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A Symmetry Rule for Predicting Molecular Structures

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Abstract: Using the second-order Jahn–Teller effect as a basis of calculation, the stable structures of molecules XY_n are predicted for n = 2–7. The symmetry argument is used that $\langle\psi_0|\partial U/\partial Q|\psi_k\rangle$ is nonzero only if the direct product of the representations of ψ_0 and ψ_k contains the representation of $(\partial U/\partial Q)$. Only the lowest lying one or two excited states are considered for ψ_k. In spite of this severe approximation, the results are remarkably good for a large variety of molecules and complex ions. The method provides a good test for molecular orbital calculations.

Symmetry arguments have been used recently to predict the course of a number of chemical reactions.[1] There is a symmetry rule due to Bader[2] which predicts the specific way in which any molecule will react upon activation. This rule, which has been largely overlooked, is potentially of great value since, in principle, it can be applied to all molecules, including activated complexes.

The basis of the rule is the second-order, or pseudo, Jahn–Teller effect.[3] The first-order Jahn–Teller effect[4] deals with degenerate electronic states and actually has not been of major chemical importance. The second-order effect deals with electronic states that are merely close to each other (within about 4 eV) and clearly concerns a very large number of molecules.

While a very large number of possible applications exist for the second-order Jahn–Teller (SOJT) effect,[2,5] in this paper we will consider its use in predicting the stable shapes of molecules of formula XY_n. A preliminary note on this subject has appeared.[6a] Recently Bartell[6b] has discussed a number of examples of this kind using simple graphical arguments. These are completely equivalent to the group theoretic arguments to be used here.

We start by assuming a particular nuclear configuration for a molecule. This will place the molecule in a certain point group. The wave equation is assumed to be solved giving rise to a number of eigenvalues, E_0, $E_1, \ldots, E_k$, and the corresponding eigenstates, $\psi_0, \psi_1, \ldots, \psi_k$. We now distort the nuclei from the original positions by means of one of the normal displacements and ask the question whether this raises or lowers the energy of the original system. An answer may be obtained by the use of second-order perturbation theory and group theory.

After distortion the Hamiltonian may be written as

$$H = H_0 + \left(\frac{\partial U}{\partial Q}\right)Q + \frac{1}{2}\left(\frac{\partial^2 U}{\partial Q^2}\right)Q^2 \ldots \tag{1}$$

where H_0 is the original Hamiltonian, Q is the displacement of the normal coordinate from the original position, and U is the nuclear–nuclear and nuclear–electronic potential energy. The energy becomes (in the ground electronic state)

$$E = E_0 + Q\left\langle\psi_0\left|\frac{\partial U}{\partial Q}\right|\psi_0\right\rangle + \frac{Q^2}{2}\left\langle\psi_0\left|\frac{\partial^2 U}{\partial Q^2}\right|\psi_0\right\rangle + \sum_k \frac{\left[Q\left\langle\psi_0\left|\frac{\partial U}{\partial U}\right|\psi_k\right\rangle\right]^2}{(E_0 - E_k)} \tag{2}$$

(1) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (b) D. R. Eaton, *J. Am. Chem. Soc.*, **90**, 4272 (1968); (c) F. D. Mango and J. H. Schachtschneider, *ibid.*, **89**, 2484 (1967).

(2) R. F. W. Bader, *Can. J. Chem.*, **40**, 1164 (1962).

(3) U. Öpik and M. H. L. Pryce, *Proc. Roy. Soc.* (London), **A238**, 425 (1957).

(4) H. A. Jahn and E. Teller, **A161**, 220 (1937).

(5) (a) R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960); (b) D. H. W. den Boer and H. C. Longuet-Higgins, *ibid.*, **5**, 387 (1962); (c) B. J. Nicholson and H. C. Longuet-Higgins, *ibid.*, **9**, 461 (1965); (d) L. S. Bartell and R. M. Gavin, Jr., *J. Chem. Phys.*, **48**, 2466 (1968); (e) D. P. Chock, J. Jortner, and S. A. Rice, *ibid.*, **49**, 610 (1968).

(6) (a) R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 1252 (1969); (b) L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1963).

and the wave function becomes

$$\psi = \psi_0 + \sum_k \frac{Q\left\langle \psi_0 \left| \frac{\partial U}{\partial Q} \right| \psi_k \right\rangle}{(E_0 - E_k)} \psi_k \qquad (3)$$

Now the integrals over the electronic coordinates can only be different from zero if the direct product of the representations of two of the terms contains the representation of the third. The symmetry species of $(\partial U/\partial Q)$ is the same as that of the normal coordinate. The symmetry of $(\partial^2 U/\partial Q^2)$ is totally symmetric.

If the original wave function, ψ_0, is nondegenerate, then $\langle \psi_0 | \partial U/\partial Q | \psi_0 \rangle$ is only different from zero for symmetric displacements. Accordingly, we must assume that all totally symmetric motions will occur until the energy is minimized. That is, the bond lengths and bond angles will change to the best values, but still keeping the molecule within the same point group.

If the original wave function is degenerate, then the first-order Jahn–Teller effect occurs. The exception is for linear molecules where, instead, a Renner–Teller distortion may remove the degeneracy.[7]

Assuming that the first-order changes have occurred, the energy may be written as a sum of two second-order terms.

$$E = E_0 + f_{00}Q^2 + f_{0k}Q^2 \qquad (4)$$

The first of these is the change in energy averaged over the original electron distribution. For any reasonable nuclear arrangement, it will be always be positive since the electron density was optimized for the original nuclear configuration. Hence moving the nuclei will result in a restoring force. The second quadratic term is always negative, since it corresponds to changing the wave function to fit the new nuclear coordinates. This must lower the energy.

The sum of the two constants, f_{00} and f_{0k}, is the experimental force constant for the normal mode designated by Q. Depending on the magnitudes of f_{00} and f_{0k}, three cases can arise.

(a) The original configuration is stable and there is a normal force constant for the Q mode ($f_{00} \gg f_{0k}$).

(b) The original configuration is not rigid in the sense that there is an abnormally small force constant for the Q mode ($f_{00} \simeq f_{0k}$). This will lead to a wide amplitude of vibration for this particular displacement. With only small activation the molecule will go over into another structure, differing little in energy from the first.

(c) The original configuration will be unstable, changing spontaneously into another structure dictated by the nature of Q ($f_{00} \ll f_{0k}$). In order to draw conclusions as to the probable value of f_{0k}, a rather drastic approximation must now be made. The infinite sum over the excited states in eq 2 and 3 is replaced by one or two terms corresponding to the lowest one or two excited states. Bader[2,5a] has shown that this approximation is justified in certain cases. We can only justify it if it works in the application at hand. The symmetries of the ground state and the first excited state(s) now determine which kind of nuclear displacement occurs most easily, *i.e.*, the mode of decomposition or rearrangement of the molecule. From a practical point of view, the symmetry properties of electronic states can only be expressed in terms of molecular orbital theory. The representation of $\psi_0\psi_k$ is then the same as that of $\Phi_i\Phi_j$, where Φ_i is the MO occupied in ψ_0 and Φ_j is the MO occupied in its place in ψ_k. They correspond to the highest occupied and lowest unoccupied MO's and are just the levels with which visible and uv spectroscopy is concerned. An assumed structure which gives an MO scheme with a large energy gap between these levels must be a stable one. Some other, more stable structure may exist, but a complex reaction path of high activation energy would be needed to attain it, starting with the original structure.

