raman spectra of TPT in the 500−1200 cm^{-1} region.

Table 2. Fundamental Frequencies of Tetrahalogeno Molecules[34b] and Tetracoordinated Titanium Species (cm^{-1})

molecule	ν_1 (R) p (A$_1$)	ν_2 (R) dp (E)	ν_3 (R, IR) dp (T$_2$)	ν_4 (R,IR) dp (T$_2$)
CCl_4	460	214	765, 792	314
$SiCl_4$	423	145	617	220
$TiCl_4$	389	114	498	136
$TiBr_4$	232	69	393	88
$Ba_2[TiO_4]^a$	761	306	770	371
$Ti(O^iPr)_4{}^b$	561	155	611	329

[a] Reference 29. [b] These wavenumbers are for neat TPT.

spectrum of 2-propanol, consistent with a previous tentative assignment.[4] This band is not completely removed in the perpendicularly polarized Raman spectrum ($\rho \neq 0$; Table 1), indicating that it does not belong to an A$_1$ mode of a species with T_d symmetry. The presence of a least three bands at 557, 583, and 611 cm^{-1} in the corresponding region of the IR spectrum (Figure 5) is also indicative of an effective lowering of TiO_4 symmetry from the ideal T_d. This lowering of symmetry can be attributed to molecular association. The bands at 557 and 583 cm^{-1} are assigned to ν_{as}(Ti−O) modes of associated species, as their intensities are reduced upon dilution, and the band at 611 cm^{-1} also contains a component of an associated species, as this band shifts upon dilution (see next section).

Table 3. Band Assignments and Wavenumbers of Skeletal Modes in Isopropyl Compounds ^{i}PrX^a

X	ν_s(CCC)	$\rho_r(CH_3)^{f,j}$	$\rho_r(CH_3)^{g,j}$	ν(C−O)	ν_{as}(CCC)
H^k	870	1155	923		1053
OH^b	818	1161^c	934, 951	1130^c	1109^c
	R vvs p	R vvw p	R vvw dp, vw dp	R vw p	R vvw sh dp
	IR m	IR w	IR vvw sh, vvs	IR m	IR w
SH^l	893	1089,^{i} 1125^h	929,^{i} 956^h		1162
Cl^m	884^d	1059,^{d} 1161	932, 949		1126
	R p	R p, −	IR w		R dp
	IR s	IR s, s			(IR 1131 m)
Br^m	879^d	1038,^{d} 1154	931, 946		1119
	R dp	R p	IR w, −		R dp
	IR s	IR s			(IR 1133 w)
$PH_2{}^n$	891	1062,^{i} 1110^h	923,^{h} 1044^h		1160
	R m	R m, w	R vw, −		R w
	IR m	IR s, m	IR m, m		IR m
$PF_2{}^o$	878	1020, 1090	928, 968		1167
	R m p	R w p	R w dp		R w p
	IR w	IR w	IR w, vw		IR vw
$NH_2{}^p$	919	942,^{i} 1135^h	981,^{h} 1035^h		1175^i
	R w p	R m p	R w p, m dp		R m dp
	IR w	IR w, s	IR vs, m		IR m
NCO^q	906	1101, 1166	931, 947		1133
	R m p	R m p, w p	R w, w dp		R w dp
	IR s	IR vs, s	IR w, vw		IR vs
OC(O)H^r	820	1106, 1184	933, 946	907, 1193^e	1148
	R vvs	R w sh, w	R w, m	R m	R w
	IR s	IR vs, s	IR w, vw	IR m	IR s
ONO^s	881	1127, 1181	891, 922	933, 958	1144
	R s	R w p	R s sh p, vvw	R vw	R w p
	IR vs	IR m	IR sh, s	IR m	IR m

