contribution of the hydrophobic interactions between the probes and PSS ions, because the hydrophobic interactions are generally reinforced with rising temperature.[11]

The possibility of the dynamic and/or static quenching of the probe with PSS macroanion itself must also be considered in interpreting our results. Photophysical properties of NaPSS have not been studied in detail. We find that NaPSS does not significantly quench the luminescence of several fluorescence and phosphorescence probes such as bis(α-binaphthylmethyl)ammonium chloride, α-naphthylmethylammonium chloride, and *n*-(4-bromo-1-naphthoyl)alkyltrimethylammonium bromides. We also found the strong monomer and excimer emission for NaPSS aqueous solution.[12] Furthermore, the absorption maxima of 6-In-11$^+$ did not show any change in the presence of NaPSS as is seen in Figure 3. These results are consistent with small or negligible dynamic quenching of the probe by NaPSS. In addition, very strong association between the cationic probes and the macroanions will not be favorable to the dynamic quenching with NaPSS.

Acknowledgment. We thank the National Science Foundation for its generous support of this work.

Registry No. NaPSS, 9080-79-9; 6-In-11$^+$·Br$^-$, 51097-79-1.

---

[11] Sheraga, H. A.; Nemethy, G.; Steinberg, I. Z. *J. Biol. Chem.* **1962**, *237*, 2506.

[12] Turro, N. J.; Okubo, T. *J. Phys. Chem.*, submitted for publication.

On the Connection between the Photochemistry and the Jahn–Teller Effect of the Excited Doublets in Octahedral Cr(III) Complexes

A. Ceulemans, D. Beyens, and L. G. Vanquickenborne*

Contribution from the Department of Chemistry, University of Leuven, 3030 Heverlee, Belgium.
Received January 26, 1981

Abstract: In octahedral Cr(III) complexes, the lowest excited doublets are more reactive than the (equiconfigurational) ground state but less than the lowest excited quartets. Moreover, the spatially degenerate doublets are characterized by negligible Jahn–Teller interactions while the degenerate quartets are subject to a large Jahn–Teller energy splitting. Both effects are shown to be related to certain specific features of half-filled shell states.

I. Introduction

It is the purpose of this paper to discuss two apparently unrelated features of the lowest excited doublet states of the octahedral Cr(III) complexes. In the first place, these states are claimed to exhibit an enhanced substitution activity with respect to the ground state; in the second place, although they are orbitally degenerate, they do not appear to be subject to any significant Jahn–Teller distortions.

It is well-known that the dominant reaction modes of the Cr(III) photosubstitutions proceed via the first excited quartet states.[1] Yet, the photoactivity of the doublets is measurable, and the substitution rates are definitely larger than in the ground state. Since both the ground state and the first excited doublets correspond to the same configuration, one generally assumes that substitutions in both cases take place along the same (associative) reaction mechanism. Recently Adamson[2] formulated a set of empirical rules connecting the doublet photoactivity and the phosphorescence lifetime of the Cr(III) complexes. Although this proposal has been stimulating further work on the doublet reactivity,[3] the basic reason for the difference in behavior between quartet ground state and doublet excited states remains unclear.

Several discussions on the photochemistry of octahedral Cr(III) complexes refer to a vacant t_{2g} orbital, supposedly characterizing the excited $t_{2g}{}^3$ doublet states.[4,5] The picture of two electrons, paired in a single d orbital while leaving one t_{2g} orbital "entirely vacant",[4] suggests a certain similarity to the ground state of the very labile d^2 systems, such as Cr(IV) or V(III) complexes. On these grounds, the $t_{2g}{}^3$ doublet states are predicted to be very reactive toward bimolecular association reactions.

A closer examination of the detailed properties of the relevant Cr(III) doublet states might contribute to a better understanding of their behavior. In the present paper, we intend to show that the vacant orbital idea is not valid and that the association reactions of the Cr(III) complexes are determined by the specific properties of half-filled shell systems. In the last sections of this paper, we will show that the same properties are also at the basis of the Jahn–Teller behavior.

II. t_{2g} Occupation and Associative Interactions

Figure 1 shows the well-known state energy diagram corresponding to the $t_{2g}{}^3$ configuration in octahedral symmetry. Representative wave functions are shown schematically (only one component is given for each state). The functions are based on the three usual real t_{2g} orbitals (d_{xz}, d_{yz}, d_{xy}); more explicit and complete sets of functions can be found in the literature.[6,7]

The first excited doublet states ^2E and $^2T_{1g}$ are degenerate to first order in perturbation theory. As a result of configuration interaction (mainly with $t_{2g}{}^2e_g{}^1$ states), ^2E_g is slightly stabilized with respect to $^2T_{1g}$.

Because of the generalized Unsöld theorem, the three t_{2g} orbitals are equally occupied in any octahedral eigenstate, in the present

---

[1] (a) Adamson, A. W. *Pure. Appl. Chem.* **1979**, *51*, 313. (b) Ballardini, R. W.; Varani, G.; Wasgestian, H. F.; Moggi, L.; Balzani, V. *J. Phys. Chem.* **1973**, *77*, 2947. (c) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1978**, *100*, 475.

[2] Walters, R. T.; Adamson, A. W. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 53. See also: Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.

[3] Shipley, N. J.; Linck, R. G. *J. Phys. Chem.* **1980**, *84*, 2490; Forster, L. S.; Castelli, F. *ibid.* **1980**, 2492. Adamson, A. W.; Gutierez, A. R. *Ibid.* **1980**, 2492.

[4] Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967.

[5] Balzani, V.; Carasitti, V. "Photochemistry of Coordination Compounds"; Academic Press: London, 1970. Adamson, A. W., Fleischauer, P. D., Eds.; "Concepts of Inorganic Photochemistry"; Wiley-Interscience: New York, 1975.

[6] Perumareddi, J. R. *J. Phys. Chem.* **1967**, *71*, 3144.

[7] Griffith, J. S. "The Theory of Transition-Metal Ions"; University Press: Cambridge, 1971.

