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Geometrical Consequences of the Jahn-Teller Effect

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The conditions which define the subgroups which may arise by a reduction in symmetry of a parent point group consequent upon a Jahn-Teller distortion are given. Accessible subgroups are listed for all important molecular point groups. The occurrence of the Jahn-Teller effect in some five cordinate complexes is briefly discussed.

Introduction

Solutions of the electronic eigenvalue problem for a molecule with appreciable symmetry frequently lead to symmetry-required degeneracies. Jahn and Teller were the first to recognise[1] that, for *non-linear* molecules, there will invariably be non-isoergic mixing between members of such a degenerate set of eigenfunctions [Φ] caused by certain non-totally symmetric vibrations of the molecule, leading to a relief of the electronic degeneracy; effectively, the members of the degenerate set 'repel' each other, so that one members becomes more stable than the others. Formally, Jahn and Teller showed that there are non-zero matrix elements of the form $\langle \Phi_i \mid V_r \mid \Phi_j \rangle$ where V_r is the operator which represents the dependence of the energy of the distorted molecule on the non-totally symmetric normal coordinate n_r. Such matrix elements can only be non-zero if they transform as the totally symmetric irreducible representation of the point group of the undistorted molecule. Since Φ_i and Φ_j are members of a degenerate set this requirement is, explicitly, that the irreducible representation under which the normal coordinate n_r transforms be contained in the *symmetric* direct product of the irreducible representation of the set [Φ].

Subsequent to the publication of their paper there has been a wide-spread search for static distortions of molecules which are consistent with the operation of the Jahn-Teller effect. Part of the difficulty lies in the fact that the Jahn-Teller theorem is permissive only; a distortion may be very small or dynamic; in either case it may escape detection.

Orbitally degenerate ground states are common amongst complexes formed by the transition metal ions and this is a field in which the Jahn-Teller effect is frequently invoked. Particularly well known is the fairly common occurrence of six co-ordinate complexes of copper(II) in which the molecular geometry often corresponds to a tetragonally distorted octahedral coordination.

Although in the case of 'octahedral' complexes the geometries which are consistent with the operation of the Jahn-Teller effect are reasonably well known, this is not the case for complexes of lower inherent symmetry (five cordinate complexes and complexes containing multidate ligands, for example). One consequence of this has been that on occasions it has been assumed that any distortion which removes orbital degeneracy does so by virtue of the Jahn-Teller theorem. This is not so. For any given molecular geometry only certain vibrations are Jahn-Teller active and only certain sub-group geometries are accessible by their operation. So, only vibrations of an octahedral complex which do not remove the centre of symmetry can be Jahn-Teller active. However, some of the vibrations whichi retain the centre of symmetry cannot be Jahn-Teller active.

In the present paper we give a complete list of subgroups of a point group which are accessible by virtue of a Jahn-Teller distortion. If a sub-group is not included in our list then it is not accessible. Because the accessible sub-groups depend not only on molecular geometry but also on the symmetry of the degenerate electronic state, we sub-divide our tabulation accordingly. A number of authors have already given very useful discussions of the detailed calculations of Jahn-Teller distortions in cubic and planar sistems.[2-5] Sturge in particular gives an extensive account of the experimental manifestations of both static and dynamic distortions.[2] The data which we now present is perhaps most informative when used in the negative sense; from it we can immediately determine those point groups which are *not* accessible from any idealised geometry. The possibility of an erronious invocation of the Jahn-Teller effect is thereby significantly diminished. We also emphasise that, although a geometry is listed as accessible, those energy terms which stabilise it may be small relative to those favouring one of the alternative Jahn-Teller distortions; furthermore the sense of the distortion is not given. For example, in an octahedral Cu^{II} complex the ^2E_g electronic ground state is subject to a Jahn-Teller distortion of E_g symmetry. Suitable vibrations of the six-coordinate ligand system have the angular forms $\pm 1/\sqrt{6}\,(2z^2-x^2-y^2)$ or $\pm 1/\sqrt{2}\,(x^2-y^2)$, lead-

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(1) H.A. Jahn and E. Teller, *Proc. Roy. Soc.*, *161A*, 220 (1937).