If the energy gap, $E_0 - E_k$, is less than about 4 eV, then instability of the structure may be indicated. Either a spontaneous rearrangement will occur, or one of low activation energy. However, for this to happen, the symmetry of $\Phi_i\Phi_j$ must be the same as that of a normal coordinate which exists for the molecule. Further, the particular vibration should be one which, if continued, will lead to a plausible alternative structure. It should be noted that eq 4 predicts equal energy changes for either $\pm Q$. As Q becomes large, then cubic and higher terms would be needed in the energy expansion. These would fix the sign of Q leading to a new structure.

Since bending force constants are much smaller then stretching force constants, rearrangements involving mainly bond angle changes are more likely than those involving bond stretching (and breaking). That is, $|f_{0k}|$ is likely to be larger than f_{00} for bending modes since f_{00} is small.

The product $\Phi_i\Phi_j$ is proportional to a quantity, ρ_{0k}, called the transition density.[8] It represents the amount of electronic charge transferred within the molecule as a result of the nuclear motion. Bader[2] has shown pictorially how the transition density favors the nuclear motion of the same symmetry as ρ_{0k}. Bartell[6b] also has shown how the symmetry of ρ_{0k} must match up with the correct nuclear motions.

In the remainder of this article we will see what predictions are made about structures for a number of simple molecules of formula XY_n. For these cases structures of high symmetry are possible. It is for such structures that arguments based on group theory will give the greatest amount of information, since the possible nuclear motions are classified in detail. It is intuitively obvious that molecules XY_n and $XY_{n-m}Z_m$ will assume similar structures, if Y and Z are similar atoms. Hence the conclusions to be drawn below can be extrapolated to many related molecules, even though a strict group theoretic justification is not possible. The atom Y may even be replaced by a group of atoms treated as a single unit.

The procedure to be followed is to test each class of molecules in the two structures of highest symmetry for second-order Jahn–Teller instability. There are always two such structures which are interconvertible by a simple continuation of one of the normal modes. The critical modes are shown in Figure 1. References 9a and b show the vibrations of these molecules in more detail.[9] Table I summarizes the symmetry designations.

(7) R. Renner, *Z. Physik*, **92**, 172 (1934).

(8) H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A235**, 537 (1956).

(9) (a) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945; (b) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

Table I. Normal Modes Needed to Interconvert Symmetric Structures

Formula	Conversion
XY_2	Linear, $D_{\infty h} \underset{A_1}{\overset{\pi_u}{\rightleftharpoons}}$ bent, C_{2v}
XY_3	Planar, $D_{3h} \underset{A_1}{\overset{A_2''}{\rightleftharpoons}}$ pyramidal, C_{3v}
XY_4	Planar, $D_{4h} \underset{E}{\overset{B_{2u}}{\rightleftharpoons}}$ tetrahedral, T_d
XY_5	Trigonal bipyramid, $D_{3h} \underset{B_1}{\overset{E'}{\rightleftharpoons}}$ square pyramid, C_{4v}
XY_6	Octahedral, $O_h \underset{A_1''}{\overset{T_{2u}}{\rightleftharpoons}}$ trigonal prism, D_{3h}

XY_2 Molecules

The molecular orbital sequences for the dihydrides have been worked out in detail for several of the first-row elements. In the linear form the MO scheme, in order of increasing energy, is

$$(\sigma_g)(\sigma_u)(\pi_u)(2\sigma_g)(2\sigma_u)$$

where only the valence electrons are included. A four-electron molecule (BeH_2, BH_2^+) will have $\rho_{0k} = (\sigma_u)(\pi_u) = \Pi_g$. Since there is no vibration of this symmetry for a linear triatomic molecule, the linear form is stable. For five, six, seven, and eight electrons (NH_2, CH_2, BH_2, H_2O) $\rho_{0k} = (\pi_u)(2\sigma_g) = \Pi_u$. This vibration bends the linear molecule. Since the energy gap is not large, the SOJT effect dominates the force constant, and the molecules bend spontaneously. For a ten-electron molecule (NeH_2), $\rho_{0k} = (2\sigma_g)(2\sigma_u) = \Sigma_u$, and the molecule is stable to bending.

We should next consider stability in the bent form. However, this cannot be done by the present method, since the vibration that takes a bent triatomic molecule into a linear one is of A_1 symmetry. It is necessary, as shown earlier, to assume that all A_1 vibrations have already led to the best values of the bond angles and bond distances.

The above conclusions on structure for H_2X molecules agree with experiment, where known. They also agree with the well-known Walsh rules, based on quite different lines of argument.[10] For nonhydride molecules the MO scheme given by Walsh[10b] for s and p atomic orbitals is

$$(1\sigma_g)(1\sigma_u)(2\sigma_g)(2\sigma_u)(1\pi_u)(1\pi_g)(2\pi_u)(3\sigma_g)(3\sigma_u)$$

This order has been found not to be an invariant one for all molecules, by exact SCF MO calculations using Gaussian basis sets.[11] Such a result is not too surprising. Fortunately, the small variations do not affect the conclusions drawn from the simple Walsh sequence, except as described below.

The Walsh rules for XY_2 molecules are that molecules containing 16 or less valence electrons would be linear, 17–20 electrons would be bent, and 22 electrons would be linear. The predictions based on the second-order Jahn–Teller effect are given in Table II, using the Walsh MO sequence.

(10) (a) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953); (b) *ibid.*, 2266 (1953); (c) *ibid.*, 2296 (1953); (d) *ibid.*, 2301 (1953).

(11) (a) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966); (b) S. Peyerimhoff, R. J. Buenker, and J. L. Whitten, *ibid.*, **46**, 1707 (1967).

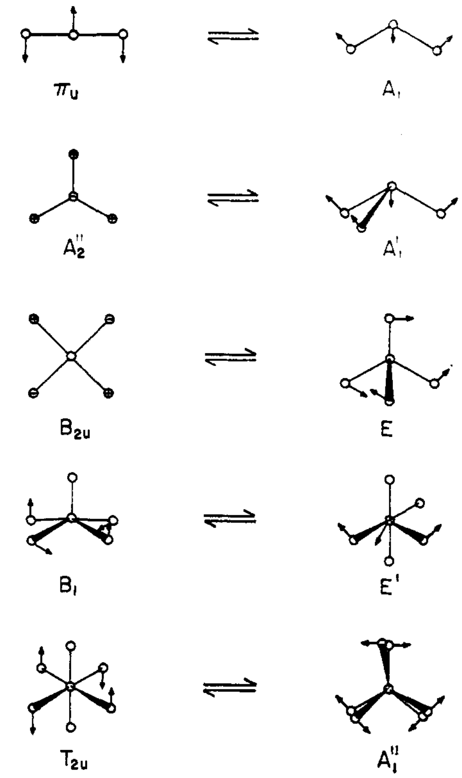

Figure 1. Symmetry species of normal modes that interconvert common structures of XY_n molecules. Only one example of each degenerate species is shown. The trigonal twist that converts an octahedral to a prismatic structure requires all three T_{2u} components.

