Theoret. Chim. Acta (Berl.) 33, 51—62 (1974)

# Jahn-Teller Instability and the Magnetic Circular Dichroism of a Tetragonal Molecular System

D. J. Robbins*

Inorganic Chemistry Laboratory, South Parks Road, Oxford

Received October 5, 1973

The consequences for the absorption and magnetic circular dichroism (m.c.d.) spectra of Jahn-Teller coupling in an $E$ orbital state of a molecule with $C_{4v}$ symmetry are investigated. The models used cover both static and dynamic Jahn-Teller interactions, the former allowing simple illustration of the interactions and their effects on the m.c.d. spectra. The moments of the spectra are discussed, as is the orbital reduction factor which is found to be oscillatory as a function of excitation energy in the presence of Jahn-Teller coupling.

*Key words:* Magnetic circular dichroism – Jahn-Teller

## 1. Introduction

During a recent investigation of the magnetic circular dichroism (m.c.d.) spectra of a series of tetragonal vanadyl complexes of general formula $(VOX_5)^{n-}$ we were prompted to consider the possible effects of a Jahn-Teller distortion of the lowest energy $^2E$ state on the m.c.d. spectrum [1]. It was first shown by Ham [2] that the expectation values of the Zeeman operator within a Jahn-Teller distorted state are dependent upon the degree of vibronic interaction, and it is this effect which makes the m.c.d. line-shape sensitive to the detailed molecular potential energy surfaces. On the other hand it has also been shown [3, 4] that the first moment of the m.c.d. spectrum taken over the whole vibrational envelope accompanying excitation of the distorted electronic state represents a parameter which is independent of any vibronic interactions within that excited state.

In tetragonal molecular systems it is certain non-degenerate vibrational modes which can produce Jahn-Teller instability in an $E$ orbital state, and the relative simplicity of this "one-dimensional" vibronic problem has led to several theoretical treatments of tetragonal systems in the literature [5–7]. In particular Ballhausen [7] has demonstrated the way in which the profile of the absorption band envelope associated with electronic excitation of a distorted $E$ state is affected by the inter-play between the Jahn-Teller and spin-orbit coupling operators. Here we extend this treatment to the m.c.d. spectra of tetragonal molecular systems.

The molecular species $(VOX_5)^{n-}$ with point group symmetry $C_{4v}$ has the following normal modes of vibration [7, 8]: $4a_1 + 2b_1 + b_2 + 4e$. The symmetric direct product $[E \times E]$ reduces to $A_1 + B_1 + B_2$, so that only the $b_1$ and $b_2$ modes

---

* Present address: Royal Radar Establishment, St. Andrews Road, Gt. Malvern, Worcs.

can be Jahn-Teller active. In order to simplify the problem we follow Ballhausen [7] and treat in detail only one active $b_1$ mode, since then the matrix elements of the vibronic interaction operator are diagonal in the real electronic basis set $(E_x, E_y)$. We have adopted this simplified model firstly because it represents a natural extension of Ballhausen's treatment of the corresponding absorption spectra, and secondly because it allows a simple pictorial illustration of the consequences of vibronic instability on the Zeeman splittings and on the selection rules for absorption of circularly polarised light which we believe is helpful in revealing the essential physical situation. Although this approximation does not allow quantitative calculations for the vanadyl ion it is sufficient to illustrate the principal effects of Jahn-Teller interaction on the m.c.d. spectrum, and it could be later generalised to include other active modes.

Here we also note a recent paper [9] treating the effects of Jahn-Teller coupling on the m.c.d. spectra of molecules with three- and six-fold symmetry axes, in which case the active modes are doubly degenerate. This calculation predicts that the orbital reduction factors for the vibronic excited states are oscillatory as a function of excitation energy, and it is clearly of interest to compare this situation with that occurring in molecules with a four-fold symmetry axis.

We shall therefore present our results in two sections. The first illustrates for a few particular vibronic states the way in which the Zeeman splittings and the circularly polarised selection rules are affected by a static Jahn-Teller distortion of the $^2E$ state, and the second reports the numerical solution of the dynamic Jahn-Teller problem with the aim of predicting the vibronic profile and the moments of the $^2E$ band in the m.c.d. spectrum.