[a] s = strong; m = medium; w = weak; b = broad; sh = shoulder. [b] This work. [c] This mode is likely to be strongly coupled to the other modes in this region of the spectrum. [d] The ν_s(CCC) and $\rho_r(CH_3)$ assignments given here are the reverse of those in ref 20. [e] Two ν(C−O) modes will be expected for this molecule; cf. $(C_3H_7)_2O$ ν(C−O) 798 and 1125 cm^{-1}.[32b] [f] In-phase. [g] Out-of-phase. [h] In-plane. [i] Out-of-plane. [j] In this table, the assignment of the CH_3 rocking modes to in- and out-of-phase components is made on the basis of assignments by other authors or by the current authors. In the latter case, this assignment is made on the basis of the polarization data given in the references, where the in-phase mode is polarized and the out-of-phase mode is depolarized. [k] Reference 18. [l] Reference 19. [m] Reference 20. [n] Reference 21. [o] Reference 22. [p] Reference 23. [q] Reference 24. [r] Reference 25. [s] Reference 26.

The Raman band at 608 cm^{-1} appears to coincide with a ν_{as}(Ti−O) mode at 611 cm^{-1} in the IR spectrum (Figure 5). However, the band at 608 cm^{-1} in the Raman spectrum cannot itself be assigned to a ν_{as}(Ti−O) mode, as it is polarized ($\rho = 0.14$), in contrast to a previous assignment.[4] Therefore, this second polarized band in the ν(Ti−O) mode region cannot be assigned to monomeric TPT and is therefore assigned to an associated species (Table 1). This is confirmed by dilution studies (see below).

The ν_{as}(Ti−O) mode of the monomer would however be expected in this region of the Raman spectrum. Gonzalez-Vilchez and Griffith[29] observed that, for tetrahedral $[MO_4]^{n-}$ ions, the antisymmetric M−O stretching mode mostly appears at slightly higher wavenumbers than the symmetric mode, as a strong band in the IR spectrum, but is usually weak or even absent in the Raman spectrum (e.g., see $Ba_2[TiO_4]$ in Table 2). This mode is observed as a weak depolarized band at 618 cm^{-1} in the Raman spectrum and as a strong band at 619 cm^{-1} in the IR spectrum of diluted TPT (see next section).

On the basis of the assignments of the titanium tetrahalides (Table 2), the ν_2 (E) and ν_4 (T$_2$) bending modes of the TiO_4

---

(29) Gonzalez-Vilchez, F.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1972**, 1416−21.

unit are also expected in this region. The band at 155 cm^{-1} is assigned to the doubly degenerate ν_2 mode, as it is depolarized in the Raman spectrum (Figure 6) and is not observed in the IR spectrum (Figure 4). This band has a shoulder at 178 cm^{-1}, which is attributed to an associated species (see below). As in the assignments of the titanium tetrahalides, this mode has the lowest wavenumber of the normal modes of the TiO_4 oscillator. The weak shoulder at 329 cm^{-1} in the Raman spectrum is assigned to the triply degenerate ν_4 mode of the TiO_4 unit, on the basis that this mode is depolarized in the Raman spectrum (Figure 6) and is observed in the IR spectrum as a broad band at 343 cm^{-1} (Figure 4). A comparison of the assignments of the Ti−O modes of TPT with other tetrahedral species, treating the isopropoxy group as a single entity, is given in Table 2.

By a process of elimination, these assignments imply that the polarized Raman bands at 227, 253, 292, 422, and 434 cm^{-1} (Figure 6) cannot be assigned to one of the normal modes of the TiO_4 unit in monomeric $Ti(O^iPr)_4$. The IR spectrum (Figure 4) also shows two bands at 430 and 469 cm^{-1}, which approximately correspond to weak bands in the perpendicularly polarized Raman spectrum (Figure 6b). In the Raman spectrum of 2-propanol (Figure 2), a polarized band of weaker intensity appears at 426 cm^{-1}. On the basis of previous assignments of the spectra of ^{i}PrSH[19] and ^{i}PrCl,[20] the bands at ca. 292 and 422 cm^{-1} are assigned to δ_s(CCO) and δ_s(CCC) modes, respectively. The Raman bands at 227 and 253 cm^{-1} are assigned to δ_s(CCO) modes of associated species (see below).