0002-7863/82/1504-2988$01.25/0

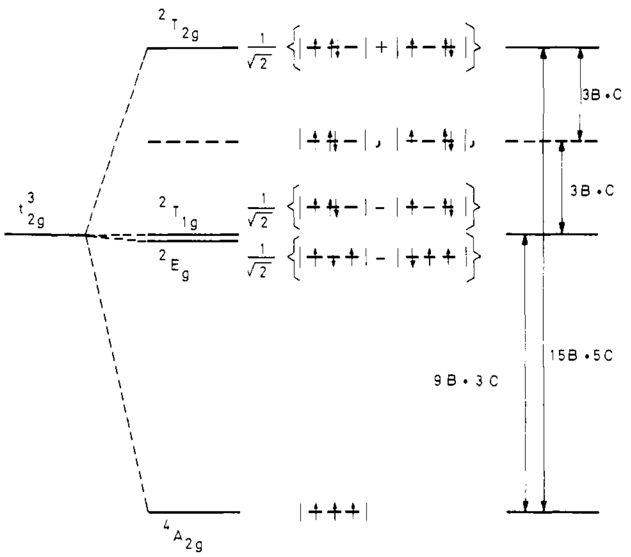

Figure 1. Energy diagram of the t_{2g}^3 states in O_h symmetry. The schematic representation of the state functions is based on the real orbital set (d_{xz}, d_{yz}, d_{xy}). As usual, B and C are Racah parameters; $B \simeq 0.07\ \mu m^{-1}$, $C \simeq 0.28\ \mu m^{-1}$.

case corresponding to the configuration $(d_{xz})^1(d_{yz})^1(d_{xy})^1$. However, the schematic representations in Figure 1 show that this situation holds true, even *for each individual component* of these states, so that no single t_{2g} orbital remains "entirely vacant". Indeed, in functions of the type $\{|(xz)\alpha\ (xz)\beta\ (yz)\alpha| \pm |(xy)\alpha\ (xy)\beta\ (yz)\alpha|\}$, each one of the three t_{2g} orbitals is clearly occupied by one electron. It is interesting to compare these functions to the quartet components such as $|(xz)\alpha\ (yz)\alpha\ (x^2-y^2)\alpha|(^4T_{2g})$ or $|(xz)\alpha\ (yz)\alpha\ (z^2)\alpha|(^4T_{1g})$; the latter are definitely characterized by an unequal occupation of both the t_{2g} and the e_g orbitals (although here again, the generalized Unsöld theorem imposes equal occupations for the states as a whole).

Doublet functions satisfying the vacant orbital condition should be of the type

$$\frac{1}{\sqrt{3!}}|xz\alpha\ xz\beta\ yz\alpha|,\ \frac{1}{\sqrt{3!}}|xz\alpha\ yz\alpha\ yz\beta|,... \qquad (1)$$

The energy corresponding to these functions is shown by a dotted line in Figure 1. Clearly, these functions do not correspond to octahedral eigenstates, but instead they are linear combinations of $^2T_{1g}$ and $^2T_{2g}$ functions.

The possibility of an associative reaction is conditioned by the availability of a σ interaction between a vacant metal orbital and an occupied ligand orbital. Therefore, one of the octahedral doublet components has to be forced to change into a function of the type described in eq 1. The modification of any octahedral function along an associative reaction path is thus necessarily accompanied by an increase in interelectronic repulsion energy; to first order this energy is described by the exchange integral $K(xz, yz) = K(yz, xy) = ... = 3B + C$.

It is well to stress, however, that the quartet ground state will have an even higher activation energy along the same associative reaction path. If the same transition state had to be reached, the change would require 4 times more energy, namely $12B + 4C$. As a matter of fact, the actual activation energy of the ground state is calculated to be lower than $12B + 4C$ if the molecule remains on the lowest quartet potential surface but still higher than $3B + C$. Therefore, as a conclusion, it remains valid to state that the doublets are characterized by an enhanced association reactivity (with respect to the ground state),[8] but the idea of a vacant t_{2g} orbital and the spontaneous formation of a seven-coordinated intermediate cannot be supported from ligand field arguments.

III. Orbital Occupation in Half-Filled Shell Functions

In the discussion on Figure 1, the t_{2g} basis chosen was the usual (xz, yz, xy) set. The question might arise whether it would be possible to find another (equivalent) basis (t_{2g}^a, t_{2g}^b, t_{2g}^c), allowing the construction of doublet functions such as

$$\frac{1}{\sqrt{3!}}|t_{2g}^a\alpha\ t_{2g}^a\beta\ t_{2g}^b\alpha| \qquad (2)$$

that are suitable octahedral basis functions while at the same time satisfying the vacant orbital condition. In other words, is it possible to find an alternative set of t_{2g} orbitals such that the first-order response of the octahedral doublets to an association reaction can be simply described by a σ-bonding stabilization? It will be shown that the answer to this question is negative, provided one restricts attention to real orbitals. This restriction does not imply any loss of generality, however, since the functions have always to be written in real form, in view of the symmetry lowering connected with any association reaction.

It is possible to discuss this problem in a very concise way from the point of view of density matrices.[9] Instead, we want to relate the nonexistence of valid "vacant-orbital functions" to a general symmetry restriction, imposed on wave functions describing half-filled shells.[10] Indeed, Griffith[11] has shown that the hole–particle equivalence, relating states from complementary configurations, e.g., t_{2g}^n and t_{2g}^{6-n}, takes the form of a symmetry property when the number of holes equals the number of electrons.

Consider a shell, described by r orthogonal one-electron spin orbitals of the proper symmetry: ϕ_1, ϕ_2, ... ϕ_r. The n-electron ($n \leq r$) determinantal wave function $D^e{}_k(1,2, ... n)$ is defined by

$$D^e{}_k(1,2, ... n) = \frac{1}{\sqrt{n!}}|\phi_{k_1}(1)\ \phi_{k_2}(2)\ ...\ \phi_{k_n}(n)| \qquad (3)$$

where k denotes a specific selection of n orbitals among the set of r available spin orbitals, where the ith column of the determinant contains only the functions ϕ_{k_i}. In what follows, $D^e{}_k$ will be represented as a row of function labels: k_1, k_2, ... k_n. Unless specified otherwise, we will let $k_i < k_{i+1}$.