Table II. Structural Predictions for XY_2 Molecules

System	ρ_{0k} symmetry	Structure (exptl)
8 electrons, Li_2O	Π_g	Linear
12 electrons, C_3	Σ_u, Δ_u	Linear
16 electrons, CO_2 NO_2^+, N_3^-, BeF_2	Σ_u, Δ_u	Linear
17 electrons, NO_2	Π_u	Bent
18 electrons, NO_2^- O_3, CF_2, SO_2	Π_u	Bent
19 electrons, NF_2, ClO_2	Π_u	Bent
20 electrons, F_2O, Cl_2O, $TeCl_2$, SCl_2, ICl_2^+	Π_u	Bent
22 electrons, XeF_2, I_3^-, ICl_2^-	Σ_u	Linear

While the agreement seems to be perfect between experimental structures and both the Walsh predictions and those based on SOJT effects, some discrepancies exist if more accurate MO schemes are used.

For example, the MO sequence for Li_2O becomes[11a]

$$(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^4(2\sigma_g)^0$$

which gives a transition density of Π_u symmetry. Hence Li_2O, like H_2O, should be bent. The Walsh rule, if applied to the new sequence, would also predict a bent structure. Calculations on the total energy of Li_2O as a function of angle show a linear structure as the most stable.[11a] However, the curve is very flat. This means that the force constant for the bending mode is small.[12] This is an example of case b where the two energy corrections are of comparable magnitude.

Another example is the molecule C_3, where the MO order is probably[13]

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(2\sigma_u)^2(1\pi_g)^0$$

again giving ρ_{0k} of π_u symmetry. The molecule is predicted to be bent, in disagreement with experiment. The bending frequency for C_3 is only 63 cm^{-1}, which means a small force constant.[14] We can see that an electronic transition with $E_k - E_0 = 3$ eV has reduced the force constant by a factor of 100, compared to CO_2, for example, where the bending frequency is 667 cm^{-1}.

Accurate SCF MO calculations on CO_2 and BeF_2 confirm the predictions based on the Walsh sequence, though the order is changed slightly.[11b] One would expect linear structures for the divalent metal halides in general, if the same sequence applied. In fact, a number such as CaF_2, $SrCl_2$, and $BaBr_2$ appear to be bent.[15] It would be of interest to see if MO calculations on these molecules predict a different ordering than for BeF_2.

Transition metal dihalides should be considered separately since the MO levels produced by the d orbitals of the metal are in the critical energy range. An MO scheme is given as

$$(1\sigma_g)(1\sigma_u)(1\pi_u)(1\pi_g)(2\sigma_g)(2\sigma_u)\vdots(\delta_g)(2\pi_g)(3\sigma_g)\vdots(4\sigma_g)(2\pi_u)$$

with the d manifold enclosed by dashed lines.[16] The ordering of the d orbitals is quite certain from ligand field theory, but the placing of the other orbitals is largely by educated guessing. However, the scheme has the virtue of correctly predicting all of the structures. Thus for d^1 to d^{10} metal ions ρ_{0k} is always of *gerade* symmetry. Hence bending is not favored and the structures should be linear, as found.[17]

For the post-transition elements we must add electrons beyond the d manifold. Stannous chloride has two electrons in $(4\sigma_g)$. This gives a ρ_{0k} of Π_u symmetry and a bent structure.

Triatomic molecules, HXY, are of $C_{\infty v}$ symmetry, if linear. A π vibration takes them into the bent form, and a totally symmetric vibration restores the bent form to linearity. The SCF MO scheme for HCN is[18]

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(2\pi)^0(4\sigma)^0$$

which predicts $\rho_{0k} = \Sigma$ or Δ, and a linear structure. For the hypothetical molecule HOF, the MO order is the same as for HCN.[11a] With four more electrons to fill in, this gives $\rho_{0k} = \pi$, and a bent structure is predicted. Hypochlorous acid, HOCl, is bent and is isoelectronic.

LiOH has the configuration $(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^0$ and is predicted to be bent. Calculation indicates it to be linear, but with a very small bending force constant.[11a]

(12) See K. S. Seshadri, D. White, and D. E. Mann, *J. Chem. Phys.*, **45**, 4697 (1966), for experimental results on Li_2O.
(13) (a) K. S. Pitzer and R. E. Clementi, *J. Am. Chem. Soc.*, **81**, 4477 (1959); (b) K. E. Clementi, *J. Chem. Phys.*, 36, 45 (1962).
(14) G. Herzberg, *Discussions Faraday Soc.*, **35**, 113 (1963).
(15) L. Wharton, R. A. Berg, and W. Klemperer, *J. Chem. Phys.*, **39**, 2023 (1963); see E. F. Hayes, *J. Phys. Chem.*, 70, 3740 (1966), for an explanation.
(16) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).
(17) K. R. Thompson and K. D. Carlson, *J. Chem. Phys.*, 49, 4379 (1968).
(18) D. C. Pan and L. C. Allen, *ibid.*, **46**, 1797 (1967).

XY_3 Molecules

As planar structures of D_{3h} symmetry the hydrides of the lighter elements have an MO order[11c,19]

$$(1a_1')(1e')(1a_2'')(2a_1')(2e')$$

For molecules with six valence electrons such as BH_3 and CH_3^+, we have $\rho_{0k} = (e')(a_2'')$ of E'' symmetry. No such vibration exists and the structure is stable. For eight electrons, NH_3, CH_3^-, PH_3, and H_3O^+, $\rho_{0k} = (a_2'')(2a_1')$ of A_2'' symmetry. This is just the normal vibration needed to take the planar molecule into the pyramidal form.

It is of interest to consider the hypothetical molecule ClH_3, which has two more valence electrons than NH_3. The symmetry of ρ_{0k} is that of $(2a_1')(2e')$ or E'. This vibration takes the equilateral planar structure (120° angles) and changes it into a T-shaped molecule (180 and 90° angles). This is the structure for ClF_3 and BrF_3. It may be noted that the same structures are always predicted, both by Walsh's rules and by second-order Jahn–Teller theory, for molecules XH_3 and XY_3, as long as X is the same and Y is a halogen atom. It is not possible to check the stability of pyramidal structures of SOJT theory, since again it is an A_1 vibration that converts the pyramidal form to planar.