The 800−1200 cm^{-1} Region. The C−O stretching, symmetric and antisymmetric C−C stretching, and CH_3 rocking modes of the isopropyl group are expected to lie in this region of the spectra. To establish the characteristic band wavenumbers and intensities of these modes, the previously published assignments for compounds ^{i}PrX were analyzed. The data are presented in Table 3.

Two trends in Table 3 are worthy of further discussion. The first of these relates to the symmetric and antisymmetric C−C stretching modes. It is known that, for secondary and tertiary alcohols, extensive coupling exists between C−O and C−C stretching modes.[30,31] In general, an increase in the interaction between C−O and C−C bond frequencies occurs as these frequencies approach one another in magnitude.[31] The effect of coupling is to further separate the admixed bands, resulting in an increase in the wavenumber of the ν(C−O) mode (and a decrease in the wavenumber of the ν(C−C) mode), as evidenced in the wavenumbers of the ν(C−O) mode of the series methanol (1030 cm^{-1}), 2-propanol (1130 cm^{-1}), and 2-methylpropanol (1205 cm^{-1}). For 2-propanol, the Raman bands at 818 and 1130 cm^{-1} have been assigned to symmetric (ν_s(CCC) in Table 3) and antisymmetric (ν(C−O) in Table 3) stretching modes of the C_3O oscillator, respectively.[32] The remaining antisymmetric stretching mode can be assigned as the ν_{as}(CCC) mode.

In Table 3, the ν_s(CCC) and ν_{as}(CCC) stretching modes of ^{i}PrX ($X \neq H$) shift to higher wavenumbers relative to those of 2-propanol. This occurs even when the mass of X is greater than that of the OH group. A reduction in the vibrational coupling between the ν(C−C) and ν(C−X) modes would be expected as the difference in their individual vibrational frequencies increases. Hence, the shift in the ν_s(CCC) and ν_{as}(CCC) modes of isopropyl compounds to higher wavenumbers, relative to those of 2-propanol, appears to be diagnostic of a reduction in the coupling between the ν(C−C) and ν(C−X) modes.

Such a reduction in coupling of the ν(C−O) and ν(C−C) modes, accompanied by a shift of the ν_s(CCC) mode to higher wavenumbers, would be expected for TPT, as the oxygen atom of the isopropoxy group is directly bonded to a transition metal center. The formation of a Ti−O bond would reduce the electron density, the force constant, and hence the vibrational frequency of the C−O bond. The observation that the stretching and bending modes of the C−H bond of the secondary carbon in TPT show on average a 16 and a 9 cm^{-1} shift, respectively, to lower wavenumbers, relative to those of 2-propanol, is evidence that electron density is also being removed from the C−H bond. Therefore, the polarized band of only medium intensity at 851 cm^{-1} (cf. 2-propanol, 818 cm^{-1}, Table 1) is assigned to the ν_s(CCC) mode, with the depolarized band of weak intensity at 1125 cm^{-1} (2-propanol 1109 cm^{-1}) assigned to the ν_{as}(CCC) mode (Figure 7). The ν_s(CCC) mode has a corresponding band at 849 cm^{-1} in the IR spectrum (Figure 5). This indicates that this mode is not coupled to ν(Ti−O) modes as strongly as the intense ligand modes at 1024, 1180 (Raman), 988, and 1115 cm^{-1} (IR) (see below), as there is little separation in the wavenumbers of the Raman and IR bands. Note the shoulder at 839 cm^{-1} in the Raman spectrum and the 826 cm^{-1} band in the IR spectrum are assigned to associated species. The 849 cm^{-1} IR band also contains a component of an associated species, as this band shifts upon dilution (see next section).