Any open-shell function, characterized by the symmetry labels Γ, M_Γ and spin quantum numbers S and M_S, can generally be written as a linear combination of the $D^e{}_k$ functions:

$$\Psi^e{}_K = \sum_k c_{kK} D^e{}_k \qquad (4)$$

where K stands for the set of state labels: $K = \{\Gamma, M, S, M_S\}$.

It is possible to introduce an operator $\mathcal{P}$, defined by eq 5, when applied to a half-filled shell ($n = r/2$):

$$\begin{aligned}\mathcal{P}D^e{}_k(1,2, ... n) &= D^h{}_k(1,2, ... n)\\ &= \frac{(-1)^{q_k}}{\sqrt{n!}}|\phi_{k_{n+1}}(1)\phi_{k_{n+2}}(2)\ ....\ \phi_{k_r}(n)|\end{aligned} \qquad (5)$$

The operator $\mathcal{P}$ depopulates the spin orbitals that were populated in $D^e{}_k$ and populates the orbitals that were vacant in $D^e{}_k$; therefore $D^h{}_k$ can be regarded as a hole function and $\mathcal{P}$ as an electron hole exchange operator. The phase factor is defined by $q_k = 1 + 2 + ... + n + k_1 + k_2 + ... k_n$, by the convention $k_i < k_{i+1}$, and by introducing a standard order for the spin-orbital basis; in the t_{2g}^3 application, we will always adopt the Griffith order convention:[14] ($yz\alpha\ yz\beta\ xz\alpha\ xz\beta\ xy\alpha\ xy\beta$). In general, the row ($k_{n+1}$, k_{n+2}, ... k_r) can be obtained from the row (1,2,3, ... r) by eliminating all function labels k_1, k_2, ... k_n already used in eq 3.

A general theorem[12] proves that the D^e and D^h functions have complex conjugate symmetry properties: $(D^e{}_k|\mathcal{R}|D^e{}_l)^* = (D^h{}_k|\mathcal{R}|D^h{}_l)$, where $\mathcal{R}$ is any symmetry operator. If the basis

---

(8) Jamieson, M. A.; Serpone, N.; Henry, M. S.; Hoffmann, M. Z. *Inorg. Chem.* **1979**, *18*, 214.

(9) Davidson, E. R. "Reduced Density Matrices in Quantum Chemistry"; Academic Press: New York, 1976.

(10) In the octahedral complex the t_{2g} orbitals are considered to form a single shell.

(11) Reference 7, Chapter 9, § 7.

(12) Vanquickenborne, L. G.; Ceulemans, A. *Chem. Phys. Lett.* **1980**, *75*, 494. In this reference, the matrix element theorem for $\mathcal{R}$ is formulated in a more general way, for $0 < n < r$, and not only for half-filled shells.

Table I. Hole–Electron Exchange Parity for a Number of States,[13] Corresponding to Some Exemplary Configurations of Octahedral Complexes[c]

	$^{2S+1}\Gamma$	exchange parity		parentage ($t_{2g}^3 \times e_g^2$)	$^{2S+1}\Gamma$	exchange parity[a]
t_{2g}^3	$^4A_{2g}$	−	$t_{2g}^3e_g^2$	$^4A_{2g} \times {}^3A_{2g}$	$^6A_{1g}$	+
	^2E_g	−		$^4A_{2g} \times {}^3A_{2g}$	$^4A_{1g}$	−
	$^2T_{1g}$	−		$^2T_{1g} \times {}^3A_{2g}$	$^4T_{2g}$	+
	$^2T_{2g}$	+		$^2T_{2g} \times {}^3A_{2g}$	$^4T_{1g}$	−
				$^4A_{2g} \times {}^1A_{1g}$	$^4A_{2g}$	−
e_g^2	$^3A_{2g}$	−		$^4A_{2g} \times {}^1E_g$	$^4E_g(^4G)$	+[b]
	^1E_g	−		$^2E_g \times {}^3A_{2g}$	$^4E_g(^4D)$	+[b]
	$^1A_{1g}$	+		$^2E_g \times {}^1E_g$	$^2A_{2g}$	+

[a] The parity of the states, resulting from the coupling of two open-shell states, is simply the product of the individual parities. [b] Although eq 8 does not generally apply when two states of the same (Γ, *S*) type are available, the parity assignment is possible in the present case, where the free-atom ^4G and ^4D functions remain unaffected by the octahedral field. [c] Throughout Griffith conventions for the orbital sequence[14] were adopted.

orbitals are taken to be real, D^e_k and D^h_k behave *identically* under spatial symmetry operators. Therefore, if we construct

$$\Psi^h_K = \sum_k c_{kK} D^h_k \qquad (6)$$

where the c_{kK} coefficients are the same as in eq 4, the functions Ψ^h_K and Ψ^e_K will be characterized by the *same* symmetry labels (Γ, M_Γ).

The spin quantum numbers of Ψ^h_K, however, are determined by the commutation properties of $\mathscr{P}$ and the spin operators. In the Appendix it is shown that

$$\mathscr{S}_z\mathscr{P} + \mathscr{P}\mathscr{S}_z = 0 \qquad (7a)$$

$$\mathscr{S}^{\mp}\mathscr{P} + \mathscr{P}\mathscr{S}^{\pm} = 0 \qquad (7b)$$

$$\mathscr{S}^2\mathscr{P} - \mathscr{P}\mathscr{S}^2 = 0 \qquad (7c)$$

Since $\mathscr{S}^2$ commutes with $\mathscr{P}$, the quantum number S is conserved under $\mathscr{P}$. Since $\mathscr{S}_z$ and $\mathscr{P}$ anticommute, M_S changes sign upon application of $\mathscr{P}$. Therefore $\bar{K} = \{\Gamma, M_\Gamma, S, -M_S\}$. The successive application ($2|M_S|$ times) of the spin-step operators $\mathscr{S}_+$ or $\mathscr{S}_-$ on $\Psi^h_{\bar{K}}$ yields a function Ψ^h_K, again characterized by the labels K = $\{\Gamma, M_\Gamma, S, M_S\}$.