(2) M.D. Sturge, *Solid State Physics*, *20*, 91 (1967).

(3) A.D. Liehr, *Progr. Inorg. Chem.*, 3, 281 (1962).

(4) A.D. Liehr, *ibid.*, *4*, 455 (1963).

(5) A D. Liehr, *J. Phys. Chem.*, *67*, 389, 471 (1963).

ing respectively to a tetragonal elongation or compression or to a biaxial distortion. If the distorting potential is both linear and harmonic any of these four distortions is equally probable; additionally all these structures would be smoothly interconverted by the eight other equally probable distortions defined with respect to the x or y axes of quantisation. However these distortions are generally anharmonic, and a section of the potential well might be described by the familiar Morse curve. The restoring forces for this case would normally follow the sequence: tetragonal compression > biaxial distortion > tetragonal elongation. Experiment strongly suggests that the static Jahn-Teller distortions in these cases are usually tetragonal elongations. Our data for O_h is general, and applies for all variations such as cube, octahedron or even the full 48 co-ordination. The detailed vibronic forces in each case must be examined in a similar fashion at least qualitatively before the *permissable* distortions can be distinguished from one another. In addition there will be many cases in which quadratic terms such as $\partial^2 Q/\partial x \partial y$ in the potential energy equation cannot be ignored.[2,6] Finally the spin-orbit coupling often provides an alternative mechanism for the relief of certain electronic degeneracy and must also be included in any detailed discussion.[7]

Static Jahn-Teller distortions are often small because the restoring potential is usually large and frequently the interaction between the electronic state and the vibrating parts of the molecule is not great (for example, suitable ligand vibrations do not greatly affect the $^2T_{2g}$ ground state of octahedral Ti^{III}. Even when the static distortion is large enough to be detected crystallographically, the distortions may well average out to zero during an experiment with a long characteristic time (such as n.m.r.). Dynamic Jahn-Teller distortions are manifest in the very general Ham effect;[8] as a result of Jahn-Teller mixing of otherwise pure electronic states, off-diagonal elements in the energy equations are reduced. This consideration is particularly relevant to the spin-orbit coupling integrals because these energies and the Jahn-Teller stabilisation energies are often similar. Explicitly, a dynamic Jahn-Teller distortion may contribute significantly to the reduction of the spin-orbit coupling constant from the free-ion value in suitable complexes.

Method. The condition under which a sub-group of a point group (the parent point group) is accessible by virtue of a Jahn-Teller active vibration may conveniently be divided into two parts.

(a) A point group is accessible if and only if the irreducible representation of the Jahn-Teller active vibration in the parent point group subduces the totally symmetric irreducible representation of the subgroup.

(b) A point group is accessible if and only if there exists no intermediate point group (such that there is an ordered reduction in symmetry passing from the parent to the intermediate and thence to the final subgroup) such that a vibration satisfying condition (a) for the final subgroup also satisfies it for the intermediate subgroup.

Note that when the Jahn-Teller active vibration is itself degenerate (as it normally is) a reduction in symmetry is possible by any of the component vibrations. Consequently each component must be followed by a systematic reduction of symmetry until each has separately spanned a totally symmetric representation. When a sub-group does not satisfy condition (b) above but is itself an immediate subgroup of two subgroups which are not themselves related by a reduction in symmetry and which separately satisfy this condition, then this subgroup is also accessible by a linear combination of the degenerate fundamentals.

In practice, the problem is simplified by a preliminary application of special conditions implicit in those above. Consider, for example, a Jahn-Teller vibration which is doubly degenerate. Any operation or set of operations of the parent point group having a character of 2 for the irreducible representation of the Jahn-Teller active vibration cannot be destroyed by the vibration and must therefore be contained in the group of elements of the final sub-group (frequently, such operations immediately identify the final subgroup). Further, any operation or set of operations with characters of –2 or –1 for the irreducible representation must be destroyed in proceeding to an acceptable sub-group (thus, a doubly degenerate Jahn-Teller-active vibration invariably destroys all threefold axes of the parent point group).

Results

We illustrate the method by reference to a coordination complex with parent point group O_h, having an orbitally degenerate ground state.