Nonhydride molecules of formula XY_3 already contain enough electrons so that accurate SCF calculations are not possible at the present time. Consequently we find, as expected, that there are quite a variety of MO sequences in the literature, even for the same molecule.[20] The original Walsh sequence[10d] is satisfactory as far as structures are concerned.

$$\ldots(a_1')(e')(a_2'')(2e')(2e'')(a_2')(2a_2'')(2a_1')(3e')$$

The dots indicate that the valence shell s orbitals of the three Y atoms are not considered.

Systems containing 24 valence electrons, such as CO_3^{2-}, NO_3^-, SO_3, BF_3, BO_3^{3-}, $GaCl_3$, $AlCl_3$, etc., would have a transition density of the same symmetry as $(a_2')(2a_2'')$, or A_1''. These would be stable in the D_{3h} planar form. For 26 valence electrons, such as NF_3, PCl_3, $AsBr_3$, SbI_3, XeO_3, SO_3^{2-}, BrO_3^-, etc., the symmetry of ρ_{0k} would be that of $(a_2'')(2a_1')$, or A_2''. This is the vibration which takes the planar form into a pyramidal one. Molecules with 28 valence electrons, such as BrF_3 and ClF_3, would have $\rho_{0k} = (2a_1')(3e')$ of E' symmetry. This vibration takes the symmetric planar form into the T-shaped planar form, as already mentioned.

Not all of the MO schemes of ref 20 will correctly make these predictions. For this reason they must be regarded with some suspicion as far as being valid energy level representations. The 23-electron molecule, NO_3, and the 25-electron molecule, BrO_3, are predicted to be planar and pyramidal, respectively, by the Walsh MO sequence. The actual structures are unknown in these cases. All of the above predictions as to planarity or nonplanarity are also made by the Walsh rules.

XY_4 Molecules

The hydrides such as CH_4, NH_4^+, BH_4^- in tetrahedral forms have been accurately solved by the SCF

(19) S. D. Peyerimhoff, R. J. Buenker, and L. C. Allen, *ibid.*, **45**, 734 (1966).
(20) Some examples are R. F. W. Bader, ref 2; W. Moffitt, *Proc. Roy. Soc.* (London), **A200**, 409 (1950); S. J. Strickler and M. Kasha in

method.[21] The MO sequence is

$$(a_1)(t_2)(2a_1)(2t_2) \text{ or } (a_1)(t_2)(2t_2)(2a_1)$$

For the eight-electron molecules above, the transition density can be $(t_2)(2t_2)$, giving rise to $T_1 + T_2 + E + A$ symmetries. While the E vibration converts to square-planar form, this may be safely ignored in this case because of the large energy gap ($\sim$10 eV) between the bonding and antibonding orbitals. A molecular form, in which all the stable MO's are occupied and all the unstable ones are empty, must correspond to a stable structure.

Systems with six or seven electrons will have orbitally degenerate ground states and will distort toward a planar form. However, the distortion can stop at D_{2d} symmetry, for example. Fortunately, it is possible to test the planar configuration for stability. Using only s and p orbitals on the central atom, the MO sequence must be

$$(a_{1g})(e_u)(a_{2u})(b_{1g}) \text{ or } (a_{1g})(e_u)(b_{1g})(a_{2u})$$

Both (a_{2u}) which is the p_z orbital of X and b_{1g}, a linear combination of H orbitals, are nonbonding. For either MO sequence an eight-electron molecule has $\rho_{0k} = (a_{2u})(b_{1g})$, of B_{2u} symmetry. This vibration takes the planar form into the stable tetrahedral structure.

We can also see that a seven-electron system, such as CH_4^+, will not be stable as a planar molecule and must move to the tetrahedral form. It will stop at a D_{2d} structure because of the first-order Jahn–Teller effect. A six-electron system will have $\rho_{0k} = (e_u)(a_{2u})$ or $(e_u)(b_{1g})$, giving E_g or E_u symmetry. The E_u vibration exists for XH_4, but it does not remove the planarity. Accordingly BH_4^+ and CH_4^{2+} will be planar, and probably square.

Because of the large number of electrons, XY_4 molecules cannot be solved accurately, and a large number of MO schemes can be found in the literature for tetrahedral structures.[22] A typical example, for CCl_4, is due to Helmholz and Robinson, and is of interest because it represents the first application of the Wolfsberg–Helmholz method to organic molecules.[23] Considering only s and p valence electrons, the MO order is

$$(a_1)^2(t_2)^6(2a_1)^2(2t_2)^6\underline{(3t_2)^6(e)^4(t_1)^6}(3a_1)^0(4t_2)^0$$

with the three underlined orbitals very close in energy.

Clearly this ordering predicts stability for tetrahedral CCl_4 only because of the large energy gap (experimentally 7 eV) between the filled and empty orbitals, and not because of symmetry. The same is true for most of the other calculations mentioned in ref 22. The top of Helmholz–Robinson MO order coincides with that of Lohr and Lipscomb[24] done for XeF_4 in an assumed tetrahedral form. Adding four more electrons to the 28 electrons of CCl_4, we find that XeF_4 has a triply degenerate ground state $(t_2)^2$ and hence will distort toward a planar structure. Also TeF_4 or SF_4, two more electrons than CCl_4, will have $\rho_{0k} = (3a_1)(3t_2)$, of T_2 symmetry. As Gavin and Bartell have shown,[5d] this vibration takes SF_4 into the structure of C_{2v} symmetry which is found experimentally. SnF_4 or SiF_4 would be stable as tetrahedral molecules for the same reason CCl_4 is.

Several workers have calculated MO level schemes for planar XeF_4, using semiempirical methods.[25] The Lohr and Lipscomb sequence for the higher levels is[25a]

$$\ldots(b_{2u})^2(3e_u)^4(a_{2g})^2(3b_{1g})^2(4a_{1g})^2(2a_{2u})^2(4e_u)^0$$

This gives $\rho_{0k} = (2a_{2u})(4e_u)$, of E_g symmetry, and planar XeF_4 is predicted stable.

TeF_4, or SF_4, would have two fewer electrons. This leads to $\rho_{0k} = (4a_{1g})(2a_{2u})$, of A_{2u} symmetry. However, the energies of the $(3b_{1g})$ and $(4a_{1g})$ orbitals are nearly equal, and the energy gap between them and the $(2a_{2u})$ is only 2.5 eV. Hence the normal vibration of B_{2u} symmetry is also favored by the $(3b_{1g})$–$(2a_{2u})$ excitation. The combination $A_{2u} + B_{2u}$ vibration leaves two *trans* F atoms in the plane and moves the two others down. This gives rise to the SF_4 structure. SnF_4, or SiF_4, or CCl_4, has two fewer electrons than SF_4. The lowest energy transitions are then of B_{1g} and B_{2u} symmetry. The first of these is an irrelevant bond distortion, but the second takes the planar molecule into the tetrahedral form.