The second trend in Table 3 relates to the CH_3 rocking modes. For each methyl group, there are two rocking modes, either in or out of plane.[33a] In the isopropyl $(CH_3)_2C(H)-$ group, the rocking modes of individual methyl groups may couple, either in-phase or out-of-phase, producing four modes. In Table 3, the in-phase rocking modes appear at higher wavenumbers than the out-of-phase rocking modes; the in-phase modes are polarized in the Raman spectrum, and the out-of-phase modes are depolarized. In Table 3, the wavenumber separation of the in- and out-of-plane components for the out-of-phase coupling is smaller (average 37 cm^{-1}) compared to the respective components of the in-phase couple (average 73 cm^{-1}).

The remaining bands in the 800−1200 cm^{-1} region of the Raman spectrum of TPT can be assigned to C−O stretching and the various CH_3 rocking modes described above. A comparison of these strong ligand bands and the ν_s(Ti−O) mode reveals similar characteristic intensities and depolarization ratios (ν_s(Ti−O): 561 cm^{-1}, $\rho = 0.06$; 1024 and 1180 cm^{-1}, $\rho = 0.05$). These bands are also noncoincident in the Raman and IR spectra, which is indicative of coupling to the ν(Ti−O) modes.

It is known that C−O stretching and CH_3 rocking modes of the same symmetry species in secondary and tertiary alcohols can also be coupled.[33b] Given the appearance of two polarized bands, intensity enhancement for both bands in the resonance Raman spectrum,[28] and the previous assignments of the CH_3 rocking modes in Table 3, these two Raman bands are assigned to combinations of a C−O stretching and an in-phase CH_3 rocking mode. The band at 1024 cm^{-1} is assigned to a predominantly ν(C−O) mode, since coordination of the oxygen atom to the transition metal center is likely to result in a weaker C−O bond and therefore in a shift to lower wavenumber relative

---

(30) Stuart, A. V.; Sutherland, G. B. B. M. *J. Chem. Phys.* **1956**, *24*, 559−70.

(31) Zeiss, H. H.; Tsutsui, M. *J. Am. Chem. Soc.* **1953**, *75*, 897−900.

(32) Dollish, F. R.; Fateley, W. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; Wiley-Interscience: New York, 1974; (a) p 29, (b) p 31.

(33) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964; (a) p 192, (b) p 274.

to that of the free alcohol (2-propanol 1130 cm^{-1}). The band at 1180 cm^{-1} is assigned to a predominantly in-phase $\rho_r(CH_3)$ mode.

The weak, depolarized bands in the Raman spectrum at 916 and 926 cm^{-1} (Figure 7) are assigned to the out-of-phase, out-of-plane and in-plane $\rho_r(CH_3)$ modes (A″), respectively, on the basis of their weak intensity, small splitting in the Raman spectra, and the previous assignments in Table 3. These weak modes are not coupled to the ν(Ti−O) modes, since they are not of the same symmetry type as the ν(C−O) mode.

The noncoincidence of the strong ligand modes in the Raman (1024 and 1180 cm^{-1}) and IR spectra (988 and 1115 cm^{-1}) can be explained by interligand coupling (Figure 5). Skeletal vibrational modes of an isopropoxy ligand vibrate in-phase and out-of-phase with those modes of other isopropoxy ligands. In other words, these ligand modes are coupled to the ν(Ti−O) modes. The ν(C−O) and in-phase $\rho_r(CH_3)$ modes can be coupled to the ν_s(Ti−O) mode, yielding strongly polarized, predominantly Raman-active modes assigned to the bands at 1024 and 1180 cm^{-1}, respectively. The same ligand modes can be coupled to the triply degenerate ν_{as}(Ti−O) mode, yielding predominantly IR-active modes, assigned to the strong, broad band at 988 cm^{-1} and the strong band at 1115 cm^{-1}, respectively (Figure 5; see Table 1). These IR bands contain components of associated species (see next section).