The complex is susceptible to a Jahn-Teller distortion if the ground state is of E_g, T_{1g}, T_{2g}, E_u, T_{1u}, or T_{2u} symmetry. The symmetric direct-product of each of these representations is:

$$\{E_g^2\} = A_{1g} + E_g$$
$$\{T_{1g}^2\} = A_{1g} + E_g + T_{2g}$$
$$\{T_{2g}^2\} = A_{1g} + E_g + T_{2g}$$
$$\{E_u^2\} = A_{1g} + E_g$$
$$\{T_{1u}^2\} = A_{1g} + E_g + T_{2g}$$
$$\{T_{2u}^2\} = A_{1g} + E_g + T_{2g}$$

The totally-symmetric vibration indicated in these products cannot lead to any distortion of the octahedral symmetry. It follows[1] that components of a T_{2g} vibration are Jahn-Teller active for electronic states of T_{1g}, T_{2g}, T_{1u} ,and T_{2u} orbital symmetry, while components of an E_g vibration are Jahn-Teller active for any orbitally degenerate ground state. In Figure 1 we indicate some of the point groups which are accessible by a reduction in symmetry of the parent O_h point group.[9] This diagram includes only those subgroups of O_h which contain the inversion operation,

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(7) C.J. Ballhausen «Introduction to Ligand Field Theory», McGraw-Hill (1962).
(8) F.S. Ham, *Phys. Rev. 138*, 1727A (1965).
(9) G.F. Koster, J.O Dimmock, R.G. Wheeler, and H. Statz, «Properties of the 32 Point Groups», M.I.T. (1963).

because no component of an E_g or a T_{2g} vibration can destroy a centre of symmetry.

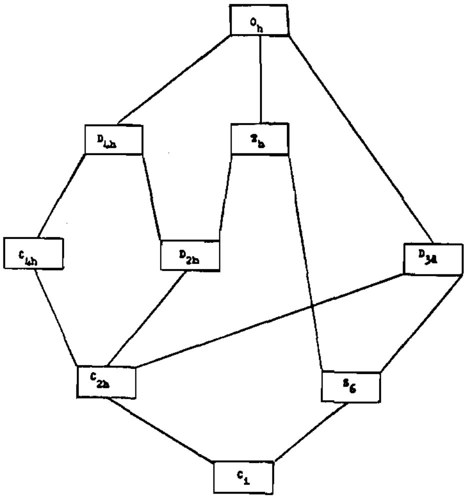

Figure 1. Centro-symmetric sub-groups of the point group O_h.

For electronic states which are more than two-fold orbitally degenerate, certain distortions may only partially remove this degeneracy. For example, the ground state of octahedral Ti^{III} is $^2T_{2g}$. If this is distorted by a tetragonal elongation, the ground state becomes ^2E_g (in D_{4h}) and as such it would be susceptible to further static distortion. For a tetragonal compression, however, the ground state would be $^2B_{2g}$.

i) *The E_g Vibrations.* The E_g irreducible representation has a character of 2 for the E, i, $3C_2$, and $3\sigma_h$ classes of symmetry operations of the octahedron. Therefore none of these symmetry elements may be destroyed by a Jahn-Teller distortion of E_g symmetry. It follows that a distortion occurring by virtue of a vibration of this symmetry may only lead to the subgroups D_{4h} and D_{2h} of Figure 1. From correlation tables,[10] we find that for $O_h \rightarrow D_{4h}$, $E_g \rightarrow A_{1g}+B_{1g}$. Thus one component of E_g (*e.g.* the tetragonal distortion, usually elongation, observed for Cu^{II} complexes), may be effective in reducing the symmetry from O_h to D_{4h}. It is readily established that this vibration transforms as the angular function $1/\sqrt{3}\,(3\cos^2\vartheta-1)$. The second component of E_g (transforming as $\cos 2\Phi \sin^2\vartheta$) cannot reduce the symmetry to D_{4h}, but instead leads to D_{2h} symmetry. It follows that for a six-coordinate complex the D_{2h} structure must be rhomboid rather than rectangular.

ii) *The T_{2g} Vibration.* In this case no major simplification of Figure 1 is possible.

