An   Application   of   the   Jahn-Teller   Theorem   to   the

VCl₄   Molecule

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The tetrahedral molecule VCl_4 is expected to distort due to the implications of the Jahn-Teller theorem. Explicit calculations reveal that at temperatures above approximately 200° Kelvin the molecule undergoes a pseudo rotation in the sense that each chlorine atom is displaced from the regular tetrahedral position and rotates around the tetrahedral bond with a radius of 0.11 Å. However, at temperatures below 200° Kelvin VCl_4 assumes a static distortion in which two of the tetrahedral angles are closed 6°, and four of the angles are opened 3°. The consequences of the above distortions are enummerated, and paths for further experimental studies are indicated.

A great many papers [1–8] have in the past dealt with the theoretical consequences of the Jahn-Teller theorem [9], but only in a very few cases has it been possible to verify experimentally the predictions put forth [6,10]. Indeed, it often seems as if nature goes to great length in this matter in order to prevent us from obtaining any answers to our questions. The results arrived at here are no exception to this rule; however, it is hoped that they will stimulate experimentation designed toward clarifying this frustrating situation. We submit this note because it should be possible, in the special case to be discussed, either to prove or to disprove the theoretical predictions which we have recently derived.

We shall show that the compound VCl_4 should experience a configurational instability of the Jahn-Teller type. We shall further compare its behavior with that of the very closely related compound $TiCl_4$, a molecule unaffected by the implications of the Jahn-Teller theorem. Both VCl_4 and $TiCl_4$ are liquids at room temperature and both possess a tetrahedral structure [11,12] in the vapor
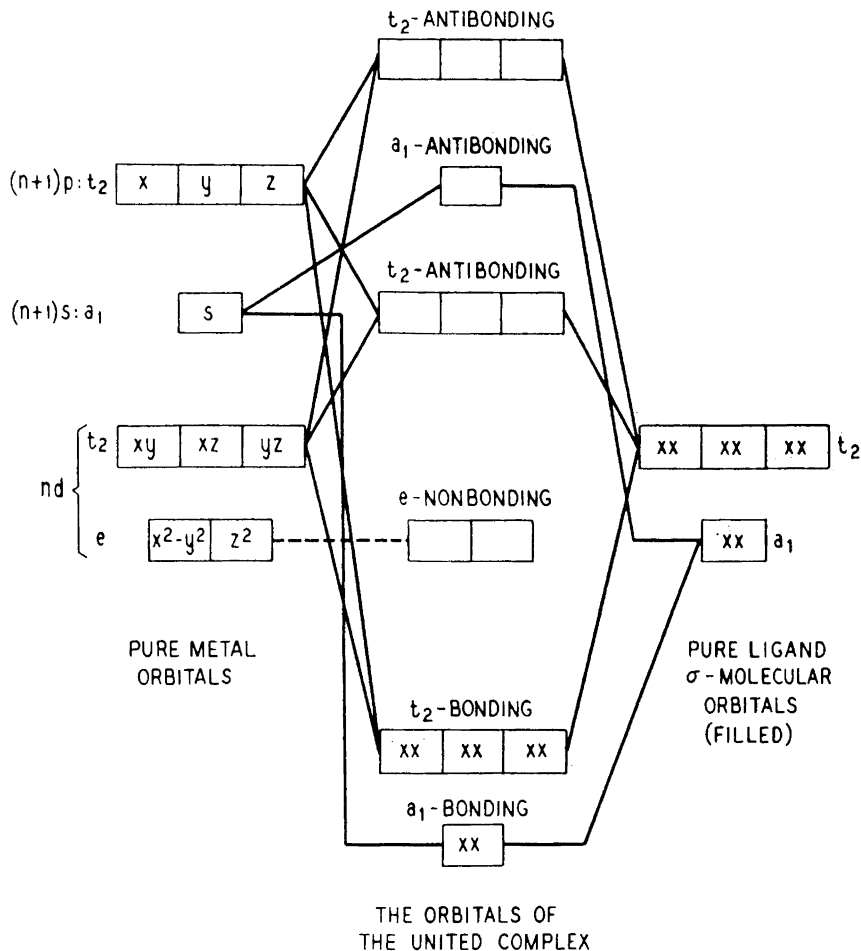
Fig. 1. Energy levels for the tetrahedral molecule VCl_4 in the σ-bonding approximation.

phase. The major difference between VCl_4 and $TiCl_4$ is that the former has one electron more than the latter. A comparison between them should therefore be of some interest.