Unlike 2-propanol, TPT has two levels of vibrational coupling: mixing of the modes of the ligand itself (as for 2-propanol), i.e. intraligand coupling, but also interactions between ligands, i.e. interligand coupling. Not surprisingly, intraligand coupling is a strong feature of the spectra. This is well illustrated by an H−D difference plot of the IR spectra of $Ti(OCH(CH_3)_2)_4$ and $Ti(OCD(CH_3)_2)_4$, where the bands at 849, 988, and 1115 cm^{-1} all contain $(H_3C)_2$**C−H** character.[15] This demonstrates that the major coupling within the isopropoxy ligand of TPT occurs between ν(C−O) and in-phase $\rho_r(CH_3)$ modes, as opposed to strong coupling between the ν(C−O) and ν_s(CCC) modes for 2-propanol.

For interligand coupling, the modes coupled with ν_s(Ti−O) (ligand modes in-phase) appear at higher wavenumber than those coupled with ν_{as}(Ti−O) (ligand modes out-of-phase), in contrast to the ν(Ti−O) modes themselves. The in-phase (symmetric) correlation coupling of the $\nu_s(CO_3)$ mode in the calcite system[34a] and the $\nu_s(SO_3)$ mode of metal salts of bis(2-ethylhexyl)-sulfosuccinate[35] also yielded strong Raman bands at higher wavenumbers than the out-of-phase (antisymmetric) mode, which was strongly IR-active in the latter case.

Vibrational Spectra of TPT in Solution. For several titanium alkoxides, dilution is known to decrease the concentration of associated species.[36] To confirm the assignment of the Raman band at 608 cm^{-1} (Figure 8) and the IR bands at 557, 583, and 611 cm^{-1} (Figure 9) to associated species, the spectra of 0.5 mol dm^{-3} TPT in various solvents (2-propanol, cyclohexane, and carbon tetrachloride) were recorded. Carbon tetrachloride and cyclohexane were chosen because they have very weak bands above and below ca. 800 cm^{-1} in the Raman spectra, respectively. 2-Propanol was chosen to investigate changes observed by other workers in the ν(Ti−O) mode region of the Raman spectrum of TPT in 2-propanol.[28] However, there were no significant differences between the spectra of TPT diluted in the various solvents. These changes in the ν(Ti−O) mode region of TPT in 2-propanol were most probably due to partial hydrolysis of the alkoxide, as the bands are similar to those observed in the spectra of partially hydrolyzed TPT.[4] The Raman spectrum in CCl_4 solution and the IR spectrum in cyclohexane are shown in Figures 8 and 9.

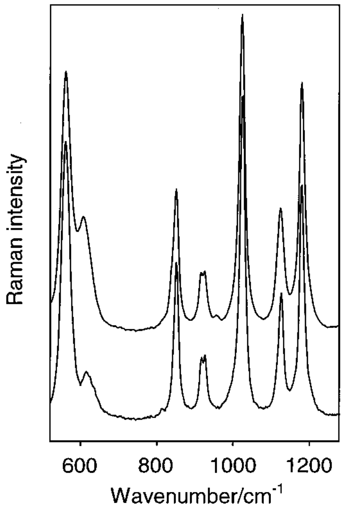

Figure 8. Comparison of the Raman spectra of TPT in the 500−1200 cm^{-1} region: (a) top, neat; (b) bottom, 0.5 mol dm^{-3} CCl_4 solution (solvent bands subtracted).

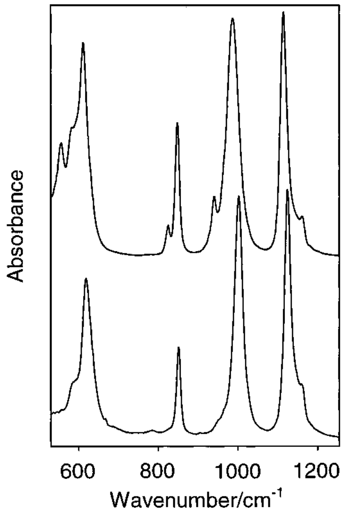

Figure 9. Comparison of the IR spectra of TPT in the 500−1200 cm^{-1} region: (a) top, neat; (b) bottom, 0.5 mol dm^{-3} C_6H_{12} solution (solvent bands subtracted).