From correlation tables we find the following correspondances

O_h	D_{4h}	T_h	D_{3d}	C_{4h}	D_{2h}
T_{2g}	$B_{2g}+E_g$	T_g	$A_{1g}+E_g$	B_g+E_g	$A_g+B_{2g}+B_{3g}$

C_{2h}	S_6	C_i
$2A_g+E_g$	A_g+E_g	$3A_g$

We at once conclude that the D_{4h}, T_h, and C_{4h} subgroups are not accessible by virtue of the distortion of an octahedron by any T_{2g} vibration. Deleting these from Figure 1 we obtain Figure 2.

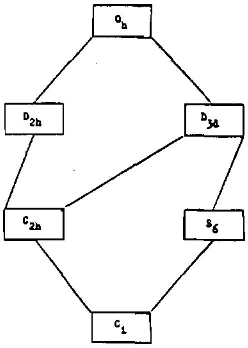

Figure 2.

It is at once evident that both D_{2h} and D_{3d} point groups are Jahn-Teller accessible. S_6 is not, for its A_g vibration correlates with that of A_{1g} symmetry in D_{3d}. The two A_g vibrations of C_{2h} correlate with those of A_g and A_{1g} symmetry in D_{2h} and D_{3d} respectively. This does not mean that C_{2h} is not accessible, for, if a combination of these two degenerate vibrations of the original O_h group is activated, this combination will also have symmetry A_g in C_{2h}, but will *not* correlate directly with the single A_g or A_{1g} vibrations of D_{2h} and D_{3d}. C_{2h} is accessible by virtue of this combination vibration. Such cases are readily found by following, for each parent point group, all possible routes for a descent in symmetry. We conclude that the D_{2h}, D_{3d}, C_{2h}, and C_i subgroups of O_h are accessible through a T_{2g} vibration. It should be noted that for six co-ordinate complexes the D_{2h} geometry will be rectangular not rhomboid (*c.f.* the E_g vibration).

The *permissable* Jahn-Teller distortions for all point groups of interest are given in Table I. All degenerate electronic states are included. The double-group representations are included, however, only for those cases where the representation has a degeneracy of four or more, as Kramers degeneracy cannot be lifted by a Jahn-Teller distortion.[11] For these states, it is the *antisymmetric* direct product which must include the symmetry of the vibration.

Discussion

In this discussion we illustrate the application of Table I by a brief discussion of the Jahn-Teller effect in some five coordinate species. Such species are of particular interest in this respect because it appears that the inter-ligand repulsion contributions to the total energy are relatively insensitive to the molecular geometry for monodentate ligands.[12] In such a situation a distortion consequent upon a Jahn-Teller effect may well be magnified. However, the probability of

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(12) M. Ciampolini, *Struct. and Bonding*, 6, 52 (1969).

Table I.