THEORY

The electronic structure of V^{+4} is $[A]3d^1$, where $[A]$ represents the closed, eighteen electron argon shell. A consideration of the bonding possible in a tetrahedral molecule reveals that the four ligands can produce σ-bonding orbitals of the symmetry a_1 and t_2. The 3d, 4s and 4p orbitals span the irreducible representations (t_2,e), a_1 and t_2, respectively. Thus if π bonding is neglected,

$S_1(\alpha_1)$ $S_{2a}(\epsilon)$ $S_{2b}(\epsilon)$
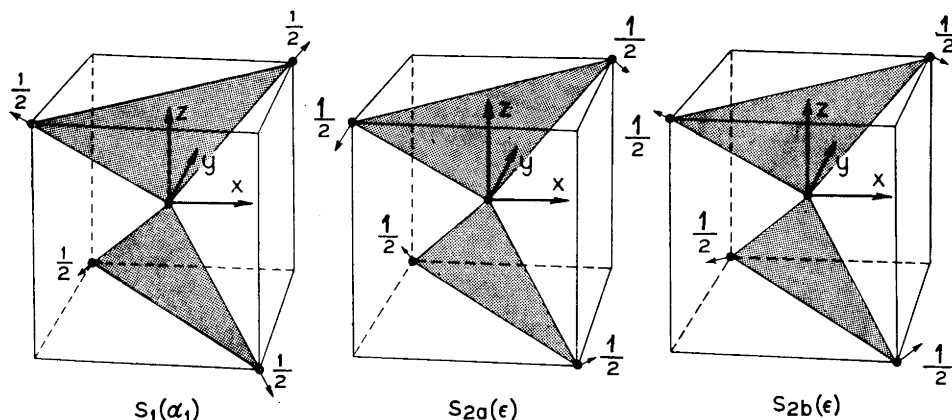
Fig. 2. The tetrahedral symmetry coordinates of species a_1 and ϵ.

the bonding scheme may be represented as in Fig. 1. The electronic structure of the molecule VCl₄ can then be written $(a_1^b)^2(t_2^b)^6(e)^1$, with the one unpaired electron present being placed in the σ-nonbonding, doubly degenerate, metal orbital.

In order for any molecule to possess a stable configuration it is obvious that the total energy of the system must be at a minimum. This means that the change in energy due to small displacements of the nuclei, must contain no terms linear in these displacements. Hence, it is necessary to minimize the total electronic energy with respect to all possible nuclear distortions of the molecular framework, if the equilibrium conformation is to be determined. After the removal of the translational and rotational degrees of freedom, it is found (by means of the usual methods[13]), that the nuclear symmetry coordinates span the irreducible representations a_1, ϵ and $2\tau_2$ of the point group T_d. The symmetry coordinates S_1 $(= a_1)$ and $S_{2a}, S_{2b}(= \epsilon)$ are represented in Fig. 2.

By expanding the coulombic potential energy V around the equilibrium configuration in powers of the symmetry coordinates we obtain:

$$V = V_0 + \sum_i S_i V_i + \sum_{i,j} S_i S_j V_{ij} + \dots \tag{1}$$

If at first only terms linear in the symmetry coordinates are retained, the change in the coulombic potential energy may be expressed

$$\Delta V = \sum_i S_i V_i \tag{2}$$

Here the expansion coefficients, V_i, are functions of the electronic coordinates only while the symmetry coordinates, S_i, are functions of the coordinates of the nuclei.

