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Far-infrared Dichroism of Vanadyl bis(acetylacetonate)

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It is shown that although VO(acac)$_2$ crystallises in the triclinic system meaningful single-crystal polarised i.r. absorption experiments can be performed on it. The results are used to establish the assignment of the molecular (C_{2v}) B_2 modes. Comparison with powder Raman data allows further comment.

Introduction

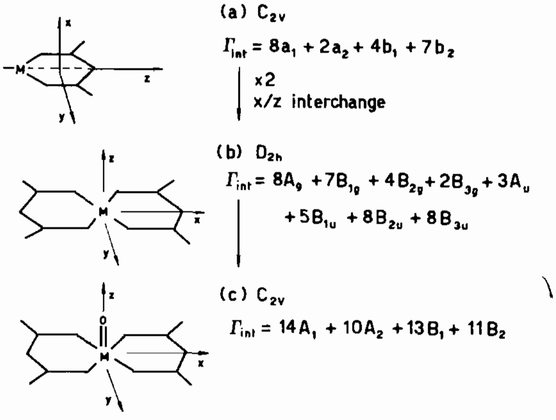
Fundamental laws of optics require that in studying the Raman spectra of oriented single crystals in polarised light the input and collection directions must be coincident with indicatrix axes if the results are to be capable of a simple interpretation. For triclinic crystals, in contrast to the higher symmetry systems, the axes of the indicatrix bear no necessary relation to the crystal axes and may also show dispersion. This makes triclinic single crystal Raman work difficult and rather unrewarding. However, the situation in respect of the analogous i.r. absorption experiments is less restrictive. It is our contention that since very thin crystal slices are used, with thickness comparable to that of far-i.r. wavelengths, splitting into ordinary and extraordinary rays will be so slight as to be readily ignored. In other words, it is possible to select *any* direction of interest in a triclinic crystal for study by i.r. absorption in polarised light and to interpret the results in a direct manner In this paper we report the results of applying this approach to a crystal of VO(acac)$_2$. The general features of the vibrational spectra of acetylacetonate complexes are well understood, but direct evidence for assignment of the structure-sensitive lowfrequency region is generally lacking. Only i.r. powder spectra in the region above 300 cm^{-1} have been reported previously for the title compound.[1]

Selection Rules

VO(acac)$_2$ crystallises in the triclinic system, P1, Z = 2.[2] The modes of the two C_{2v} molecules in the unit cell will couple via the site field (C_1) with each mode yielding an A_g (Raman) + A_u(i.r.) pair in the factor group C_i. Thus, for the i.r. or Raman spectrum alone the *number* of internal modes will be just that due to one molecule, see Tables I and II. The two spectra will be coincident unless there is significant interaction between the two molecules, in which case the frequency differences will indicate the strength of the correlation field. There are 3A$_u$ rotatory lattice modes, plus 6A$_g$ lattice modes, nominally three of each kind.

We have studied VO(acac)$_2$ crystals in transmission using naturally-occurring faces containing the *a*- and *b*-axes, with radiation polarised either parallel or perpendicular to the *b*-axis. The relation between the molecular and crystal axes is shown in Figure 1.

TABLE I. Vibrational Modes for Acac Complexes.



(a) C_{2v}

$\Gamma_{int} = 8a_1 + 2a_2 + 4b_1 + 7b_2$

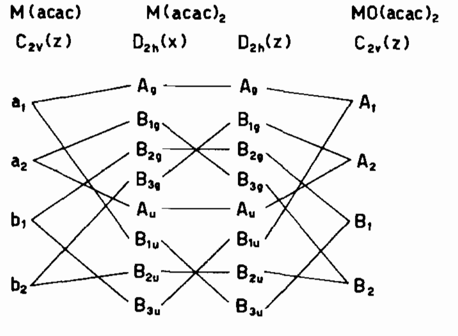
x2
x/z interchange

(b) D_{2h}

$\Gamma_{int} = 8A_g + 7B_{1g} + 4B_{2g} + 2B_{3g} + 3A_u + 5B_{1u} + 8B_{2u} + 8B_{3u}$

(c) C_{2v}

$\Gamma_{int} = 14A_1 + 10A_2 + 13B_1 + 11B_2$



Correlation from one- and two-ring (acac) systems to selection rules for MO(acac)$_2$ structure.

TABLE II. Approximate Descriptions of the Low-frequency Internal Modes (<790 cm^{-1})^{a} Expected for VO(acac)$_2$, together with the Symmetry of Their Counterparts for the Planar One- and Two-ring (acac) Systems.

