all lose oxygen before melting when heated in air; the temperatures at which oxygen loss begins is indicated in Table I. Reactions between $Na_2TeO_4 \cdot 2H_2O$ and a chloride gave small crystals which were suitable for single-crystal X-ray diffraction studies.

TABLE I

CRYSTALLOGRAPHIC[a] AND STABILITY DATA

Compound	a, Å	b, Å	c, Å	Angle,[b] deg	d_x[c]	d_m	Dec pt,[d] °C
$MgTeO_4$	4.6860	5.5848	5.0198	93.211	5.466	5.43	630
$CdTeO_4$	5.0036	12.5254	4.9881		6.458	6.43	630
$CaTeO_4$	5.2299	12.6785	4.9809		4.658	4.64	700
$SrTeO_4$	5.5757	13.1144	5.0032		5.068	5.02	730
$BaTeO_4$	5.9224	13.5117	5.0230	93.483	5.444	5.49	790
$PbTeO_4$	5.4129	4.9471	6.0185	99.596	8.333	8.28	740

[a] Errors estimated from standard deviations are ±0.0004 Å for the 4–5 Å edges, ±0.0008 Å for 12–13 Å edges, and ±0.006° on the angles. [b] The angle is β for $MgTeO_4$ and $PbTeO_4$ but γ for $BaTeO_4$. [c] Calculated density based on crystallographic data. [d] Decomposition temperature by tga.

Single crystals of $SrTeO_4$ were found to be orthorhombic with a space group of $Pca2_1$ or $Pcam$. The refined cell dimensions are given in Table I. $CaTeO_4$ and $CdTeO_4$ were judged isomorphous with $SrTeO_4$ by comparison of their X-ray powder patterns; the refined cell dimensions of $CaTeO_4$ and $CdTeO_4$ are given in Table I. Density measurements (Table I) indicate four formula units per unit cell for these tellurates.

Single crystals of $BaTeO_4$ found to be monoclinic with a space group of $P2_1/c$ where $a = 5.9225$ Å, $b = 5.0229$ Å, $c = 15.0796$ Å, and $\beta = 116.56°$. The cell may also be described by $a = 5.9225$ Å, $b = 5.0229$ Å, $c = 13.5117$ Å, $\beta = 93.48°$, and a space group of $P2_1/n$. This cell has an obvious similarity to the cells of $CdTeO_4$, $CaTeO_4$, and $SrTeO_4$. Consequently, in Table I the cell dimensions have been rearranged to facilitate comparison. It appears that $BaTeO_4$ has a distorted version of the structure which exists for $CdTeO_4$, $CaTeO_4$, and $SrTeO_4$.

Single crystals of $PbTeO_4$ were found to be monoclinic, and the refined cell dimensions are given in Table I. The space group is $C2$, Cm, or $C2/m$, and there are two formula units per unit cell.

The powder pattern of $MgTeO_4$ was readily indexed by assuming it had a wolframite-type structure. Intensities were calculated using the published[3] positional parameters for $NiWO_4$, and a comparison of observed and calculated intensities supports this structure type for $MgTeO_4$.

Discussion

Of the tellurates prepared only $MgTeO_4$ appears to be of a known structure type. These tellurates are clearly not isostructural with the analogous sulfates and selenates. This is probably due to the preference of Te^{6+} for octahedral rather than tetrahedral coordination to oxygen. $MgTeO_4$ is isostructural with several tungstates; however, in this structure all cations are six-coordinated to oxygen. The other A^{2+}-TeO_4 tellurates are not isostructural with known structures of analogous tungstates, molybdates, or uranates.

X-Ray powder patterns of $BaTeO_4$ have been given by Engelbrecht and Sladky[1] and by Knyazeva and Kurapova.[2] These agree very well with our powder pattern, and thus it is certain that we all have the same phase.

Knyazeva and Kalugina[4] have reported the preparation of $SrTeO_4$; however, their powder pattern is entirely different than ours. Furthermore, their preparation temperature (750°) is very close to the decomposition temperature of $SrTeO_4$.

Natansohn[5,6] has reported the preparation of $MgTeO_4$, $CaTeO_4$, $SrTeO_4$, and $BaTeO_4$. However, preparative temperatures of 900–1000° were used, and such tellurates are not stable under these conditions.

It is possible that the valence states in $PbTeO_4$ are 4–4 instead of 2–6. However, $PbTeO_4$ is not merely a solid solution of PbO_2 and TeO_2 because it is not isomorphous with any form of PbO_2 or TeO_2. Furthermore, varying the reactant ratios in the PbO_2–TeO_2 system did not indicate a significant range of stoichiometry for $PbTeO_4$.