Provided each (Γ, *S*) state occurs just once in the open-shell configuration—a condition which is obviously satisfied for the t_{2g}^3 shell—the function Ψ^h_K can be nothing but the original function Ψ^e_K, except possibly for changes in sign

$$\mathscr{P}\Psi^e_K = \Psi^h_K$$

$$\Psi^h_K = \pm\Psi^e_K \qquad (8)$$

No function of the general type of eq 2 can satisfy eq 8; if t_{2g}^c is entirely vacant in Ψ^e_K, it will be doubly occupied in Ψ^h_K. This observation completes the proof of section II.

Equation 8 associates an "electron–hole exchange parity" to the state function Ψ^e_K. For a specified Γ, the exchange parity can be shown[11] to be independent of M_Γ. Indeed, the (Γ, M_Γ) and (Γ, M_Γ') functions are related by shift operators, which are specific linear combinations of the symmetry operators. Because of the theorem mentioned before,[12] as applied to real functions, the shift operators will affect Ψ^e_K and Ψ^h_K in an identical way. Therefore the sign in eq 8 is independent of M_Γ.

For a specified value of *S*, the so-obtained exchange parity is not independent of M_S, however. Indeed, by use of eq 7b, it can be shown (see Appendix) that any M_S function has the opposite parity of its $(M_S + 1)$ and $(M_S - 1)$ partners. Therefore, for a given set of $\{\Gamma, M_\Gamma, S\}$ labels, the parity alternates all the way from $M_S = S$ to $M_S = -S$. In Table I, the exchange parity is given for a number of half-filled shells for the maximum value of M_S.

IV. Jahn–Teller Effect in the Doublet States

In the previous sections, we have shown that the excited Cr(III) states will not be inclined to undergo spontaneous association reactions. Since all the doublets under consideration are orbitally degenerate, another possible source of instability and (reactive or nonreactive) distortion is the Jahn–Teller (J–T) effect.[15]

In fact, several very accurate experimental observations suggest the total absence of a first-order Jahn–Teller effect in the excited $^2E_g(t_{2g}^3)$ state. Perhaps the best example can be found in the studies on hexafluoromanganate(IV) which is isoelectronic with Cr(III).[16,17] A vibronic analysis of the absorption and emission spectra indicates that the vibrational frequencies of ground and excited states are virtually identical—even for those modes that would be expected to be J–T active for symmetry reasons. Moreover, the intensity distribution indicates that levels derived from ^2E_g and $^4A_{2g}$ with different vibrational quantum numbers are very nearly orthogonal.[18] Similar observations[19-21] have been made for $Cr(NH_3)_6^{3+}$ and $Cr(CN)_6^{3-}$. The same conclusions are also valid for the $^2T_{2g}(t_{2g}^3)$ state, as exemplified by the luminescence spectra of $ReCl_6^{2-}(5d^3)$.[22] In CrF_6^{3-}, the observation of a Franck–Condon progression has been attributed to a second-order J–T effect, due to spin–orbital coupling with the nearby $^4T_g(t_{2g}^2\,e_g)$.[23-25]

No detailed explanation of these remarkable observations appears to be available in the literature. It is quite often assumed that the potential energy surfaces of the $^4A_{2g}$ state and the excited doublets are parallel because they correspond to the same t_{2g}^3 configuration.[4,5] However, the property of belonging to the same configuration is not by itself sufficient for the states to have similar potential surfaces; Jahn–Teller distortions are obviously state specific rather than configuration specific.

Another line of reasoning focuses attention on the sharp contrast between doublet and quartet states. The weakness of π interactions between the ligands and the t_{2g} orbitals is supposed to be responsible for the absence of J–T effects in the doublet states. One anticipates quite a different situation in the excited quartet $^4T_{2g}(t_{2g}^2\,e_g^1)$, where the occupation of the e_g orbital is responsible for a strong σ* interaction. The $^4T_{2g}$ state is indeed found to be strongly J–T unstable along the e_g stretching mode.[26-27] Similar effects have been observed[28] in the $^3T_{1g}$ and $^1T_{1g}$ states ($t_{2g}^5\,e_g$) of $Co(NH_3)_6^{3+}$. This simple orbital view is consistent with the fact that J–T effects involving e_g orbitals are generally much larger than J–T effects involving only t_{2g} orbitals. But the fact that t_{2g}^1 and t_{2g}^2 systems are characterized by small though readily detectable J–T splittings (of the order 100 cm⁻¹ or more),[29-31] while $^2E_g(t_{2g}^3)$

---

(13) Another interesting application of the present classification (not included in Table I) is the π^2 configuration of O_2. Adopting the orbital sequence $(\pi_x\alpha, \pi_x\beta, \pi_y\alpha, \pi_y\beta)$, one obtains the following exchange parities: $^3\Sigma_g^-(-)$, $^1\Delta_g(-)$, $^1\Sigma_g^+(+)$.

(14) Reference 7 Table A24.

(15) Jahn, H. A.; Teller, E. *Proc. R. Soc. London, Ser. A.* **1937**, *161A*, 220. Bersuker, I. B. *Coord. Chem. Rev.* **1975**, *14*, 357.

(16) Pfeil, A. *Theor. Chim. Acta* **1971**, *20*, 159.

(17) Flint, C. D. *J. Mol. Spectrosc.* **1971**, *37*, 414.

(18) Kupka, J. *Chem. Phys. Lett.* **1976**, *41*, 114.

(19) Flint, C. D.; Greenough, G. *J. Chem. Soc., Faraday Trans 2* **1972**, *68*, 897.

(20) Flint, C. D.; Greenough, P.; Matthews, A. P. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 23.

(21) Flint, C. D.; Greenough, P. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 815.

(22) Black, A. M.; Flint, C. D. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 877.

(23) Ferguson, J.; Guggenheim, H. J.; Wood, D. L. *J. Chem. Phys.* **1971** *54*, 504.

(24) Greenough, P.; Paulusz, A. G. *J. Chem. Phys.* **1979**, *70*, 1967.

(25) Dubicki, L.; Ferguson, J.; Van Oosterhout, B. *J. Phys. C* **1980**, *13*, 2791.

(26) Güdel, H. U.; Snellgrove, T. R. *Inorg. Chem.* **1978**, *17*, 1617.

(27) Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1978**, *17*, 1729.

