Modification of the Jahn-Teller theorem: Temperature-dependent rhombic distortion of the $^2E_{1g}$ ground state of cobaltocene inferred from susceptibility and NMR measurements

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The Jahn-Teller theorem has been modified on the basis of statistical physics: The ensemble average of the molecular energy is supposed to be minimal with respect to distortions of the nuclear framework. The consequences of this formulation are discussed for the D_{5d}-coordinated cobaltocene having the degenerate electronic ground state $^2E_{1g}$. At low temperatures $T < 155$ K, the symmetrical structure is unstable, and the strength of the rhombic distortion depends on temperature. At moderate temperatures $T \geq 155$ K, however, the symmetrical configuration D_{5d} is stable. The three adjustable parameters of the theory were successfully fitted to susceptibility data reported in the literature.

I. INTRODUCTION

The Jahn-Teller theorem[1] can be formulated as follows: Symmetrical molecules with degenerate electronic states are unstable. Such molecules therefore take up a distorted shape in order to remove the degeneracy. The group-theoretical proof is guided by the assumption that the total energy of the electronic ground state is minimal with respect to distortions of the nuclear framework. The observation of this symmetry-reducing effect, however, particularly as revealed in electron paramagnetic resonance (EPR) studies, is restricted to low temperatures[2] $T < T_0$, where T_0 is a characteristic temperature of the molecular complex. For $T > T_0$, the EPR and NMR (Ref. 3) spectra exhibit the high symmetry of the degenerate ground state of the symmetrical molecule. In order to maintain the general nature of the Jahn-Teller theorem, it has been customary to describe the symmetrical high-temperature region by the concept of a dynamic Jahn-Teller effect, where vibronic couplings are taken into account. Although such an improved theory may account for many complex features of the experimental spectra, group-theoretical reasoning still expects the low Jahn-Teller symmetry to be reflected in the dynamic effects also.

The present paper shows that problems connected with the previous formulation of the Jahn-Teller theorem disappear, if the underlying physical assumption of the theorem is guided by statistical considerations. Again we investigate the conditions under which a polyatomic molecule can have a stable equilibrium configuration when its electronic ground state has orbital degeneracy. For physical reasons, however, we give an alternative interpretation of the minimal principle, namely, the average of the molecular energy at a given temperature must be minimized with respect to distortions of the nuclear framework. The interesting consequence of this formulation is the occurrence of a transition temperature T_0. In the range $T \geq T_0$, the symmetrical structure of the molecule is stable, in contrast to the Jahn-Teller theorem. At low temperatures $T < T_0$, the symmetrical structures are unstable, and the strength of the low symmetry splitting of the electronic ground state depends on temperature.

As an illustration we report here the temperature-dependent rhombic distortion $\kappa(T)$ of the D_{5d}-coordinated cobaltocene inferred from the $^2E_{1g}$ ground-state splitting. The three adjustable parameters of the theory were successfully fitted to the susceptibility data.[4]

II. ELECTRONIC GROUND STATE AND SUSCEPTIBILITY OF COBALTOCENE

The electronic structure of the $3d^7$ configuration of cobaltocene has been discussed in a previous paper[3] (we refer to this paper for definitions and notation): the fourfold degenerate spin multiplet ($S = \frac{1}{2}, M_L = \pm 1$) of the ground state is split by the spin-orbit interaction and lower-symmetry ligand fields into two Kramers doublets with eigenvalues $\pm D$,

$$|\pm, +D\rangle = \cos(\alpha/2)|\pm\tfrac{1}{2}, \pm 1\rangle + \sin(\alpha/2)|\pm\tfrac{1}{2}, \mp 1\rangle ,$$

$$\tag{1}$$

$$|\pm, -D\rangle = -\sin(\alpha/2)|\pm\tfrac{1}{2}, \pm 1\rangle + \cos(\alpha/2)|\pm\tfrac{1}{2}, \mp 1\rangle ,$$

where the energy splitting D and the angle α are given by the spin-orbit coupling constant λ and the rhombic perturbation strength κ,

$$D = \tfrac{1}{2}(\lambda^2 + \kappa^2)^{1/2} ,$$

$$\cos\alpha = \lambda/(2D) , \tag{1a}$$

$$\sin\alpha = \kappa/(2D) .$$

The magnetization of the molecule is induced by the interaction with the applied magnetic field

$$H_S = -\mu_B \mathbf{H}(k\mathbf{L} + g\mathbf{S}) , \tag{2}$$

where $g = 2.0023$, μ_B is the Bohr magneton, and k is the orbital reduction factor resulting from covalent delocalization of the d electrons. The evaluation of the temperature-dependent magnetization up to second-order