Systems containing d electrons are found as T_d, D_{2d}, or D_{4h} structures. These can all be accurately predicted by the use of SOJT theory. The details have already been published.[6a]

XY_5 Molecules

The alternative structures for five-coordinated central atoms are trigonal bipyramidal, D_{3h} symmetry, and square pyramidal, C_{4v} symmetry. The simplest known example would be CH_5^+, for which detailed MO calculations are apparently not available in either form. However, a calculation has been made[26] for the related, but hypothetical, molecule PH_5 in D_{3h} symmetry. The MO order for the valence electrons is

$$(1a_1')^2(1a_2'')^2(1e')^4(2a_1')^2(2e')^0(2a_2'')^0$$

The transition density has the symmetry of $(2a_1')(2e')$ which is E'. This vibration takes a trigonal bipyramid into a square pyramid. The calculated energy gap between $(2a_1')$ and $(2e')$ is 5 eV, which makes the effect somewhat marginal.

Almost by inspection, we can conclude that the MO order in CH_5^+ must also be

$$(1a_1')^2(a_2'')^2(1e')^4(2a_1')^0$$

Again we have a transition density of E' symmetry, and instability toward the square-pyramidal structure. The logical order for CH_5^+ in C_{4v} symmetry is

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(25) (a) L. L. Lohr, Jr., and W. N. Lipscomb in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 347; (b) J. Jortner, E. G. Wilson, and S. A. Rice, *ibid.*, p 358.

(26) K. Issleib and W. Gründler, *Theor. Chim. Acta*, **8**, 70 (1967).

$$(1a_1)^2(1e)^4(2a_1)^2(b_1)^0(3a_1)^0$$

Here we have ρ_{0k} of B_1 symmetry, which is the vibration that takes a square pyramid into a trigonal bipyramid. Also for PH_5, with two more electrons, the symmetry of ρ_{0k} is B_1, and instability is likely.

Complete MO schemes, including π bonding, have been calculated for PF_5, AsF_5, and BrF_5 in both C_{4v} and D_{3h} symmetry.[27] In the square pyramid form the sequence is

$$\ldots\underline{(5e)^4(3b_1)^2(1a_2)^2(1a_2)^2(6a_1)^0(6e)^0(2b_2)^0}$$

with the $(6a_1)$ orbital empty for PF_5 and AsF_5 and filled for BrF_5. The $(3b_1)$–$(6a_1)$ transition has B_1 symmetry and makes PF_5 and AsF_5 unstable. However, BrF_5 would be stable since ρ_{0k} is of E or B_2 symmetry.[28]

In D_{3h} symmetry the sequence is

$$\ldots(2e'')^4(4a_1)^2(4e')^4(5e')^0(3e'')^0$$

Since $E' \times E' = A_1' + A_2' + E'$, PF_5 and AsF_5 are also unstable as trigonal bipyramids. BrF_5 would have the $(5e')$ orbital half-filled and would show first-order Jahn–Teller instability.

In the case of PF_5 and AsF_5 the calculated[26] energy gaps between the filled and unfilled orbitals are too large to be correct. Nevertheless, these molecules are colorless, so rather high-energy transitions must be invoked to create structural instability. PCl_5 does not absorb light until about 2500 Å, or 5 eV, for example.

It is of considerable interest that we have concluded in all cases but BrF_5 and IF_5 that both the square-pyramidal and trigonal-bipyramidal structures readily interconvert. This is, of course, exactly the situation that exists experimentally for a large number of five-coordinated systems, especially those of P, As, and Sb.[29] The extra pair of electrons in BrF_5 stabilizes it in the square-pyramidal form.

A number of MO calculations have been made for transition metal complexes, both for D_{3h}[30] and C_{4v}[31] symmetry. Unfortunately the MO sequences do not always agree with one another. The ordering of Chastain, *et al.*,[30c] is

$$\ldots(3a_1')(3e')(3a_2'')\,\vdots\,(3e'')(4e')(4a_1')\,\vdots\,(5e')$$

with the d manifold enclosed by dashed lines. For C_{4v} the corresponding order is

$$\ldots(a_2)(e)\,\vdots\,(e)(b_2)(a_1)(b_1)\,\vdots\,(a_1)\ldots$$

The ordering of the MO's derived from the d orbitals is fairly certain as is the expectation that low-energy transitions can occur between them. The positions and symmetries of the orbitals outside the dotted lines are much less certain. Assuming that (a_2'')–$(3e'')$, (e)–(e), and $(4a_1')$–$(5e')$ transitions can occur without undue energy expenditure, we can now predict stability of d^n complexes in both the trigonal-bipyramidal and the square-pyramidal structures. The results are summarized in Table III. The predictions that are based only on the d manifold are starred, and are much more certain. A number of systems will show first-order Jahn–Teller effects. These also lead to D_{3h}–C_{4v} interconversion.

Table III. Stability of Five-Coordinated Transition Metal Complexes in Trigonal-Bipyramidal (D_{3h}) and Square-Pyramidal (C_{4v}) Forms[a]

	D_{3h}		C_{4v}	
	High spin[b]	Low spin	High spin	Low spin
d^1	u*[c]	u*[c]	u*[c]	u*[c]
d^2	u	u	u	u
d^3	u*[c]	u*[c]	u	u*[c]
d^4	u*[c]	s*	u*	s*
d^5	u*	u*[c]	u*	s*
d^6	u*[c]	u*	u*[c]	s*
d^7	u*	u*[c]	u*	u*
d^8	u*[c]	u*	u*	u*
d^9	u*	u*	u*	u*
d^{10}	u	u	u	u

[a] u = unstable with respect to E′ vibration for D_{3h} and B_1 vibration for C_{4v}; s = stable. [b] Starred systems show predictions on the basis of the d manifold only, and are more certain. [c] These systems show first-order Jahn Teller instability. Since $(E'' \times E'')^+ = A_1' + E'$ and $(E \times E)^+ = A_1 + B_1 + B_2$, D_{3h} structures will move towards C_{4v} structures, and *vice versa*.

It can be seen that in most cases it is predicted that a ready interchange between trigonal-bipyramidal and square-pyramidal structures will occur. Only low-spin d^5 and d^6 complexes are predicted to be stable as square pyramids. Low-spin d^4 complexes are predicted stable in both structures. This presumably means a large energy barrier for their interconversion.

The predictions of Table III may be compared with those of Eaton,[1b] which differ in several cases. Experimentally the situation is not very certain. Many five-coordinated complexes have been observed in either one structure or the other.[32] However, this does not rule out a facile interconversion between structures, one of which is more stable. There is evidence that some d^8 metal complexes do readily interconvert between square-pyramidal and trigonal-bipyramidal structures.[1b,33]

The case of spin-paired d^6 is interesting because this includes the five-coordinated complexes of cobalt(III) postulated for many substitution reactions of octahedral cobalt(III) complexes.[34] The intermediates $Co(NH_3)_5{}^{3+}$ $Co(en)_2NH_3{}^+$, and $Co(en)_2H_2O^{3+}$ do appear to have a stable C_{4v} structure as predicted.[35] However, intermediates such as $Co(NH_3)_4NH_2{}^{2+}$, $Co(en)_2Cl^{2+}$, and $Co(en)_2OH^{2+}$ rearrange, presumably by way of a trigonal-bipyramidal form. These species are outside of

(27) R. S. Berry, M. Tamres, C. J. Ballhausen, and H. Johansen, *Acta Chem. Scand.*, 22, 231 (1968).