Parent Point Group	Jahn-Teller active vibrations	Electronic States split	Ground-state symmetries consistent with the operation of a Jahn-Teller effect
O_h	E_g	$E_g,E_u,T_{1g},T_{1u},T_{2g},T_{2u},G_{3/2g},G_{3/2u}$	D_{4h},D_{2h} (rhombus)
	T_{2g}	$T_{1g},T_{1u},T_{2g},T_{2u},G_{3/2g},G_{3/2u}$	D_{3d},D_{2h} (rectangle), C_{2h},C_i
T_d	E	$E,T_1,T_2,G_{3/2}$	D_{2d},D_2
	T_2	$T_1,T_2,G_{3/2}$	C_{3v},C_{2v},C_s,C_1
T_h	E_g	$E_g,E_u,T_g,T_u,G_{3/2g},G_{3/2u}$	D_{2h}
	T_g	$T_g,T_u,G_{3/2g},G_{3/2u}$	C_{2h},S_6,C_i
O	E	$E,T_1,T_2,G_{3/2}$	D_4,D_2
	T_2	$T_1,T_2,G_{3/2}$	D_3,D_2,C_2,C_1
T	E	$E,T,G_{3/2}$	D_2
	T	$T,G_{3/2}$	C_3,C_2,C_1
D_{6h}	E_{2g}	$E_{1g},E_{2g},E_{1u},E_{2u}$	D_{2h},C_{2h}
D_{4h}	B_{1g}	E_g,E_u	D_{2h} (rhombus)
	B_{2g}	E_g,E_u	D_{2h} (rectangle)
D_{3h}	E'	E', E''	C_{2v},C_s
C_{6h}	E_{2g}	$E_{1g},E_{1u},E_{2g},E_{2u}$	C_{2h}
C_{4h}	$2B_g$	E_g,E_u	C_{2h}
C_{3h}	E'	E', E''	C_s
C_{6v}	E_2	E_1,E_2	C_{2v},C_2
C_{4v}	B_1	E	$C_{2v},$
	B_2	E	$C_{2v},$
C_{3v}	E	E	C_s,C_1
D_{3d}	E_g	E_g,E_u	C_{2h},C_i
D_{2d}	B_1	E	D_2
	B_2	E	C_{2v}
D_6	E_2	E_1,E_2	D_2,C_2
D_4	B_1	E	D_2
	B_2	E	D_2
D_3	E	E	C_2,C_1
C_6	E_2	E_1,E_2	C_2
C_4	$2B$	E	C_2
C_3	E	E	C_1
S_6	E_g	E_g,E_u	C_i
S_4	$2B$	E	C_2
I_h	G_g	$G_g,G_u,H_g,H_u,I_{5/2g},I_{5/2u}$	$T_h,D_{3d},C_{2h},S_6,C_i$
	$2H_g$	$T_{1g},T_{1u},T_{2g},T_{2u},G_g,G_u,H_g,H_u$ $G_{3/2g},G_{3/2u},I_{5/2g},I_{5/2u}$	$D_{5d},D_{3d},D_{2h},C_{2h},C_i$
I	G	$G,H,I_{5/2}$	T,D_3,C_3,C_2,C_1
	$2H$	$T_1,T_2,G,H,G_{3/2},I_{5/2}$	D_5,D_3,D_2,C_2,C_1
$D_{\infty h}$	none[1]		
D_{5h}	E_1'	E_2',E_2''	C_{2v},C_s
	E_2'	E_1',E_1''	C_{2v},C_s
C_{5h}	E_1'	E_2',E_2''	C_s
	E_2'	E_1',E_1''	C_s
$C_{\infty v}$	none[1]		
C_{5v}	E_1	E_2	C_s,C_1
	E_2	E_1	C_s,C_1
D_{6d}	B_1	E_3	D_6
	B_2	E_3	C_{6v}
	E_2	E_1,E_5	D_2,C_{2v},C_2
	E_4	E_2,E_4	D_{2d},S_4
D_{5d}	E_{1g}	E_{2g},E_{2u}	C_{2h},C_i
	E_{2g}	E_{1g},E_{1u}	C_{2h},C_i
D_{4d}	B_1	E_2	D_4
	B_2	E_2	C_{6v}
	E	E_1,E_3	D_2,C_{2v},C_2
D_5	E_1	E_2	C_2,C_1
	E_2	E_1	C_2,C_1
C_5	E_1	E_2	C_1
	E_2	E_1	C_1
S_{12}	$2B$	E_3	C_6
	E_2	E_1,E_5	C_2
	E_4	E_2,E_4	S_4
S_{10}	E_{1g}	E_{2g},E_{2u}	C_i
	E_{2g}	E_{1g},E_{1u}	C_i
S_8	$2B$	E_2	C_4
	E_2	E_1,E_3	C_2

occurrence of a dynamic phenomenon is also increased.

Two idealised geometries are recognised for five coordinate complexes, namely the trigonal bipyramid (D_{3h}) and the square pyramid (C_{4v}). Molecules of D_{3h} symmetry may have ground states of E' and E'' symmetry and those of C_{4v} symmetry may have E ground states. In both of the most symmetrical five-coordination geometries, therefore, the possibility of a Jahn-Teller distortion exists. In the C_{4v} case, as shown by Table I, the final geometry will be C_{2v}.