(28) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(29) Englman, R. "The Jahn-Teller Effect in Molecules and Crystals"; Wiley-Interscience: New York, 1972. Lever A. B. P. "Inorganic Electronic Spectroscopy"; Elsevier: Amsterdam, 1968.

(30) Bacci, M. *Chem. Phys. Lett.* **1978**, *58*, 537.

(31) Bacci, M. *Chem. Phys.* **1979**, *40*, 237.

does not show any detectable J–T splittings at all, remains unexplained. The experimental data on the $^2T_{1g}(t_{2g}{}^3)$ doublet are much more limited and less clear-cut. The $\Delta v = 1$ rule is not followed as neatly as in ^2E_g, but a possible Jahn–Teller effect, if at all present, appears to be very small. The sharpness of some sextet–quartet absorption bands[32] in $Mn(H_2O)_6{}^{2+}$ $(t_{2g}{}^3\ e_g{}^2)$ suggests that these degenerate quartets are J–T inactive in spite of their considerable σ-antibonding character.

Occasionally, the absence of a significant Jahn–Teller effect appears to have been linked in a phenomenological way to the half-filled shell character of the states under consideration.[33,34] On a calculational basis, Davidson and Borden[35] showed that, in the specific case of the cyclopropenyl anion, the half-filled shell component of the $^1E'$ state has a zero contribution to the Jahn–Teller effect.

In the next section, we intend to show analytically that the peculiar Jahn–Teller properties of $t_{2g}{}^3$ doublets or of $t_{2g}{}^3\ e_g{}^2$ quartets are not artificial or accidental but that they are essentially related to the electronic structure of half-filled shells.[36]

V. Jahn-Teller Inactivity of Half-Filled Shells

Consider two components $\Psi^e{}_K$ and $\Psi^e{}_L$ of a given $^{2S+1}\Gamma$ state in a half-filled shell; the labels K and L stand for $\{\Gamma, M_\Gamma, S, M_S\}$ and $\{\Gamma, M_\Gamma', S, M_S'\}$, respectively. The first-order J–T coupling elements for some nontotally symmetric distortion Q are given by the general expression

$$V_{KL} = \left(\Psi^e{}_K \left| \frac{\partial \mathcal{H}}{\partial Q} \right| \Psi^e{}_L \right) \Bigg|_{Q=0} \tag{9}$$

In what follows, the numerical specification $Q = 0$ will be omitted to alleviate the notation. Obviously, if $M_S \neq M_S'$, $V_{KL} = 0$; the only matrix elements contributing to a first-order Jahn–Teller coupling have $M_S = M_S'$. From now on K and L will be taken to have the same spin quantum number. Since both components belong to the same state, they are characterized by the same exchange parity, in the sense of eq 8. Moreover, V_{KL} is independent of the M_S value, and therefore, using eq 6 and 8:

$$V_{KL} = \left(\Psi^e{}_K \left| \frac{\partial \mathcal{H}}{\partial Q} \right| \Psi^e{}_L \right) = \left(\Psi^h{}_K \left| \frac{\partial \mathcal{H}}{\partial Q} \right| \Psi^h{}_L \right) = \left(\Psi^h{}_K \left| \frac{\partial \mathcal{H}}{\partial Q} \right| \Psi^h{}_L \right) \tag{10}$$

The matrix element V_{KL} can thus equally well be expressed in terms of the hole functions. From eq 4 and 6, V_{KL} can be written in two different ways as a sum of matrix elements of the individual D_k determinants:

$$V_{KL} = \sum_k \sum_l c^*{}_{kK} c_{lL} \left(D^e{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^e{}_l \right) = \sum_k \sum_l c^*{}_{kK} c_{lL} \left(D^h{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^h{}_l \right) \tag{11}$$

First consider the diagonal elements in these expressions. Since $\partial\mathcal{H}/\partial Q$ is a sum of one-electron operators, $\partial\mathcal{H}/\partial Q = \sum_{j=1}{}^n \partial h_j/\partial Q$, one obtains

$$\left(D^h{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^h{}_k \right) = (-1)^{2q_k} \sum_{i=n+1}^{r} \left(k_i \left| \frac{\partial h}{\partial Q} \right| k_i \right) = \sum_{i=1}^{r} \left(k_i \left| \frac{\partial h}{\partial Q} \right| k_i \right) - \sum_{i=1}^{n} \left(k_i \left| \frac{\partial h}{\partial Q} \right| k_i \right)$$

The first summation of the right hand side expression can be interpreted as the expectation value of the r-electron determinant, corresponding to the closed-shell configuration. This determinant is always totally symmetric, and since Q is not totally symmetric, one obtains

$$\sum_{i=1}^{r} \left(k_i \left| \frac{\partial h}{\partial Q} \right| k_i \right) = 0 \tag{12}$$

and

$$\left(D^h{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^h{}_k \right) = -\sum_{i=1}^{n} \left(k_i \left| \frac{\partial h}{\partial Q} \right| k_i \right) = -\left(D^e{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^e{}_k \right) \tag{13}$$

This means that the diagonal elements of the hole determinants are equal in magnitude but opposite in sign to the diagonal elements of the corresponding electron determinants.

Next, turning to the off-diagonal elements in eq 11, it is clear that D_k and D_l will interact only if they differ in one spin orbital, say ϕ_{k_s} vs. ϕ_{l_t}. For evaluation of the interaction elements $(D_k|\partial\mathcal{H}/\partial Q|D_l)$, the determinants must be rearranged so as to carry the k_s and l_t orbitals to the same place on the principal diagonal. Let us assume that $k_s < l_t$ (the proof can be adapted without difficulty if $k_s > l_t$). The notation for the D_k functions is such that the orbitals are listed in order to ascending labels:

$$D^e{}_k = (k_1, k_2, \ldots k_s, \ldots k_n) \tag{14a}$$

$$D^e{}_l = (l_1, l_2, \ldots l_t, \ldots l_n) \tag{14b}$$

The number of permutations necessary to shift the two orbitals k_s and l_t to the first position (while maintaining the standard order for the other ones) equals the number of orbitals preceding ϕ_{k_s} and ϕ_{l_t}, i.e., $(s - 1)$ and $(t - 1)$, respectively. Hence:

$$D^e{}_k = (-1)^{s-1}\ (k_s; k_1, k_2, \ldots k_{s-1}, k_{s+1}, \ldots k_n) \tag{15a}$$

$$D^e{}_l = (-1)^{t-1}\ (l_t; l_1, l_2, \ldots l_{t-1}, l_{t+1}, \ldots l_n) \tag{15b}$$

and

$$\left(D^e{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^e{}_l \right) = (-1)^{s+t} \left(k_s \left| \frac{\partial h}{\partial Q} \right| l_t \right) \tag{16}$$