(3) R. O. Keeling, *Acta Crystallogr.*, **10**, 209 (1957).

(4) R. N. Knyazeva and Z. I. Kalugina, *Russ. J. Inorg. Chem.*, **15**, 895 (1970).

(5) S. Natansohn, U. S. Patent 3,509,064 (1970).

(6) S. Natansohn, Abstracts, Spring Meeting of the Electrochemical Society, Los Angeles, Calif., May 1970, No. 61.

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The Application of Symmetry Ascent Selection Rules to a Factor Group Analysis of Red Mercuric Iodide

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The study of metal–ligand vibrations[1,2] has played an important role in the development of coordination chemistry. However ambiguity in band assignment has often vitiated the value of such studies. Recently single-crystal infrared and Raman studies, *e.g.*,[3,4] have become more common and present the possibility of unambiguous band assignment. However, even in such cases where high-resolution polarized data are obtained, the number of observed vibrations may be less than that calculated on the basis of a factor group analysis. In such circumstances the polarization data may allow assignment of a vibration to a particular symmetry species but it may be impossible to distinguish whether the vibration concerned is internal to a molecular species in the crystal or is external thereto, *i.e.*, is a lattice mode.

For example, vibrational studies of red mercuric iodide[5,6] were recently substantiated by a single-crystal Raman study.[7] This revealed only four of the six expected Raman-active transitions down to an ob-

(1) D. M. Adams, "Metal-Ligand and Related Vibrations," E. Arnold, London, 1967.

(2) I. Nakagawa, *Coord. Chem. Rev.*, **4**, 423 (1969).

(3) D. M. Adams, M. A. Hooper, and M. H. Lloyd, *J. Chem. Soc. A*, 946 (1971).

(4) D. M. Adams and R. R. Smardzewski, *ibid.*, 8, 10, 714 (1971).

(5) J. P. Mon, *C. R. Acad. Sci., Ser. B*, **262**, 493 (1966).

(6) R. P. J. Cooney, J. R. Hall, and M. A. Hooper, *Aust. J. Chem.*, **21**, 2145 (1968).

(7) D. M. Adams and M. A. Hooper, *ibid.*, **24**, 885 (1971).

servation limit of 2.5 cm^{-1}. The factor group analysis predicts three E_g modes (two internal to HgI_2 and one external) and two B_{1g} modes (one internal and one external) as well as an internal A_{1g} mode. Of the four bands observed, two were assigned to *internal* E_g modes, one was assigned to an *internal* B_{1g} mode, and one was assigned to the internal A_{1g} mode. No evidence was presented to substantiate that the E_g and B_{1g} modes were in fact internal rather than external. Since the internal E_g modes have energies of 17 and 29 cm^{-1}, remarkably low for vibrations of a covalent metal–ligand bond, it was of especial interest, from the viewpoint of metal–ligand bonding, to substantiate that these vibrations were indeed correctly assigned as internal modes. The conclusions can be confirmed by an examination of the selection rules of these translational modes after requiring the crystal symmetry to ascend from the D_{4h}^{15} ($P4_2/nmc$) space group to an equivalent octahedral group.

The distortion of the red mercuric iodide lattice from an octahedral space group is very small. Cubic close packing would be perfect if the ratio c/a were 2.828 rather than the observed[8] 2.84. The removal of the tetragonal distortion from each sublattice results in the ascent in symmetry of the mercury sites from D_{2d} to O_h and of the iodide sites from C_{2v} to T_d symmetry (Figure 1). The new octahedral space group is unequivocally O_h^5 ($Fm3m$) in which all Hg–Hg, I–I, and Hg–I distances, respectively, become equal.

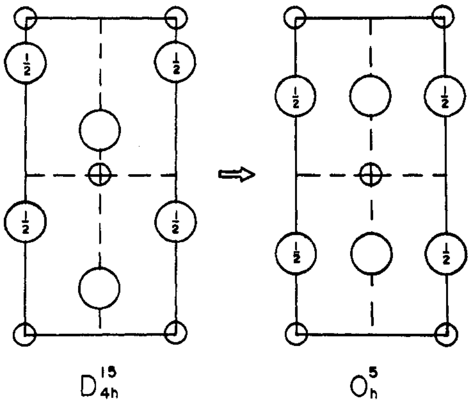

Figure 1.—The ascent in symmetry of the D_{4h}^{15} space group to O_h^5.