A_1	ν (M–O)	A_g, a_1
	δ (C–Me)	
	δ ring def.	
	δ ring def.	
	π (C–Me)	B_{1u}, b_1
	π ring def.	
	π ring def.	
	π ring scissors	B_{1u}, ν_R
A_2	ν (M–O)	B_{1g}, b_2
	δ (C–Me)	
	δ ring def.	
	π (C–Me)	A_u, a_2
	π ring def.	
	ring torsion	A_u, ν_R
B_1	π (C–Me)	B_{2g}, b_1
	π ring def.	
	π ring def.	
	ν (M–O)	B_{3u}, a_1
	δ (C–Me)	
	δ ring def.	
	δ ring def.	
	δ (V=O)	
B_2	π (C–Me)	B_{3g}, a_2
	π ring def.	
	ν (M–O)	B_{2u}, b_2
	δ (C–Me)	
	δ ring def.	
	δ ring def, δ (OMO)	B_{2u}, ν_R
	δ (V=O)	

[a] Known high frequency modes omitted, their positions are approximately constant, see for example ref. 3.

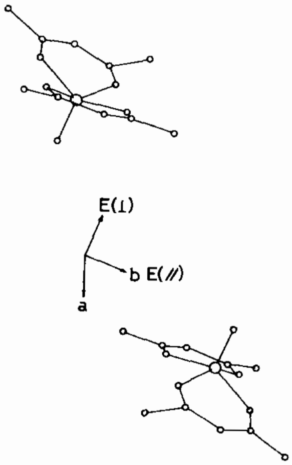


Figure 1. The structure of crystalline VO(acac)$_2$, showing the relative positions of the molecules, the crystallographic *a* and *b* directions, and the polarisation directions used.

Since the two molecules are related by a centre of inversion the same directions apply for both. The E(||) experiments will excite vibrations having a resultant dipole moment in the *y*-direction (*i.e.* B_2 modes in C_{2v}), but both A_1 and B_1 modes will be excited by E(⊥). The dihedral angle (163°) between the rings precludes any simple distinction between in-plane and out-of-plane modes relative to each ring; on coupling the two rings both π- and δ- modes have resultant moments in the molecular x, y, and z-directions. Further, the metal atom is slightly above the plane of the four oxygens subtended by the rings so complete extinctions are not expected for ν(V–O) modes.

It must be emphasised that strictly speaking all the i.r.-active modes are of A_u symmetry. What we seek to show is that for well-chosen directions only certain modes are excited and that these may be approximately described by molecular C_{2v} labels.

Results and Discussion

The spectra, Figure 2, show pronounced dichroic effects in the far-i.r. region and to this extent support the postulate upon which the experiment was based. In the E(||) spectrum six bands are found between 120 and 500 cm^{-1} which compares well with seven B_2 modes expected in this region: the weak band at 460 cm^{-1} is regarded as a residual of the much stronger one in E(⊥). The E(⊥) spectrum contains many more bands; ten of the theoretical sixteen low-frequency

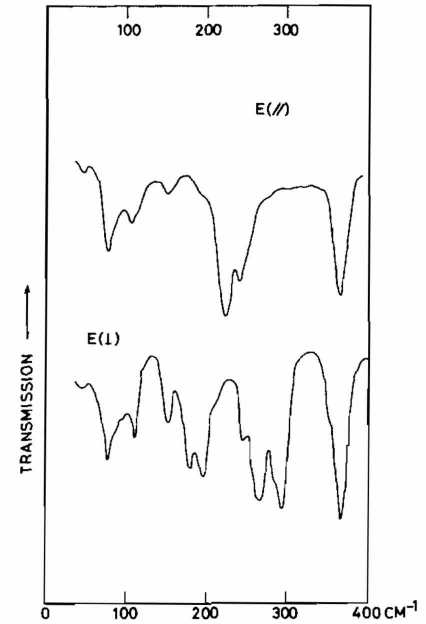


Figure 2. Polarised far-i.r. transmission spectra of VO (acac)$_2$ at liquid nitrogen temperature.

TABLE III. Frequencies (cm^{-1}) from Polarised-i.r. Transmission Spectra for VO(acac)$_2$, and from Raman and I.r. Spectra of the Polycrystalline Solid.