The corresponding hole determinants will also differ in the very same orbitals, but now ϕ_{k_s} belongs to the $D^h{}_l$ sequence while ϕ_{l_t} belongs to the $D^h{}_k$ sequence:

$$D^h{}_k = (-1)^{q_k}(k_{n+1}, k_{n+2}, \ldots l_t \ldots k_r) \tag{17a}$$

$$D^h{}_l = (-1)^{q_l}(l_{n+1}, l_{n+2}, \ldots k_s \ldots l_r) \tag{17b}$$

Let $t' - 1$ and $s' - 1$ be the number of orbitals that precede respectively l_t and k_s in the rows of eq 17. Then it can be readily shown that

$$s' + t' = k_s + l_t - s - t + 1 \tag{18}$$

and therefore[37]

$$\left(D^h{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^h{}_l \right) = (-1)^{q_k+q_l+s'+t'} \left(l_t \left| \frac{\partial h}{\partial Q} \right| k_s \right) = (-1)^{s+t-1} \left(l_t \left| \frac{\partial h}{\partial Q} \right| k_s \right) \tag{19}$$

If the orbitals are taken to be real—which can be done without loss of generality—the combination of eq 16 and 19 gives:

$$\left(D^h{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^h{}_l \right) = -\left(D^e{}_k \left| \frac{\partial \mathcal{H}}{\partial Q} \right| D^e{}_l \right) \tag{20}$$

and from eq 11, 13, and 20, one obtains $V_{KL} = 0$, which concludes the proof.

The experimental relevance of this result depends on the extent to which a given electronic state can be described by a half-filled

---

(32) Heidt, L. J.; Koster, G. F., Johnson, A. M. *J. Am. Chem. Soc.* **1959**, *80*, 6471.

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

(34) Black, A. M.; Flint, C. D. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1871.

(35) Davidson, E. R.; Borden, W. T. *J. Chem. Phys.* **1977**, *67*, 2191.

(36) In section V, an algebraic procedure is followed throughout; no use is made of Kramers star operator, introduced by Griffith[7] to deal with similar problems.

(37) Since the k and l lists of orbital labels in eq 13a,b are identical, except for k_s and l_t, one has $(-1)^{q_k+q_l} = (-1)^{k_s+l_t}$.

Table II. Coupling of the Different t_{2g}^2 State Functions with $^2E_g(e_g)$

$^{2S+1}\Gamma(t_{2g}^2)$	$^{2S+1}\Gamma(t_{2g}^2e_g)^a$
$^1A_{1g}$	^2E_g
^1E_g	^2E_g, $^2A_{1g}$, $^2A_{2g}$
$^1T_{2g}$	$^2T_{1g}$, $^2T_{2g}$
$^3T_{1g}$	$^2T_{1g}$, $^2T_{2g}$, $^4T_{1g}$, $^4T_{2g}$

^{a} Column 1 entries × $^2E_g(e_g)$.

shell. In the case of the Cr(III) t_{2g}^3 doublets, the most important interacting states are of $t_{2g}^2\ e_g^1$ parentage, and to first order in the interaction element λ, one can write

$$\Psi \simeq \Psi(t_{2g}^3) + \lambda\Psi(t_{2g}^2\ e_g^1) \qquad (21)$$

The numerical value of λ is of the order of 0.1–0.2. Since λ is decreasing function of the ligand field strength, strong field complexes will have a more pronounced half-filled shell character than weak field complexes.

By using the result $V_{KL} = 0$, where V_{KL} is defined in eq 9, the relevant matrix element for the lowest ^2E_g state can be written as

$$\left(\Psi_K(^2E_g)\left|\frac{\partial\mathcal{H}}{\partial Q}\right|\Psi_L(^2E_g)\right) \simeq 2\lambda\left(\Psi_K(^2E_g;\ t_g^3)\left|\frac{\partial\mathcal{H}}{\partial Q}\right|\Psi_L(^2E_g;\ t_{2g}^2e_g)\right) \qquad (22)$$

The matrix element at the right hand side of eq 22 is zero, since both states differ in two spin orbitals. This can be seen most readily by analyzing the common part of both configurations, i.e., the (t_{2g}^2) subshell. Table II shows the symmetry of different states arising from t_{2g}^2 and the product of their coupling with $^2E_g(e_g^1)$. The only t_{2g}^2 states on the basis of which it is possible to construct a $^2E_g(t_{2g}^2\ e_g^1)$ state are $^1A_{1g}$ and ^1E_g. All the determinants contributing to $^1A_{1g}$ and ^1E_g have the two electrons in the same spin orbital. Therefore all the $^2E_g(t_2^2\ e^1)$ functions consist of determinants of the general type $|t\alpha\ t\beta\ e\alpha|$. On the other hand, as shown schematically in Figure 1, the $^2E_g(t_{2g}^3)$ state contains only determinants of the type $|t\alpha\ t'\beta\ t''\alpha|$, constructed on the basis of the $^1T_{2g}$ and $^3T_{1g}(t_{2g}^2)$ functions.

Therefore, the lowest excited doublet ^2E_g provides a rather extreme example, where no first-order Jahn–Teller effect should be expected. For the other t_{2g}^3 doublets $^2T_{1g}$ and $^2T_{2g}$, the situation is somewhat less simple in that the corresponding matrix elements (eq 22) do not vanish. We did not attempt a detailed calculation of the actual magnitude of these matrix elements. Indeed, such a calculation would necessarily also have to introduce the effect of spin-orbit coupling. In view of the very limited amount of experimental data, it did not seem worthwhile to pursue the issue any further at this point. It is to be noted, however, that a qualitative analysis (using Bacci's ligand field approach[30,31]) suggests that the Jahn–Teller effect in both $^2T_{1g}$ and $^2T_{2g}$ should be very small.