The energy change ΔE of the doubly degenerate ground state is given by first order perturbation theory as the solutions to the secular equation

$$\begin{vmatrix} \Delta V_{AA} - \Delta E & \Delta V_{AB} \\ \Delta V_{BA} & \Delta V_{BB} - \Delta E \end{vmatrix} = 0 \qquad (3)$$

where

$$\Delta V_{AB} = \Delta V_{BA} = \int \psi_A \Delta V \psi_B d\tau \qquad (4)$$

$$\Delta V_{AA} = \int \psi_A \Delta V \psi_A d\tau \qquad (5)$$

$$\Delta V_{BB} = \int \psi_B \Delta V \psi_B d\tau \qquad (6)$$

As our zero-order wavefunctions we take the two nonbonding orbitals $3d_{x^2-y^2}$ and $3d_{z^2}$. Hence $(A,B) = (d_{x^2-y^2}, d_{z^2})$. These two orbitals span the irreducible representation E in the point group T_d.

In order for the matrix elements $(4)-(6)$ to be different from zero the direct product representation of the components must contain the identity representation A_1. The complete Hamiltonian for the system transforms like A_1; hence S_i and V_i must span the same representations in the point group T_d. The symmetric product of the representation E with itself is A_1 and E. Therefore, only the $S_{2a,b}$ symmetry coordinates are capable of mixing the $d_{x^2-y^2}$ and d_{z^2} like orbitals.

An actual (electrostatic) calculation of ΔV_{AA}, ΔV_{BB} and ΔV_{AB} then yields [14],[15]

$$\Delta V_{x^2-y^2,x^2-y^2} = (2B_0 - \frac{2}{9} B_4)S_1 + \frac{a}{2} S_{2a} \qquad (7)$$

$$\Delta V_{z^2,z^2} = (2B_0 - \frac{2}{9} B_4)S_1 - \frac{a}{2} S_{2a} \qquad (8)$$

$$\Delta V_{x^2-y^2,z^2} = \Delta V_{z^2,x^2-y^2} = - \frac{a}{2} S_{2b} \qquad (9)$$

where

$$a = \frac{8\sqrt{2}}{7r_0} (G_2 - \frac{5}{9} G_4) \qquad (10)$$

with r_0 being the bond distance V—Cl. The radial integrals G_1 and B_1 are defined as [6]

$$G_1 = \int_0^\infty R^2(r) f_1(r,r_0) r^2 dr \qquad (11)$$

and

$$B_1 = \frac{dG_1}{dr_0} \qquad (12)$$

The quantities B_1 and G_1 are tabulated in Ballhausen and Ancmon.[16]

By inserting $(7)-(9)$ into (3) and solving, ΔE is found to be

$$\Delta E = (2B_0 - \frac{2}{9} B_4)S_1 \pm \frac{a}{2} \sqrt{S_{2a}^2 + S_{2b}^2} \qquad (13)$$

The total potential surface of VCl$_4$ is then given by

$$E = V_0 + \Delta E \tag{14}$$

We now assume that the potential surfaces of TiCl$_4$ and VCl$_4$ are the same, except for the terms due to ligand field effects, that is the terms in a and B_4. Making the substitutions

$$S_1 = q_1, \quad S_{2a} = q_2\cos \varphi_2, \quad S_{2b} = q_2\sin\varphi_2 \tag{15}$$

the potential surface for VCl$_4$ may be written

$$E = \tfrac{1}{2}k_1q_1^2 - \frac{2}{9} B_4q_1 + \tfrac{1}{2}k_2q_2^2 \pm \frac{a}{2} q_2 \tag{16}$$

where k_1 and k_2 are the force constants for the harmonic vibrations of symmetry a_1 and ε, respectively.