Since the wavelength of infrared radiation is very long compared to the unit cell dimensions, it is usually assumed[9] that propagation takes place only at the center of the Brillouin zone. This point may correspond in either the D_{4h} or the O_h factor groups to the center of the face adjoining two unit cells in the c direction. The relevant vibration unit in the octahedral space group is a cluster of six mercury and eight iodine atoms (Figure 2). A previous assignment[6] used only a part of this unit and it appears that the modes described as B_{1g} are essentially ungerade in character with respect to motion of the mercury atoms (see Figure 2). Since four of these atoms lie in the horizontal plane of the factor group, they cannot move parallel to the z axis in any gerade mode.

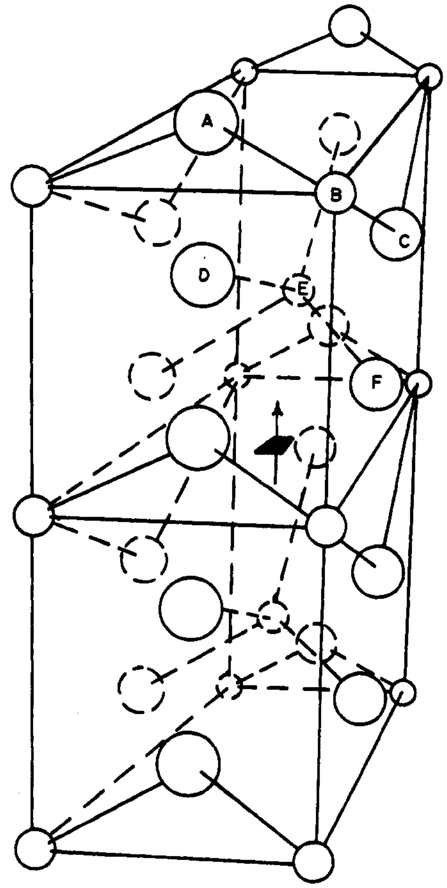

Figure 2.—The Brillouin zone of the D_{4h}^{15} space group for wave propagation parallel to the z axis: mercury, small circles; iodine, large circles. The atoms labeled A–F are the subgroup of the Bravais unit cell used for vibrational analysis in ref 2.

The upgrading of this zone to an octahedral factor group results in the addition of two orthogonal fourfold axes to the symmetry of this vibration unit. The correlation of D_{4h} vibrational wave functions (Table I) to those of the O_h factor group displays the effects of the additional operators. Some of the allowed modes correlate into partly forbidden representations in the higher symmetry. The vibrational wave functions have been normalized in the O_h group to preserve the correct number of modes, under the initial assumption that equal parts of each O_h mode are required (footnote c, Table I).

We propose that the selection rules governing the intensities of the octahedral modes are preserved on descent in symmetry to the D_{4h} factor group. This selection rule correlation has recently been discussed[10] with respect to electronic spectroscopy and magnetic phenomena and appears to be relevant to vibrational spectroscopy. Since D_{4h} is a subset of O_h, the wave function basis set is unchanged[11] on descent in symmetry from O_h to D_{4h}. If the representation in the subset is related to more than one representation of the generic octahedral group, then the intensity of the D_{4h} vibration is determined only from the proportion of the allowed generic mode.

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[8] R. W. C. Wyckoff, "Crystal Structures," Vol. 1, Interscience, New York, N. Y., 1963.

[9] S. S. Mitra and P. J. Gielisse, *Progr. Infrared Spectrosc.*, **2**, 47 (1964).

[10] B. R. Hollebone, A. B. P. Lever, and J. C. Donini, *Mol. Phys.*, **22**, 155 (1971).

[11] The selection rules are completely preserved only if configuration interaction, which may become allowed in the less symmetric group, remains insignificant.