(28) The same conclusion is reached for IF_5 where a σ orbital MO scheme has been estimated: R. E. Rundle, *J. Am. Chem. Soc.*, 85, 112 (1963).

(29) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960); R. R. Holmes and R. M. Dieters, *J. Am. Chem. Soc.*, 90, 5021 (1968).

(30) (a) R. F. W. Bader, *Can. J. Chem.*, 39, 2306 (1961); (b) W. E. Hatfield, H. E. Bedon, and S. M. Horner, *Inorg. Chem.*, 4, 1181 (1965); (c) B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Am. Chem. Soc.*, 90, 3994 (1968); (d) S. T. Spear, Jr., J. R. Perumareddi, and A. W. Adamson, *ibid.*, 90 6626 (1968).

(31) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1, 226 (1962); M. Ciampolini, *ibid.*, 5, 35 (1966); J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, 89, 3356 (1967); J. R. Perumareddi, S. T. Spees, Jr., and A. W. Adamson, *ibid.*, 90, 6626 (1968).

(32) The structures of fivefold coordination have been reviewed recently: J. A. Ibers, *Ann. Rev. Phys. Chem.*, 16, 375 (1965); C. Furlani, *Coord. Chem. Rev.*, 3, 141 (1968); E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 20, 245 (1966).

(33) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 1362 (1968).

(34) For a general review see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, Chapters 3 and 4.

(35) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, 20, 597 (1967); *J. Am. Chem. Soc.*, 90, 6654 (1968).

the scope of Table III, not because of the reduced symmetry, but because they contain ligands which are chemically too different from NH_3 (strong π bonders). Thus symmetry is technically destroyed by replacing two NH_3 ligands by one ethylenediamine ligand, but chemically there is little change.

XY_6 Molecules

In six-coordinated systems the problem is to explain the almost universal occurrence of octahedral structures. Figure 2 shows the remaining nonsymmetric normal modes of an octahedral XY_6 molecule.[9] As an example of a nontransition metal complex, we have an MO sequence for XeF_6, calculated by semiempirical methods.[36]

$$\ldots \underline{(t_{2u})^6(3t_{1u})^6(2e_g)^4(t_{1g})^6(3a_{1g})^2}(4t_{1u})^0(2t_{2g})^0$$

with the underlined orbitals very close in energy. The energy separation between $(3a_{1g})$ and $(4t_{1u})$ is 3.7 eV, experimentally. The symmetry of the transition density is T_{1u}. This vibration leads to a distorted structure which is not stable, but fluctuates, leading to an average octahedral structure.[5d] Alternatively, one can say that the force constant for the T_{1u} vibration is near zero.

Molecules such as TeF_6, SF_6, SiF_6^{2-}, PF_6^- contain two fewer electrons. More accurate calculations for XeF_6[37] indicate that the $(3t_{1u})$–$(3a_{1g})$ separation is about 7 eV. Molecules such as SF_6 are not only colorless up to 2200 Å, but are also extremely inert. It is expected that going from Xe to Te to Sn, for example, will increase the $(3t_{1u})$–$(3a_{1g})$ separation. The $(3t_{1u})$ orbital is mainly ligand π, and the $(3a_{1g})$ is largely on the central atom. The reduced nuclear charge on Te and Sn will raise the (a_{1g}) energy and increase the energy gap.

Many MO calculations have been made for octahedral complexes of the transition metal ions. For non-π-bonding ligands, such as NH_3, the order is generally given as[38]

$$(a_{1g})(e_g)(t_{1u}) \mid (t_{2g})(e_g) \mid (2a_{1g})(2t_{1u})$$

The only low-lying transitions are within the d manifold, giving rise to $T_{1g} + T_{2g}$ symmetry for ρ_{0k}. The T_{1g} vibration does not exist and the T_{2g} distortion cannot lead to a stable, alternative structure.[39] Except for first-order Jahn–Teller effects, such molecules should be stable in octahedral form.

If π-bonding ligands, such as the halide ions, are present, orbitals of T_{1g}, T_{1u}, and T_{2u} symmetry come in before the T_{2g} symmetry d orbitals.[40] The energy differences between the (t_{1u}), (t_{2u}) ligand π orbitals and the (t_{2g}), (e_g) metal d orbitals are not calculated easily, but experimentally they can be found from the charge-transfer bands.[41] Usually such bands occur in the uv, below 3000 Å. Hence the energy gap is large.

(36) E. A. Boudreaux in ref 25a, p 354.
(37) I am indebted to L. Lohr, Jr., and H. Basch for giving me additional information on energy values from their accurate calculations on XeF_6.
(38) H. Yamatera, *J. Inst. Polytech. Osaka City Univ.*, 5, 163 (1956); F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 1004 (1964).
(39) The T_{2g} vibration should have a low force constant because of SOJT effects. Some evidence exists for this: ref 9b, p 119.
(40) P. Ros, Thesis, Eindhaven, Bronder-Offset, Rotterdam, 1964; H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, 44, 10 (1966); R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, 7, 479 (1968).
(41) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, Chapter 8.

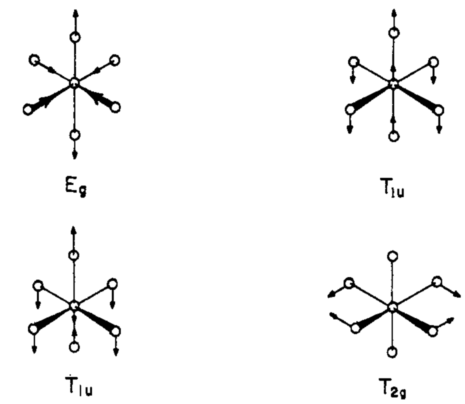

Figure 2. Remaining nonsymmetric vibrations of an octahedral molecule, showing kinds of distortion possible.

If the oxidation state of the central atom becomes very high, it is expected that the separation between the (t_{1u}), (t_{2u}), and (t_{2g}) orbitals will become small. This shows up in the charge-transfer spectra. Since T_{1u} (or T_{2u}) $\times$ T_{2g} gives rise to T_{1u} and T_{2u} symmetry, structural changes should also result. Orgel[42] has given some interesting examples of this effect. The examples are from the solid state and must be viewed with some reservations, since solids are subject to other forces which can distort structure. Metal ions of high oxidation state such as Hf^{4+}, Zr^{4+}, Nb^{5+}, Mo^{6+}, V^{5+}, often form oxide lattices with distorted octahedral structures in which the metal ion is off center.[42a] It can be seen from Figure 2 that the T_{1u} vibration does draw the central atom away from the center of the octahedron.