The result $V_{KL} = 0$ also applies for the second-order J–T effect, involving matrix elements between two *different* states of the same half-filled configuration, if at least both states are of the same parity, so that eq 10 is satisfied.

The latter observation is also of special relevance in discussing the doublet functions of Cr(III) complexes. Indeed, as shown in Figure 1, the ^2E_g and $^2T_{1g}$ states are nearly degenerate, so that in principle a large pseudo-first-order J–T effect might be anticipated. However, since both states are of the same exchange parity (Table I), the resulting off-diagonal matrix elements will be zero. It is true that ^2E_g will be subject to a second-order J–T coupling with the energetically more distant $^2T_{2g}(t_{2g}^3)$, since both states are of the opposite exchange parity. Also, on account of spin–orbit coupling, ^2E_g will be coupled to $^4T_{2g}(t_{2g}^2\ e_g)$. The details of this mechanism remain to be investigated.[38]

VI. Potential Energy Surfaces of Ground State and Excited Doublet States

The result of the previous section is valid for any operator that can be written as a sum of one-electron operators—provided hole and electron determinants are defined in accordance with the conventions outlined in eq 5. Therefore, as a corollary to the preceding conclusions, one can apply the same line of reasoning to the matrix elements of $\partial^2\mathcal{H}/\partial Q^2$ in order to describe the harmonic part of the molecular vibrations.

Since this operator is totally symmetric, its matrix elements satisfy an expression similar to eq 20 but not to eq 12. Therefore, in analogy to eq 11 and separating the diagonal and the off-diagonal terms, one obtains

$$\begin{aligned} U_{KL} &= \left(\Psi^e{}_K\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|\Psi^e{}_L\right) = \sum_k c^*{}_{kK}c_{kL}\left(D^e{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^e{}_k\right) + \\ &\sum_{k\neq l} c^*{}_{kK}c_{lL}\left(D^e{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^e{}_l\right) = \left(\Psi^h{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|\Psi^h{}_k\right) = \\ &\sum_k c^*{}_{kK}c_{kL}\left(D^h{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^h{}_k\right) + \sum_{k\neq l} c^*{}_{kK}c_{lL}\left(D^h{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q_2}\right|D^h{}_l\right) = \\ &\sum_k c^*{}_{kK}c_{kL}\left(D^h{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^h{}_k\right) - \sum_{k\neq l} c^*{}_{kK}c_{lL}\left(D^e{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^e{}_l\right) \qquad (23) \end{aligned}$$

and therefore the off-diagonal matrix elements can be expressed in terms of the diagonal elements:

$$\sum_{k\neq l} c^*{}_{kK}c_{lL}\left(D^e{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^e{}_l\right) = \left(\frac{1}{2}\right)\sum_k c^*{}_{kK}c_{kL}\left\{\left(D^h{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^h{}_k\right) - \left(D^e{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^e{}_k\right)\right\} \qquad (24)$$

Substituting the latter equation into the first line of the U_{KL} expression, one obtains

$$U_{KL} = \frac{1}{2}\sum_k c^*{}_{kK}c_{kL}\left\{\left(D^e{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^e{}_k\right) + \left(D^h{}_k\left|\frac{\partial^2\mathcal{H}}{\partial Q^2}\right|D^h{}_k\right)\right\} = \frac{1}{2}\delta_{KL}\sum_{i=1}^{n}\left(k_i\left|\frac{\partial^2 h}{\partial Q^2}\right|k_i\right) = U_Q\delta_{KL} \qquad (25)$$

Since the harmonic part of the vibrational potential is given by $^1/_2U_QQ^2$, eq 25 means that all states, corresponding to the same half-filled shell configuration, should be characterized by exactly the same harmonic vibrational frequencies.

The experimental results for Cr(III) and Mn(IV) complexes—especially in the cases where higher order effects can be neglected—indicate that the prediction is verified within a few cm^{-1}. Yet, in arriving at this prediction, one assumes that the orbitals ϕ_{K_i} are the same in the different states belonging to the configuration under consideration. While this assumption is part of the classical set of assumptions underlying ligand field theory, it is not strictly true. The fact that nevertheless the agreement between theory and experiment is excellent suggests that orbital relaxation effects have only a minute effect on the vibrational frequencies.

VII. Conclusion

The role of the doublet states in the photochemisty of Cr(III) complexes has now been questioned for over 20 years.[39] A detailed analysis of the octahedral doublet state wave functions is at variance with the simple view of one vacant orbital, supposedly responsible for spontaneous association with a nucleophilic agent.

Moreover, it is concluded that no first-order Jahn–Teller distortions are associated with the dominant component of the doublet states. As a result, the doublet state is characterized as a largely

---

(38) Flint, C. D. *Chem. Phys. Lett.* **1971**, *11*, 27.

(39) Schläfer, H. L. *J. Phys. Chem.* **1965**, *69*, 2201.

imperturbable entity. This view appears to be compatible with all evidence from inorganic spectroscopy.

Both features—absence of a vacant t_{2g} orbital and strongly reduced J–T coupling—are closely connected to the half-filled shell character of these states. To the extent that a state is adequately described by a half-filled shell, it effectively protects itself against both reactive and nonreactive distortions.

Acknowledgment. We are indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid). A.C. thanks the Belgian Science Foundation (N.F.W.O.) for a postdoctoral fellowship.