In the IR spectrum, several bands almost completely disappear in 0.5 mol dm^{-3} TPT solutions (Figure 9), viz. 557, 583, 826, and 940 cm^{-1}. The strong IR bands sometimes show large apparent shifts upon dilution, viz. 611 to 619 cm^{-1}, 849 to 852 cm^{-1}, 988 to 1003 cm^{-1}, and 1115 to 1124 cm^{-1}. For the 988 and 1115 cm^{-1} bands, the magnitude of the shifts (15 and 9 cm^{-1}, respectively) and the absence of any difference in the observed shifts for 2-propanol, cyclohexane, and carbon tetrachloride do not favor the assignment of the band shifts to a solvent effect.

Instead, these shifts are actually due to a removal of a component of these bands attributable to an associated species. Hence, the IR bands at 557, 583, and 611 cm^{-1} (ν_{as}(Ti−O) mode), 826 and 849 cm^{-1} (coupled ν_s(CCC) mode), 940 and 988 cm^{-1} (coupled ν(C−O) mode), and 1115 cm^{-1} (coupled

---

(34) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; (a) p 93, (b) p 133.

(35) Moran, P. D.; Bowmaker, G. A.; Cooney, R. P.; Bartlett, J. R.; Woolfrey, J. L.; *J. Mater. Chem.* **1995**, *5*, 295−302.

(36) Barraclough, C. G.; Martin, R. L.; Winter, G. *J. Chem. Soc.* **1964**, 758−62.

$\rho_r(CH_3)$ mode) can all be assigned to associated species. In the IR spectrum of neat TPT, molecular association removes the degeneracy of these ligand modes which are coupled to the ν_{as}(Ti−O) mode (triply degenerate for T_d symmetry species). This results in the appearance of several bands in the IR spectrum for the ν_{as}(Ti−O) mode and the coupled ligand modes. The corresponding modes of monomeric TPT are observed upon dilution at 619, 852, 1003, and 1124 cm^{-1}, respectively (Figure 9). These wavenumbers all fall within the respective band profiles of the IR spectrum of neat TPT, contributing to the broadness of the band at 611, 849, 988 and 1115 cm^{-1}. The lower wavenumbers of the bands of associated species are consistent with decreases in the Ti−O, C−O, and C−C bond strengths upon molecular association.

In the Raman spectrum, the shoulder at 178 cm^{-1}, the polarized bands at 227, 253 [δ_s(CCO)], and 608 cm^{-1} [ν_s(Ti−O)] (Figure 8), and the polarized shoulder at 839 cm^{-1} [ν_s(CCC)] can be assigned to associated species (Table 1), as their intensities are reduced upon dilution. The shoulder at 178 cm^{-1} is most probably due to a removal of the degeneracy of the O−Ti−O bending mode (E) upon molecular association. The reduction in intensity of the 608 cm^{-1} band reveals a weak depolarized band at ca. 618 cm^{-1} (Figure 8), which can be assigned to the ν_{as}(Ti−O) mode of TPT. The corresponding mode in the IR spectrum appears at 619 cm^{-1} (Figure 9).

In contrast to the IR spectrum, there are no effective band shifts for the modes at 561, 851, 1024, and 1180 cm^{-1} in the Raman spectrum upon dilution. The 561 cm^{-1} band is assigned to the ν_s(Ti−O) mode of monomeric TPT. However, the absence of separate bands attributable to coupled ligand modes of associated species is likely to be due to a combination of factors: low Raman intensity of modes of associated species (as observed for the ν_s(Ti−O) mode of an associated species at 608 cm^{-1}) and a weak molecular association interaction which produces a negligible band shift of these ligand modes coupled to the nondegenerate ν_s(Ti−O) mode.

The wavenumbers of the ν(C−O) and in-phase $\rho_r(CH_3)$ modes in the Raman and IR spectra are noncoincident for both associated and monomeric TPT species, indicating that the ligand modes are coupled for both species. Given that the ν_{as}(Ti−O) mode itself is very weak in the Raman spectrum, it is not surprising that the ligand modes coupled to the ν_{as}(Ti−O) mode of monomeric TPT are not observed in the Raman spectrum.