The oxides, sulfides, and selenides of metal ions with an inert pair of electrons Tl^+, Pb^{2+}, Bi^{2+}, etc., also form distorted octahedral structures.[42] Since the inert pair is in an orbital of A_{1g} symmetry, the distortion is explained by an excitation from this orbital into a higher (t_{1u}) orbital. This is identical with the explanation given earlier for XeF_6.

A third example discussed by Orgel[43] concerns sixfold coordination of d^{10} ions such as Hg^{2+}, Au^+, Ag^+, and Cu^+, which give badly distorted octahedra in the solid state, whereas other d^{10} ions such as Zn^{2+}, Cd^{2+}, and Tl^{3+} do not. Orgel has shown that a small s–d energy gap in the metal ion leads to the distortion, whereas a large gap does not. Such an s–d mixing will be of $A_{1g} \times E_g = E_g$ symmetry and the corresponding vibration (Figure 2) will be excited. This causes a distortion in which two *trans* groups are closer to the metal than the other four, or, just as probable, two groups are further than the other four. The former distortion is characteristic of Hg^{2+}, Au^+, Ag^+, and Cu^+. In solution, the effect occurs to such an extreme that usually only two ligands are held tightly by these metal ions.

The possibility of exciting the T_{2u} vibration is particularly interesting since, as shown in Figure 2, this vibration twists an octahedron into a trigonal prism structure. Excitation from (t_{1u}) or (t_{2u}) into the (t_{2g}) orbital should favor the T_{2u}, as well as the T_{1u} vibrations, the latter distortion is much more common than the former. The only molecular examples of the trigonal-prismatic structures are the well-known dithiolate com-

(42) (a) L. E. Orgel, *Trans. Faraday Soc.*, 26, 138 (1958); (b) *J. Chem. Soc.*, 3815 (1958).
(43) L. E. Orgel, *ibid.*, 4186 (1958).

plexes, $MS_6C_6R_6$.[44] Considering the dithiolate ligand, $R_2C_2S_2{}^{2-}$, as formally divalent, the metal ions which give trigonal-prismatic structures are Mo(VI), W(VI), Re(VI), Cr(VI), and V(VI). These are all d^0 or d^1 metal ions. Metal ions of lower oxidation state, or more d electrons, are octahedral.

In these examples conditions have been optimized to make the (t_{1u}), $(t_{2u}) \rightarrow (t_{2g})$ transitions of low energy and hence to favor the T_{2u} vibration. The conditions are as follows: (1) π-bonding ligands with filled π orbitals, (2) at least one empty (t_{2g}) orbital on the central metal ion, (3) a high oxidation state for the central metal ion (to lower the (t_{2g}) energy), (4) a donor atom of the ligand which is easily oxidized (to raise the (t_{1u}) and (t_{2u}) levels), (5) strong ligand–ligand interactions due to overlap. The last condition comes from the work of Schmidtke,[45] who has considered the effect of ligand–ligand interactions in detail. A significant conclusion is that the (t_{1u}) orbital is raised with respect to the (t_{2g}) orbital. There is evidence from bond distances of strong sulfur–sulfur interactions in the trigonal-prismatic structures.[45]

To complete the argument, it is necessary to show when the trigonal-prismatic structure is stable to rearrangement into a octahedral structure. The required twisting mode is of A_1'' symmetry. There are two MO schemes available for trigonal-prismatic structures, both of the Wolfsberg–Helmholz type. That of Gray and Eisenberg[44c] is

$$\ldots(4e')\underline{(3a_1')}\,\vdots\,\underline{(2a_2')(5e')(4e'')}\,\vdots\,(2a_1'')(5e'')$$

and that of Schrauzer and Mayweg[46] is

$$\ldots(3a_1')(4e')\,\vdots\,\underline{(5e')(2a_2')(4e'')}\,\vdots\,(2a_1'')(5e'')$$

In both schemes d^0 and d^{10} are predicted to be stable as trigonal prisms. Also d^2 to d^9 are predicted to be unstable. This arises because $E' \times E'' = A_1'' + A_2'' + E''$. However, d^1 is predicted stable by the first scheme, and unstable by the second. The experimental examples of d^1 are trigonal prismatic for Re(VI) and in between trigonal and octahedral for V(IV).[47]

XY_7 Molecules

A coordination number of seven is relatively rare, but some examples are known, mainly fluorides and fluoride complexes. The molecule IF_7 has been much discussed since there is evidence that it is stereochemically nonrigid, somewhat like XeF_6.[48] The most recent conclusion is that it has a rigid D_{5h} pentagonal-bipyramidal structure on the infrared and Raman time scale.[49] On the much longer nmr time scale, IF_7 and ReF_7 have nonrigid structures, since all seven fluorine atoms have become equivalent by an intramolecular process.[50] Presumably this occurs by a pseudo-rotation process similar to that postulated for PCl_5, $AsCl_5$, etc.[29] An E_1' vibration could convert the D_{5h} structure into a capped octahedron, of C_{3v} symmetry, losing the identity of axial and equatorial positions.[48]

Only one MO calculation exists for IF_7, and it ignores π bonding.[51] The MO sequence in D_{5h} symmetry is

$$(a_1')^2(e_1')^4(a_2'')^2(2a_1')^2(e_2')^4(2a_2'')^0(2e_1')^0\ldots$$

Since $(2a_2'')$ and $(2e_1')$ are close together in energy, there is a ρ_{0k} of $E_2' \times E_1' = E_1' + E_2'$ symmetry. However, the calculated energy gap is very large (10 eV). While the calculations cannot be taken too seriously, there is probably a fairly substantial gap between (e_2') and $(2e_1')$. For example, the molecule is colorless. This suggests a moderately stable structure, at least. It is of interest that ReF_7, which is pale yellow, shows evidence of being nonrigid even on the ir time scale.[49] An estimated MO sequence exists for a pentagonal-bipyramidal complex of a transition metal ion.[30d] Whether it can be applied to ReF_7 is questionable.

An MO calculation also exists for the C_{3v} capped octahedral structure of IF_7.[51] The total energy is greater than for the pentagonal bipyramid, and again a large gap exists between the highest filled and lowest empty orbitals. A normal coordinate analysis for this structure does not seem to be available.

Conclusion

In the preceding sections we have made very successful predictions of the structures of molecules consisting of a central atom surrounded by two to seven other atoms. It is desirable to conclude with some precautionary remarks. For small displacements, Q, eq 2 is exact. It reflects accurately the requirement that a nondegenerate wave function must change from the original one if a change in nuclear configuration is to occur spontaneously, or with low expenditure of energy.