Raman	Infra-red						Assignment
	Mull		E(‖)		E(⊥)		
L.N.	R.T.	L.N.	R.T.	L.N.	R.T.	L.N.	
43s			42w	44w	43w	46w	ν_L
62m, sh							
69vs							
	80s, br	78 m	79 m	78 m	81vs, br	78 m	
89vw		92m					
111m,sh	101w	113m	101m	107w		112m	
124s							
147m	146w	152w	147w	154w	148w	154m	π
178w	174wm	184wm			173m	180s	
	195m	198wm			196ms	196s	
223w	222m	227m	224s	225s			B_2, δ
247m	243wm	245wm	243m	243m	244m	244m	
262wm	261s	264s			264s	263s	
298vw	285ms	291m			286s	288m	
376w	365s	367s	366s	367s	367s	368s	$\delta(V{=}O)$
	406w, sh	407w			406m	407m	
	425ms	423s	425m	424m	430w, sh	433wm, sh	B_2, $\nu(V–O)$
468vs	465m	467s	458w	460w, sh	463vs, br	464vs	B_1, $\nu(V–O)$
	487vs, br	485vs, br	490vs[a]	490vs[a]		485m	B_2, δ
565vs	564w	565w					A_1, $\nu(V–O)$
	612s	615s					
664w	660m	661m					
684w, sh	672m, sh	670m, sh					
693m	688vs	685vs					
	793vs	794vs					$\pi(C–H)$
	803vs	805vs					
949m	942vs	940vs					
	977sh	980sh					
993wm	993vs	994vs					$\nu(V{=}O)$
	1010vs, br, sh	1010vs, br, sh					

[a] ± 5 cm^{-1}

modes are present between 120 and 500 cm^{-1}. Below 120 cm^{-1} both spectra show absorptions which are undoubtedly associated with the three A_u rotatory modes, but which must also include very-low frequency molecular deformations which will interact strongly with them; indeed no meaningful distinction can be drawn between them. NCA of M(acac)$_2$ and M(acac)$_3$ systems[3] with all atoms included invariably generate "internal" modes in the region below 100 cm^{-1}. In particular there will be one such mode of B_2 symmetry: we note that there are three bands below 120 cm^{-1} in E(‖) and consider that an internal mode contributes to them, thereby locating the seventh B_2 mode.

The spectra of all M(acac)$_2$ complexes[3] show a clear gap between 290 and 400 cm^{-1}: VO(acac)$_2$ is also clear in this region apart from a prominent band in E(‖) at 367 cm^{-1}, another in E(⊥) at 368 cm^{-1}, and a weak Raman counterpart at 376 cm^{-1}. Nakamoto and co-workers[1] originally attributed this to a ring deformation although in fact they only found it in VO(acac)$_2$ and its pyridine adduct and not in other M(acac)$_2$ compounds, but its position and dichroic behaviour are more consistent with $\delta(V{=}O)$. Although in terms of C_{2v} molecular symmetry both B_1 and B_2 $\delta(V{=}O)$ modes are expected, the vanadyl group is in an effectively tetragonal environment and the two modes are essentially degenerate (they would transform as E in D_{4h}). Since they will suffer the same static field effect their separation from the Raman mode indicates that there is quite substantial correlation coupling for this mode, which is not altogether surprising in view of its highly dipolar nature.

One mode with a major contribution from $\nu(V–O)$ motion should be present in the E(‖) spectrum and is identified with the 425 cm^{-1} band. The modes at 225 and 243 cm^{-1} may well have some slight contribution from $\nu(V–O)$ but otherwise we regard this as too low for a metal in the +IV oxidation state. Two further

ν(V–O) modes are associated with the intense Raman bands at 468 and 565 cm^{-1}, the lower of which has a strong i.r. counterpart in E($\perp$). The weak i.r. band at 564 cm^{-1} is consistent with assignment of the equivalent Raman band as A_1 ν(V–O) as this mode only attains i.r. activity by virtue of the dihedral angle between the rings. We note, for comparison, that Hancock and Thornton[4] located a metal-sensitive [presumed ν(V–O)] mode in $V^{III}(acac)_3$ at 449 cm^{-1}.

The total number of i.r. and Raman bands found below 790 cm^{-1} is close to that predicted; some are unique to one or other spectrum. No simple description of the remaining low-frequency modes can be given without a normal coordinate analysis but our physically-based assignment of B_2 modes improves the basis upon which a full calculation might be attempted.

Experimental

A laboratory sample of $VO(acac)_2$ was recrystallised from dichloromethane which yielded large crystals, some of them twinned. Although the compound is more soluble in chloroform, it did not yield good crystals. The axial orientation was determined from X-ray photographs.

Polarised i.r. spectra were obtained in the frequency interval 10–500 cm^{-1} using a Beckman-RIIC FS-720 interferometer with the samples mounted in a home-made cryostat. Even low laser powers decomposed the material at room temperature but good spectra were obtained from a crystal at liquid nitrogen temperature using 514.5 nm excitation and a Coderg T800 instrument.

Acknowledgement

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