Appendix

Some Useful Properties of the Electron-Hole Exchange Operator. (1) The one-determinant functions of the type $D^e{}_k$ are eigenfunctions of $\mathcal{S}_z$

$$\mathcal{S}_z D^e{}_k = M_s \hbar D^e{}_k \tag{1A}$$

Since $M_S = 0$ for the closed shell, specified by the set $\{1, 2, 3, \ldots r\}$, the effect of $\mathcal{P}$ on $D^e{}_k$ leads to a determinant, which is again an eigenfunction of $\mathcal{S}_z$, but with eigenvalue $-M_s\,\hbar$

$$\mathcal{S}_z \mathcal{P} D^e{}_k = -M_S \hbar \mathcal{P} D^e{}_k = -\mathcal{P}\mathcal{S}_z D^e{}_k \tag{2A}$$

and

$$\mathcal{S}_z \mathcal{P} + \mathcal{P}\mathcal{S}_z = 0$$

(2) The effect of the step operators can be described as follows:

$$\mathcal{S}^{\pm} D^e{}_k = \sum_{i=1}^{r/2} (\ldots\ \mathrm{s}_{\pm} k_i\ \ldots) = \sum_i c_i(\ldots(\mathrm{k}_i \mp 1)\ldots) \tag{3A}$$

In this equation, it is assumed that the standard order of the spin orbitals is used throughout: $\phi\alpha$ always immediately precedes $\phi\beta$ (where ϕ is an arbitrary space orbital of the set). The coefficient c_i is only different from zero if k_i corresponds to an unmatched α or β spin, that is, if either $\phi\ \alpha$ or $\phi\ \beta$ belongs to k, but not both; therefore, if the orbitals in $D^e{}_k$ are in standard order, so will the orbitals be in all the determinants of eq 3A.

$$\begin{aligned}\mathcal{P}\mathcal{S}^{\pm} D^e{}_k &= \sum_i c_i \mathcal{P}(k_1 \ldots (k_i \mp 1) \ldots k_n) \\ &= \sum_i c_i (-1)^{q_k+1}\ (k_{n+1} \ldots k_i \ldots k_r) \\ &= -\sum_i c_i (-1)^{q_k} (k_{n+1} \ldots k_i \ldots k_r)\end{aligned}$$

The latter determinants are all characterized by $(-M_S \mp 1)$. They differ from $\mathcal{P}D^e{}_k(M_S) = D^h{}_k(-M_S)$ only in sign and in one spin orbital; they all have k_i rather than $k_i \mp 1$ in $D^h{}_k$. Therefore

$$\begin{aligned}\mathcal{P}\mathcal{S}^{\pm} D^e{}_k &= -(-1)^{q_k} \sum_i c_i (k_{n+1} \ldots k_i \ldots k_r) \\ &= -(-1)^{q_k} \mathcal{S}^{\mp} (k_{n+1} \ldots k_i \mp 1 \ldots k_r) \\ &= -\mathcal{S}^{\mp} \mathcal{P} D^e{}_k \end{aligned} \tag{4A}$$

and

$$\mathcal{P}\mathcal{S}^{\pm} + \mathcal{S}^{\mp}\mathcal{P} = 0$$

(3) Since

$$\mathcal{S}^2 = \mathcal{S}_z{}^2 + {}^1\!/_2(\mathcal{S}^+\mathcal{S}^- + \mathcal{S}^-\mathcal{S}^+)$$

and

$$\begin{aligned}\mathcal{S}_z{}^2\mathcal{P} &= -\mathcal{S}_z\mathcal{P}\mathcal{S}_z = \mathcal{P}\mathcal{S}_z{}^2 \\ \mathcal{S}^+\mathcal{S}^-\mathcal{P} &= -\mathcal{S}^+\mathcal{P}\mathcal{S}^+ = \mathcal{P}\mathcal{S}^-\mathcal{S}^+ \\ \mathcal{S}^-\mathcal{S}^+\mathcal{P} &= -\mathcal{S}^-\mathcal{P}\mathcal{S}^- = \mathcal{P}\mathcal{S}^+\mathcal{S}^-\end{aligned}$$

one obtains

$$\mathcal{P}\mathcal{S}^2 - \mathcal{S}^2\mathcal{P} = 0 \tag{5A}$$

(4) If the labels Γ, M_Γ, and S are known, specification of M_S completes K and eq 5 and eq 8 can be rewritten as

$$\mathcal{P}\Psi^e(M_S) = \Psi^h(-M_S) \tag{6A}$$

$$\Psi^h(M_S) = p\Psi^e(M_S) \tag{7A}$$

where $p = \pm 1$. Applying $\mathcal{S}^{\mp}$ to eq 6A and using eq 4A, one obtains

$$\begin{aligned}\mathcal{S}^{\mp}\mathcal{P}\Psi^e(M_S) = \mathcal{S}^{\mp}\Psi^h(-M_S) = -\mathcal{P}\mathcal{S}^{\pm}\Psi^e(M_S) = \\ -\mathcal{P}\mathrm{N}\Psi^e(M_S \pm 1) = -N\Psi^h(-M_S \mp 1)\end{aligned}$$

where N is the positive constant appearing in the step operator. Clearly,

$$\mathcal{S}^{\mp}\Psi^h(-M_S) = -N\Psi^h(-M_S \mp 1)$$

Therefore, the step-operator constant is negative for the hole functions and positive for the electron functions. Since the number of steps between M_S and $-M_S$ is a number with the same parity as the number of steps between $M_S \pm 1$ and $-M_S \mp 1$, it follows from eq 7A that

$$\Psi^h(M_S \pm 1) = -p\Psi^e(M_S \pm 1)$$

Registry No. Cr^{3+}, 16065-83-1.

Structure of Glycolic Acid Determined by Microwave Spectroscopy

C. E. Blom and A. Bauder*

Contribution from the Laboratory for Physical Chemistry, Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland. *Received September 22, 1981*

Abstract: The microwave spectra of all singly substituted D, ^{13}C, and ^{18}O species and one doubly substituted species of glycolic acid ($CH_2OHCOOH$) have been measured and analyzed. From the moments of inertia of all species the complete molecular structure was determined. It shows an intramolecular hydrogen bond in which the hydroxyl group points toward the carbonyl oxygen of the carboxylic group with an O···H distance of 2.11 Å. The structure of the free molecule in the gas phase differs largely from the molecular structure in the crystal due to strong intermolecular hydrogen bonding in the solid state.

Introduction

Glycolic acid ($CH_2OHCOOH$) is the simplest member of the α-hydroxycarboxylic acid series, which is of considerable biological importance. Hydrogen bonding is crucial for the actual conformation of glycolic acid. In the solid state the conformation is dominated by two strong intermolecular hydrogen bonds to

0002-7863/82/1504-2993$01.25/0