In order to find the stable configuration of the molecule, (16) must be minimized with respect to q_1 and q_2. This is quite straightforward and leads to the results

$$\overline{q_1} = \frac{\frac{2}{9} B_4}{k_1}, \quad \overline{q_2} = \mp \frac{a}{2k_2} \tag{17}$$

DISCUSSION

A number of interesting conclusions can be inferred from (17). First if G_4 is defined as a positive quantity, ligand field theory demands [6],[16] that B_4 must be a negative quantity. As a result $\overline{q_1}$ will be negative, and thus the V—Cl bond distance should be shorter than the Ti—Cl bond distance. This prediction is borne out by experiments, the reported values being 2.03 $\pm$ 0.02 Å, and 2.18 $\pm$ 0.04 Å for VCl$_4$ and TiCl$_4$, respectively [11],[12]. Numerically the shortening of the bond distance is found to be $\simeq$ 0.02 Å. The sign is seen to be correct, but not the order of magnitude. The discrepancy is, however, easily explained. When the derivative of the semiempirical potential, expressed by the parameters $G_l(l = 2,4)$, is taken, we cannot expect to get the correct slope of the potential since the bonding terms have not been properly included in the Hamiltonian. Since no splitting of the degenerate level takes place due to the influence of S_1 this term will be neglected in what follows.

The configurational instability of the Jahn-Teller type is apparent from the q_2 terms in (16). A positive a results in a splitting of the electronic degeneracy, and also in a continuous set of minima, found at $\overline{q_2} = \dfrac{a}{2k_2}$. The energy gain ΔE is $- \dfrac{a^2}{8k_2}$. The apparent independence of φ_2 which this result show is due to the neglect of the second order terms in (1). If these are included a more refined potential surface of the form [14],[15].

$$E = \tfrac{1}{2}k_1q_1^2 - \frac{2}{9} B_4q_1 + \tfrac{1}{2}k_2q_2^2$$
$$\pm \tfrac{1}{2}q_2\sqrt{a^2 + \beta^2q_2^2 + \gamma^2q_1^2 - 2\beta\gamma q_1q_2\cos3\varphi_2 - 2a\beta q_2\cos3\varphi_2 + 2a\gamma q_1} \tag{18}$$

is obtained, where β and γ are constants involving further derivatives of the potential. The appearance of the cos $3\varphi_2$ term in (18) makes it clear that the molecule will have a threefold potential barrier.

The minimization of (18) with respect to φ_2 gives the condition

$$\sin\ 3\overline{\varphi}_2 = 0$$

$$\overline{\varphi}_2 = \frac{n\pi}{3} \quad (n = 0,\ 1,\ 2,\ 3,\ 4,\ 5) \tag{19}$$

Three of these points will give identical potential minima, the other three yielding identical saddle points. The identification of which is which can first be made once we know the sign of β. Now β is calculated to be positive in the molecular orbital approximation and negative in the electrostatic limit [14],[15], and hence, the minima are found at $\overline{\varphi}_2 = \frac{n\pi}{3}$ ($n = 1,\ 3,\ 5$) for the covalent case and at ($n = 0,\ 2,\ 4$) in the electrostatic case. A positive β further indicates that the stable configuration takes the shape of an *elongated* tetrahedron. For VCl_4 we expect that β is greater than zero.

In order to obtain a crude numerical estimate of the effect, we place β equal to zero. Now G_4 may be estimated from the absorption spectra [17] of VCl_4, and G_2 may be found in the tables of Ballhausen and Ancmon [16]. We find a to be about 0.20×10^{-3} dyne. If for illustrative purposes $k_2 = 0.47 \times 10^5$ dyne/cm, corresponding to [18] $\nu_2 = 150$ cm^{-1}, $\overline{q}_2$ will equal 0.21 Å. The stable configuration then corresponds to an closing of $\simeq 6°$ of two of the tetrahedral angles, the four others being opened each $\simeq 3°$. The height of the threefold barrier has further been estimated to be ≈ 150 cm^{-1} [14]. The value of $\overline{q}_2$ corresponds to a Jahn-Teller Energy gain, ΔE, of 250 cm^{-1}. Note that the ordinary zero point amplitude, $\sqrt{\langle q_2^2 \rangle_0}$, is roughly one-fourth (0.055 Å) of the Jahn-Teller amplitude $\overline{q}_2$.