Now a very severe approximation has been made in assuming that only the lowest excited state can replace the infinite sum of states shown in eq 2. It is certainly expected that the magnitude of f_{0k} will fall off rapidly with increasing size of $|E_0 - E_k|$. As Bader has shown,[2] this is not because of the energy difference in the denominator, but because the integral becomes very small when the two eigenstates, ψ_0 and ψ_k, correspond to quite different energies. Nevertheless an infinite sum of terms, each of which makes a vanishingly small contribution, can still add up to an appreciable total.

We have taken $|E_0 - E_k| \geq 4$ eV as a cutoff for important contributions to f_{0k}. This is rather arbitrary and done only because it seems to fit in most cases. Nevertheless there are important SOJT effects that arise for $|E_0 - E_k| \geq 5$ eV, for example, PF_5.

The difficulty with symmetry arguments is that they can tell only if an integral is zero or not, the magnitude remaining unknown. Thus we cannot easily estimate the relative sizes of f_{00} and f_{0k}, which can vary markedly from one case to the next, even when f_{0k} is symmetry allowed.

For the symmetries of the electronic states we must rely on molecular orbitals which are far from being accurate, at least for most molecules of interest. Fur-

(44) (a) R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, 87, 3776 (1965); (b) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, 87, 5798 (1965); (c) R. Eisenberg and H. B. Gray, *Inorg. Chem.*, 6, 1844 (1967).

(45) H. H. Schmidtke, *J. Chem. Phys.*, 45, 3920 (1966); *Theor. Chim. Acta*, 9, 199 (1968).

(46) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 88, 3235 (1966).

(47) E. Stiefel, Z. Dori, and H. B. Gray, *ibid.*, 89, 3353 (1967).

(48) R. D. Burbank and N. Bartlett, *Chem. Commun.*, 645 (1968).

(49) H. H. Claasen, E. L. Gasner, and H. Selig, *J. Chem. Phys.*, 49, 1803 (1968); see E. L. Muetterties, *Inorg. Chem.*, 4, 769 (1965), for a discussion of experimental time scales for various structural techniques.

(50) E. L. Muetterties and K. J. Parker, *J. Am. Chem. Soc.*, 86, 293 (1964); N. Bartlett, S. Beaton, L. W. Reeves, and E. J. Wells, *Can. J. Chem.*, 42, 2531 (1964).

(51) R. L. Oakland and G. H. Duffey, *J. Chem. Phys.*, 46, 19 (1967).

thermore, we have made the approximation that an MO level ordering valid for one molecule is also valid for a number of related molecules in the same structure. While this appears to be true more times than one might have supposed, certainly there are many exceptions.

While the theme of this article has been the prediction of structure from MO level diagrams, it is more realistic to turn the problem about. That is, since reliable structures are often known, we should test assumed or calculated MO schemes to see if they are compatible with the known structures. The test is to show stability with respect to second-order Jahn–Teller distortions.

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Molecular Structure and Photochemical Reactivity. XIV. The Vapor-Phase Photochemistry of *trans*-Crotonaldehyde

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Abstract: The vapor-phase photochemistry of *trans*-crotonaldehyde has been studied at wavelengths longer than 2550 Å between 70 and 130°. The major photodecomposition products were CO and propylene. Small amounts of C_2H_4, allene, methylacetylene, cyclopropane, ethylketene, and *enol*-crotonaldehyde were also formed. The results are explained by a mechanism involving decomposition from, and multistage collisional deactivation of, a vibrationally excited upper singlet state, intersystem crossing to an unstable upper triplet state, and internal conversion to the ground state *via* isomerization of the upper singlet state to unstable intermediates.

The vapor-phase photochemistry of *trans*-crotonaldehyde has been the subject of many investigations. Blacet and Roof[2a] found that the molecule was extremely resistant to photodecomposition at room temperature when irradiated with any of the mercury lines between 3660 and 2399 Å. Subsequently, Blacet and Luvalle[2b] showed that photodecomposition did occur at 2380 Å and 265° to give CO, unidentified unsaturated hydrocarbons, and methane. Tolberg and Pitts[3] found $\phi_{CO} \simeq 1.5$ at 2380 Å and 265°, and identified the hydrocarbon products as CH_4, propylene, and 2-butene. Allen and Pitts[4] studied the methyl radical sensitized decomposition of *trans*-crotonaldehyde and showed that 2-butene was formed by methyl radical displacement of the formyl group. McDowell and Sifniades[5] reported that in the vapor phase at $\sim$30°, and with the wavelength range 2450–4000 Å, *trans*-crotonaldehyde isomerized to but-3-en-1-al, but neither Yang[6] nor later workers[7,8] could detect this isomer. Using a long-path-length ir spectrophotometer, Coomber, *et al.*,[7] found that ethylketene and *enol*-crotonaldehyde were unstable intermediates in the photolysis at 3130 and 2537 Å. Subsequently, Allen and Pitts[8] proposed that the photodecomposition at 2537–2654 Å involved the formation of an electronically excited molecule of crotonaldehyde which isomerized to ethylketene. This isomer then photodecomposed to propylene and CO. Although this is an attractive proposition, we felt their mechanism was not proven and so undertook the present study.

Experimental Section

Materials. *trans*-Crotonaldehyde (Matheson Coleman and Bell) was purified immediately before each run by glpc on a 15 ft × 0.25 in. Carbowax 20M (20%) column at 75° with helium as carrier gas. No impurity could be detected in the chromatographed aldehyde by ir or mass spectrometry. Nitric oxide (Matheson Gas Co.) was thoroughly degassed at −210° and then transferred to the first of two Ward-Leroy stills in series. A middle cut of the fraction volatile with the stills at −170 and −180° was stored in a blackened bulb on the vacuum line. CO_2 (Matheson Gas Co., "Bone Dry" grade) was degassed and used without further purification. 2,3-Dimethylbutene-2 (Chemical Procurement Laboratories Inc.) was better than 99% pure by glpc and was used without further purification. 3-Pentanone (Aldrich Chemical Co.) was purified immediately before use by glpc on a 20 ft × 0.25 in. 1,2,3-tris(cyanoethoxy)propane (TCEP)–Chromosorb P column at 160°. CO, C_2H_4, CH_4, allene, methylacetylene, cyclopropane, and propylene (all Matheson Gas Co.) were used for gas chromatographic calibration. Each compound, except CO and CH_4, which were used directly, was purified by low-temperature distillation in the Ward-Leroy stills. CF_3I (Peninsular Chem Research), O_2 (Matheson, Research Grade), and N_2 (American Cryogenic, prepurified quality) were used without further purification. All purified compounds were analyzed by ir or mass spectrometry or both. No impurity was detected.

Apparatus. Two apparatuses were used. One, a conventional high-vacuum system, has been described before[9] except for the following modifications. The combined gas buret–Toepler pump was connected *via* a microvolume gas-sampling valve (Carle Instruments Inc.) to a gas chromatograph with a 10 ft × 0.25 in. column of 40–60 mesh 13X molecular sieves and a Gow Mac

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