Molecular association of TPT may be expected in view of the known molecular complexity[7] of 1.4. This result, obtained from refluxing solutions of TPT in benzene, implies that the molecule in these solutions is not purely a monomer, dimer, or trimer, but an equilibrium mixture of all three. The results of a combined XANES and EXAFS study[27] showed that TPT is largely monomeric but has symmetry lower than tetrahedral. This lower symmetry is confirmed by these results from vibrational spectroscopy. However, the presence of associated species in neat TPT is also established.

In the IR spectrum of TPT, three separate regions, often containing several bands, are observed viz. 800−900 cm^{-1} [ν_s(CCC)], 900−1050 cm^{-1} [ν(C−O)], and 1050−1200 cm^{-1} [in-phase $\rho_r(CH_3)$]. The same spectral features are observed in the spectra of the following compounds: $B(O^iPr)_3$, $P(O^iPr)_3$, $Al(O^iPr)_3$;[37] $Y(O^iPr)_3$;[37,38] $Zr(O^iPr)_4$, $Hf(O^iPr)_4$, $Th(O^iPr)_4$;[39] and lanthanide isopropoxides.[38] The transition metal isopropoxides that are known to be associated in undiluted form show several bands in these respective regions, which can be assigned to modes composed of vibrations involving bridging ligands. The greater IR intensity of these ligand modes in associated species makes IR spectroscopy a more useful technique than Raman spectroscopy for the investigation of the chemistry of metal isopropoxide species.

Conclusions

There is evidence in the Raman and IR spectra for the presence of associated species in neat TPT. The Raman band at 608 cm^{-1}, previously assigned to ν_{as}(Ti−O), has been shown to be due to such a species.

Modes of isopropoxy ligands of monomeric and associated TPT species with ν(C−O) mode character can be coupled to ν_s(Ti−O) and ν_{as}(Ti−O) modes. The symmetrically coupled ligand modes give rise to intense, strongly polarized bands in the Raman spectrum. The antisymmetrically coupled ligand modes give rise to strong bands in the IR spectrum. In contrast to the ν(Ti−O) modes, the symmetrically coupled ligand modes appeared at higher wavenumbers than the antisymmetrically coupled ligand modes.

Molecular association of TPT produced negligible shifts in the ligand modes coupled to the ν_s(Ti−O) mode in the Raman spectrum. In contrast, the degeneracy of the strong ligand modes coupled to the ν_{as}(Ti−O) mode was lifted upon molecular association, yielding band shifts and splittings in the IR spectrum of neat TPT.

Except for the C−H stretching and bending modes of the methyl groups, the bands in the vibrational spectra of 2-propanol and TPT do not closely resemble each other. This is largely due to the differences in vibrational coupling within the molecules. For the alcohol, ν(C−O) and ν(C−C) coupling appears to be dominant, whereas, for TPT, ν(C−O) and $\rho_r(CH_3)$ coupling to ν_s(Ti−O) and ν_{as}(Ti−O) modes is dominant.

Acknowledgment. P.D.M. is grateful to the New Zealand Vice-Chancellors' Committee for the award of a postgraduate scholarship. We also acknowledge financial support from the New Zealand Lottery Grants Board, the Australian Department of Industry, Science and Technology, and the University of Auckland Research Committee. The technical assistance of Dr. John Seakins is also gratefully acknowledged.

IC9709436

---

(37) Bell, J. V.; Heisler, J.; Tannenbaum, H.; Goldenson, J. *Anal. Chem.* **1953**, *25*, 1720−4.

(38) Brown, L. M.; Mazdiyasni, K. S. *Inorg. Chem.* **1970**, *9*, 2783−6.

(39) Lynch, C. T.; Mazdiyasni, K. S.; Smith, J. S.; Crawford, W. J. *Anal. Chem.* **1964**, *36*, 2332−7.