perturbation theory as outlined in Sec. 4 of Ref. 5 yields for the susceptibility of a random sample and $T > \mu_B H$

$$\langle X \rangle_{RS} = N\mu_B^2 \mu_{eff}^2 / 3T \tag{3}$$

and

$$\mu_{eff}^2 = A_1 + A_2 \tanh(D/T) + A_3(T/D)\tanh(D/T) . \tag{4}$$

T is the temperature $(1 \text{ cm}^{-1} \hat{=} 1.439 \text{ K})$, and the coefficients A_μ are given by

$$A_1 = (g/2)^2(1+2\sin^2\alpha) + k^2\cos^2\alpha ,$$

$$A_2 = -gk\cos\alpha , \tag{4a}$$

$$A_3 = 2(g/2)^2\cos^2\alpha + k^2\sin^2\alpha .$$

A least-squares fit of Eq. (4) to the experimental μ_{eff} data[4] for di-π-cyclopentadienylcobalt (Cp_2Co) allows to determine the three adjustable fine-structure parameters of the theory, yielding

$$k = 0.313 ,$$

$$\lambda = 59.2 \text{ cm}^{-1} , \tag{5}$$

$$\kappa = 82.8 \text{ cm}^{-1} .$$

This treatment reveals the standard method of the current literature for analyzing paramagnetic susceptibility data. It has been tacitly assumed that the adjustable fine-structure parameters do not depend on the temperature. This supposition was fully confirmed, so far, by the satisfactory agreement between experiment and theory as shown in Fig. 1. It may be noted that $\mu_{eff}(T > 150 \text{ K})$ becomes insensible to the precise value of κ, because at high
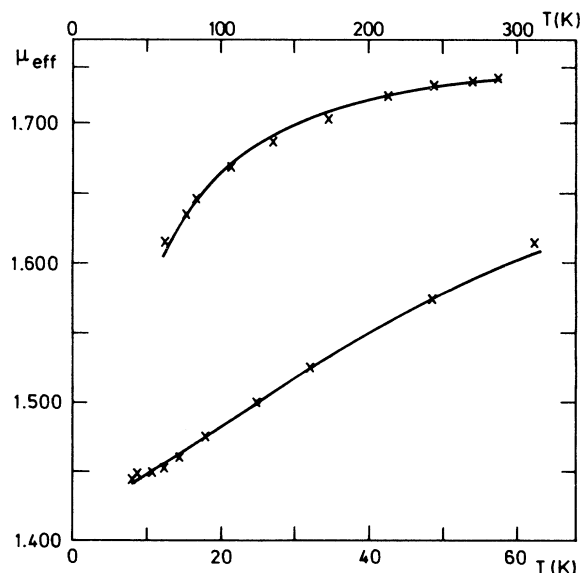

FIG. 1. Temperature dependence of the effective magnetic moment μ_{eff} for Cp_2Co between 7.91 and 289.0 K. The solid curve is calculated by means of Eqs. (4) and (5). The mean-least-squares displacement of the 19 experimental points (Ref. 4) from this standard fit, $f = 0.0033$, exceeds the limit of the experimental uncertainty ± 0.005 yielding $f_{expt} = 0.0030$.

temperatures μ_{eff} does not depend on κ and λ. According to Eq. (4), $\mu_{eff}(T \gg D) = (3.007 + k^2)^{1/2}$, where k is the orbital reduction factor. Quite recently, however, the analysis of the ^{13}C and ^{1}H NMR signal shifts of Cp_2Co yielded unambiguously the rhombic perturbation κ of cobaltocene to be exactly zero in the investigated temperature range 196–386 K.[3] Needless to say, Eq. (4) does not fit the experimental μ_{eff} data on setting $\kappa = 0$. This discrepancy will be resolved without additional parameters by the mechanism of a modified Jahn-Teller distortion, where the ensemble average of the molecular energy must be minimized.

III. TEMPERATURE DEPENDENCE OF THE RHOMBIC PERTURBATION

The orbitally degenerate spin multiplet of the Cp_2Co ground state $(S = \frac{1}{2}, M_L = \pm 1)$ transforms according to the direct product representation $^2E_{1g} = D^{1/2} \times E_{1g}$ where E_{1g} is the two-dimensional irreducible representation of the point group D_{5d}. Jahn and Teller[1] have shown that such symmetrical molecules with degenerate electronic states are unstable and take up a distorted shape. The proof of the theorem is based on the assumption that a molecule will tend to the state having the lowest possible energy. For physical reasons, however, we change the minimal principle as follows: The ensemble average of the molecular energy is minimal with respect to distortions of the nuclear framework.