TABLE I

THE CORRELATION OF VIBRATIONAL MODES FROM THE D_{4h} TO O_h FACTOR GROUP

Mode[a]	D_{4h}[b]	O_h[c,d]
Internal raman active	$\vert A_{1g}\iota\rangle$	$(1/\sqrt{2})[\vert A_{1g}0+\rangle + \vert E_g0+\rangle]$
	$\vert B_{1g}\iota\rangle$	$(1/\sqrt{2})[\vert A_{2g}0-\rangle + \vert E_g0-\rangle]$
	$2 \times \{\vert E_g\theta\rangle$	$(1/\sqrt{2})[\vert T_{1g} - 1+\rangle + \vert T_{2g} + 1-\rangle]$
	$\vert E_g\epsilon\rangle$	$(1/\sqrt{2})[\vert T_{1g} + 1+\rangle - \vert T_{2g} - 1-\rangle]$
Internal infrared active	$\vert A_{2u}\iota\rangle$	$\vert T_{1u}0+\rangle$
	$\vert B_{2u}\iota\rangle$	$\vert T_{2u}0+\rangle$
	$2 \times \{\vert E_u\theta\rangle$	$(1/\sqrt{2})[\vert T_{1u} - 1+\rangle + \vert T_{2u} + 1-\rangle]$
	$\vert E_u\epsilon\rangle$	$(1/\sqrt{2})[\vert T_{1u} + 1+\rangle - \vert T_{2u} - 1-\rangle]$
Acoustic infrared active	$\vert A_{2u}\iota\rangle$	$\vert T_{1u}0+\rangle$
	$\vert E_u\theta\rangle$	$(1/\sqrt{2})[\vert T_{1u} - 1+\rangle + \vert T_{2u} + 1-\rangle]$
	$\vert E_u\epsilon\rangle$	$(1/\sqrt{2})[\vert T_{1u} + 1+\rangle - \vert T_{2u} - 1-\rangle]$
Lattice raman active	$\vert B_{1g}\iota\rangle$	$(1/\sqrt{2})[\vert A_{2g}0-\rangle - \vert E_g0-\rangle]$
	$\vert E_g\theta\rangle$	$(1/\sqrt{2})[\vert T_{1g} - 1+\rangle + \vert T_{2g} + 1-\rangle]$
	$\vert E_g\epsilon\rangle$	$(1/\sqrt{2})[\vert T_{1g} + 1+\rangle - \vert T_{2g} - 1-\rangle]$

[a] Activity in D_{4h}. [b] Representation in the D_{4h} factor group. [c] Wave functions assume complete coupling (see text). Note that $\Sigma_\iota\int\psi^*\psi\,d\tau = 18$ in agreement with the total number of degrees of freedom in the D_{4h} factor group. [d] For the derivation of these functions see ref 10.

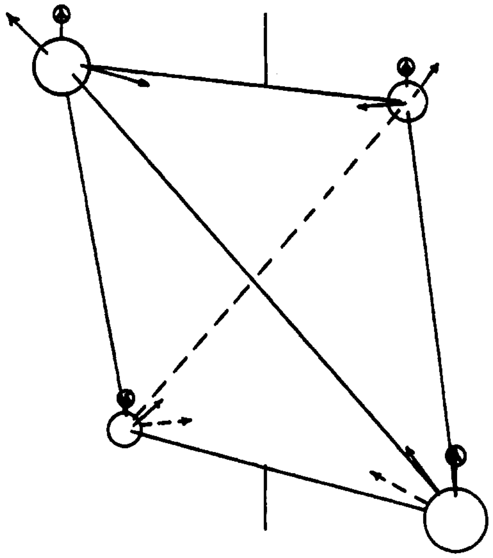

Figure 3.—The resolution of the B_{1g} mode of the D_{4h}^{15} iodine sublattice (denoted ○) into the A_{2g} mode at 45° to the z axis (forbidden) and the E_g mode in the xy plane (allowed) of O_h^5.

On ascent in symmetry to the octahedral Brillouin zone, the correlation of some of the D_{4h} representations into more than one octahedral mode can be regarded as a resolution of the motion implied by the D_{4h} mode into those implied by the O_h mode. For example, the z axis directed motion of the iodine atoms in the B_{1g} mode is resolved in the O_h group into a motion at 45° to the z axis corresponding to an A_{2g} mode and into one in the xy plane corresponding to the E_g mode (Figure 3). The former forbidden mode corresponds to the lattice translation since it causes planes of iodine atoms to interact while the allowed E_g mode of O_h can be regarded as internal. A similar analysis for the E_g modes of D_{4h} reveals again that the lattice mode is the forbidden T_{1g} vibration in O_h and thus confirms that the experimentally observed E_g modes are indeed internal.

The application of selection rules appertaining to a higher group than that actually present has been recognized informally in the past.[12] It is hoped that the publication[10] of a mathematical formalism to deal with this problem will lead to a more rigorous application in the future.

[12] H. J. Buttery, G. Keeling, S. F. A. Kettle, I. Paul, and P. J. Stamper, *Trans. Faraday Soc.*, **47**, 48 (1969).