The situation can thus be described as follows: At low temperatures the molecule will be frozen into one of the three potential traps, and it will assume the shape of an *elongated* tetrahedron. At temperatures so high that the molecule has sufficient energy to override the barriers, the complex will exhibit a sort of pseudo rotation: all of the Cl^- nuclei are forced to perform a coupled rotation about the (regular) tetrahedral bond angles, each one rolling upon a cone with an apex angle of 6° (See Fig. 3).

We must now ask ourselves: are there any experimental proofs as to this rather remarkable behavior of VCl_4? Unfortunately there are none at the time of writing. The existing electron diffraction data [12] cannot, without refinement, decide whether the predicted behavior is true *.

Three other methods of substantiating these predictions are possible however. One would be an investigation of the Raman spectrum. By this tech-

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* This is due to the fact that the molecule librates freely at the temperature at which the diffraction measurements are performed. Hence the measured Cl—Cl distance is an average distance, *i.e.*, the bond distance found for a strictly tetrahedral molecule. The Jahn-Teller motions may yet be detected, however, by their production of an anomalous temperature dependent scattering factor. This possibility should be investigated.
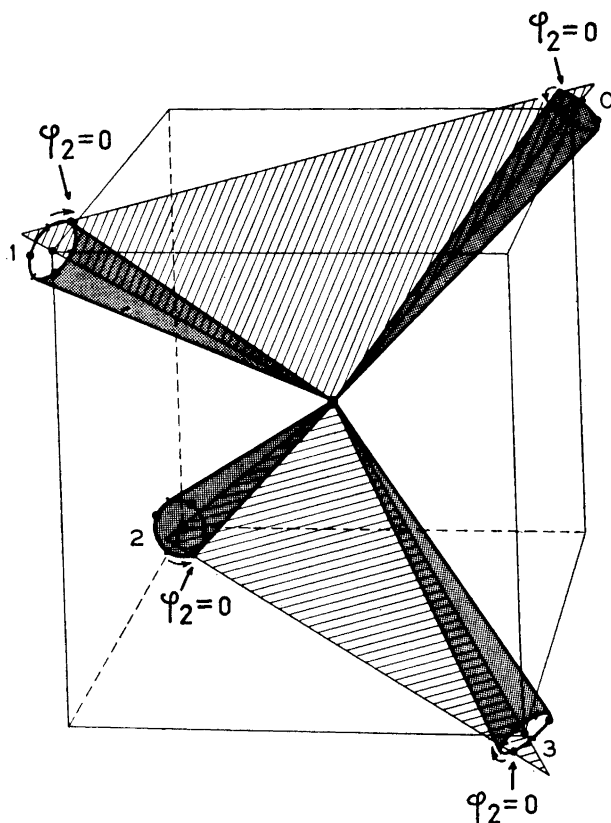
Fig. 3. Jahn-Teller motions in the VCl₄ molecule, $\beta > 0..$

nique one could decide whether the symmetry of the molecule is instantane-
ously lower than T_d.[15] Furthermore, an investigation of the paramagnetic
resonance spectrum should yield results identical to those found [6],[10] for
$Cu(H_2O)_6SiF_6$, that is, an isotropic g-factor is expected when the molecule can
interconvert freely. On the other hand we would get an anisotropic g-factor
if the molecule is trapped in one of the potential holes. As pointed out previ-
ously by the authors [6], it would furthermore be possible to estimate the sign
of β by using the result of such a measurement. Lastly, optical measurements
at low temperatures should exhibit anomalously intense vibrational progres-
sions in the ε mode *. It seems to the authors that these three experiments
are well worth doing. Such work is now in progress [19],[20],[22].

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* This last experiment is difficult to interpret for VCl₄, but has been performed [21] and analy-
zed [15] for Cu++:ZnO.

The work reported in this note is being continued in two mutually complementary directions by the authors. One direction is an attempt to include the molecular orbital approach in the calculation of the Jahn-Teller configurational instability for tetrahedral molecules in both their ground- and excited-states [14], and the second is an attempt to mathematically describe the concomitant Jahn-Teller nuclear motions in these self-same systems without regard to any specific model [15].

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