In order to exhibit the consequences of this statistical formulation, we shall consider the rhombic $(\Delta M_L = 2)$ distortion of the $^2E_{1g}$ ground state of cobaltocene. The average energy of the split ground state of Eq. (1) with the proper statistical weights of the two Kramers doublets is given by $-D\tanh(D/T)$. On the other hand, the global energy minimum of those electrons which contribute to the bonding orbitals of the molecule is obtained for the symmetrical nuclear configuration $\kappa = 0$. We may then assume the symmetry energy expanded in a Taylor series of the rhombic perturbation κ which is a measure of the nuclear displacements from the equilibrium positions. There is no linear term since the first derivative of the symmetry energy must vanish in the equilibrium configuration. Thus the average energy appropriate to the rhombic distortion κ can be written as

$$E(\kappa) = -D\tanh(D/T) + E_s(\kappa/\lambda)^2 , \tag{6}$$

where D is the energy splitting of Eq. (1a) and E_s accounts for the symmetry energy of the electrons. The stable equilibrium configuration at a given temperature $\kappa(T, \lambda, E_s)$ is defined by the condition

$$E(\kappa) = \text{minimum} . \tag{6a}$$

The symmetry energy E_s takes now the place of κ as an adjustable parameter of the fitting procedure. Thus the improved fit of Eq. (4) to the experimental μ_{eff} data[4] minimizes simultaneously Eq. (6) with respect to the rhombic distortion $\kappa(T)$, yielding

$$k = 0.370 ,$$

$$\lambda = 63.6 \text{ cm}^{-1} , \tag{7}$$

$$E_s = 8.87 \text{ cm}^{-1} .$$

The corresponding rhombic distortion $\kappa(T)$, as obtained from Eqs. (6) and (6a), respectively, is shown in Fig. 2. It can be seen that (i) the rhombic perturbation $\kappa(T)$ becomes zero for $T > 155$ K in accordance with the results of the ^{13}C and ^1H NMR shift analysis[3] of Cp_2Co, where κ was found to be exactly zero between 196 and 386 K, and (ii) the agreement of the fit values of the orbital reduction factor k and the spin-orbit coupling constant λ with the Cp_2Co results of the NMR analysis given in Table II of Ref. 3 is rather good. The small deviations should be mainly due to the parameter correlations of the NMR data fit. (iii) The mean-least-squares displacement of the experimental μ_{eff} data[4] from the improved theory, $f = 0.0023$, compares favorably with the standard fit of Fig. 1, where f was found to be 0.0033. In view of the complex curvature of $\kappa(T)$, the precise fit is a surprising result implying that the energy balance of Eq. (6) describes the physical situation.

According to Eq. (6a), the rhombic distortion at zero temperature becomes

$$\kappa(T=0)=\lambda[(\lambda/4E_s)^2-1]^{1/2} . \qquad (8)$$

The distortion disappears at $T \geq T_0$, where the transition temperature is approximately given by

$$T_0 \cong \lambda[(\lambda/4E_s)^2-0.35]^{1/2} , \qquad (9)$$

and 1 cm$^{-1} \doteq 1.439$ K.

These results obtained for cobaltocene are supposed to be qualitatively the same for any symmetrical molecule, when the electronic ground state is degenerate for sym-
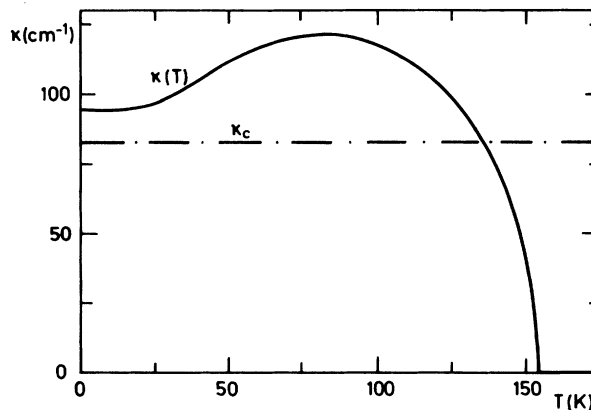

FIG. 2. Temperature dependence of the rhombic distortion $\kappa(T)$, defined in Eqs. (6) and (6a), respectively. The curve corresponds to the fit parameters of Eq. (7). The temperature-independent rhombic perturbation of Eq. (5), $\kappa_c = 82.8$ cm^{-1}, was obtained by the standard analysis of the susceptibility data.

metry reasons. In particular, at moderate temperatures $T > T_0$ symmetrical structures are generally stable.

ACKNOWLEDGMENTS

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