For the B_1 vibration the distortion will be such that the 'equivalent' bonds will distort to become either two long and two short bonds or two bonds 'up' and two bonds 'down'. In the case of a B_2 distortion, the four bond-lengths remain identical. Of these three distinct distortions, the last two seem the more probable since bond-angle changes are less energy-demanding than those involving bond length changes. Such facile distortions could however be of a dynamic nature.

In the D_{3h} case only the E′ vibrations are Jahn-Teller active. The plane defined by the equatorial ligands remains a symmetry plane but the ligands lying in this plane may each be unique (final C_s symmetry) or two may be equivalent (final C_{2v} symmetry).

If the one-electron d-orbital splitting patterns are:[12]

$$D_{3h}\ z^2(A_1') > xy,\ x^2{-}y^2(E') > xz,\ yz\ (E'')$$

$$C_{4v}\ x^2{-}y^2(B_1) > z^2(A_1) > xy(B_2) > xz,\ yz(E)$$

then the following configurations may give rise to low-lying states which, in principle, are susceptible to a Jahn-Teller distortion.

$$D_{3h}\ d^1(^2E''),\ d^2(^1E'),\ d^3(^4E',\ ^2E''),\ d^5(^2E',\ ^4E'')$$
$$d^6(^5E''),\ d^7(^2E'),\ d^8(^3E')$$

$$C_{4v}\ d^1(^2E),\ d^3(^2E),\ d^4(^3E),\ d^5(^4E),\ d^6(^5E).$$

There is a dearth of the necessary combination of structural and spectroscopic information on C_{4v} complexes that are expected to show the Jahn-Teller effect and so we restrict the following discussion to the D_{3h} case.

An interesting series is provided by $MX_3(NMe_3)_2$, $M = Ti^{III}$,[13] V^{III},[14] and Cr^{III},[15] $d^1(^2E'')$, $d^2(^3A_2')$, and d^3-$(^4E')$ respectively, $X = Br^-$ for Ti^{III} and Cl^- for the others. The idealised geometry for each compound is D_{3h}, but each shows a distortion to C_{2v} symmetry, of relative magnitude

$$d^3 > d^1 > d^2$$

This is the order one would expect on the basis of the operation of a Jahn-Teller effect. However, the distortion of the vanadium compound cannot be a consequence of vibronic effects. Whether the distortion of the other two species is similarly a consequence of inter-, rather than intra-, molecular forces, is not known. The octahedral case is much clearer. So, in the recently-determined structure of the $[Ti(urea)_6]^{3+}$ ion the distortion from O_h to D_3 symmetry cannot be due to the Jahn-Teller effect.[15]

The members of the series $[MeBr(Me_6tren)]^+$ $M = Fe^{II}$, Mn^{II}, Zn^{II}, Cu^{II}, Ni^{II}, Co^{II}[16,17,18] are all isostructural, all having rigorous (crystallographic) C_3 symmetry. This symmetry cannot arise as a consequence of the Jahn-Teller effect but must be imposed by the ligand geometry. It would be anticipated that the vibronic distortions would be in the order (in D_{3h} symmetry; C_{3v} labels are obtained by omitting the primes)

$$Ni^{II}(^3E') > Fe^{II}(^5E'') > Mn^{II}(^6A_1'),\ Cu^{II}(^2A_1'),\ Co^{II}(^4A_1'),$$
$$\text{and } Zn^{II}(^1A_1').$$

The observation that $[CoClP(\sigma{-}C_6H_4P\Phi_2)_3]^+$ has a symmetry of C_{2v} to C_s[19] is entirely consistent with the operation of a Jahn-Teller effect. The $[NiBr(Me_6tren)]^+$ ion is in a state derived from a... $(e')^3$ configuration. This nickel compound is evidently a key one, because the crystal-structure analysis gives no indication of the existence of a dynamic phenomenon, so it may well be concluded that vibronic effects are negligible. In this case their existence in, say, $TiBr_3(NMe_3)_2$, looks doubtful also.

Conclusions

It is clear that phenomena which can be unambiguously attributed to the Jahn-Teller effect are rare. Indeed, for the static effect, it is possible that is has never been observed. In such circumstances it is inevitable that the search should continue, and the data in the present paper will here prove of considerable value.

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