## 2. The One-Dimensional Static Jahn-Teller Problem

If we consider only a single active $b_1$ vibrational mode, then in the absence of a Jahn-Teller interaction, spin-orbit coupling and an external magnetic field the energy of $^2E$ state is given in the harmonic oscillator approximation by:

$$E_0 = W_e + W_N \tag{1}$$

where $W_e$ is the electronic energy of the doubly degenerate state for fixed $C_{4v}$ symmetry

$$W_N = \frac{P_N^2}{2\mu} + \frac{\mu\omega^2}{2} \cdot Q^2 , \tag{2}$$

i.e. $W_N$ is the energy of a harmonic oscillator with angular frequency $\omega$, momentum $P_N$ and reduced mass $\mu$ and $Q$ is the normal co-ordinate of the $b_1$ vibration.

The Jahn-Teller interaction may then be included using standard vibronic theory [7, 10], retaining only terms linear in $Q$. In the limit that the interaction energy is much larger than the nuclear kinetic energy it is permissible to solve first for the electronic energy and then for the vibrational energies. This approximation, which represents a static Jahn-Teller distortion, is analogous to the Born-Oppenheimer approximation for non-degenerate states. The energy of the

$^2E$ state then contains a term linear in $Q$:

$$\begin{aligned} E &= E_0 + Kh(ii)Q \\ &= W_e + \frac{P_N^2}{2\mu} + \frac{\mu\omega^2}{2}\left[Q + \frac{Kh(ii)}{\mu\omega^2}\right]^2 - \frac{K^2h(ii)^2}{2\mu\omega^2} \end{aligned} \tag{3}$$

where

$$K = \langle E_i | (dH_e/dQ)_0 | E_i \rangle \, (i = x, y)$$

$$h(ii) = +1 \quad \text{or} \quad -1 \quad \text{as} \quad i = x \quad \text{or} \quad y$$

and $H_e$ is an electronic Hamiltonian excluding the nuclear momentum operator [10].

Equation (3) shows that after inclusion of the Jahn-Teller interaction the eigenfunctions are those of harmonic oscillators with minima at $Q = \frac{-Kh(ii)}{\mu\omega^2}$ and with energy minima $\left(W_e - \frac{K^2h(ii)^2}{2\mu\omega^2}\right)$. They remain simple products of electronic and nuclear functions, and hence represent the least complicated form of Jahn-Teller interaction. The potential surfaces associated with the electronic functions $|E_x\rangle[h(ii) = 1]$ and $|E_y\rangle[h(ii) = -1]$ are shown diagramatically in Fig. 1a, where it is assumed that the ground state has the same potential surface as the undistorted excited state.

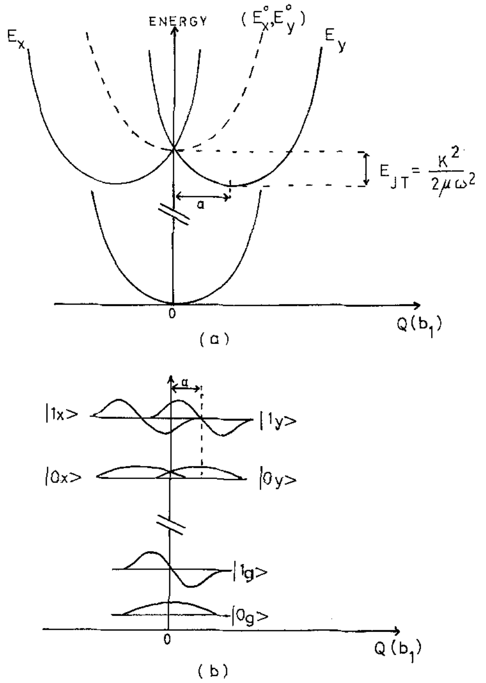

Fig. 1. a Potential energy curves for the active $b_1$ vibration, shown for the $^2B_2$ ground state and for both the distorted and undistorted configurations of the $^2E$ excited state. b Some vibrational wavefunctions for the ground state and distorted configurations of the excited state

It can than be shown that the Jahn-Teller interaction profoundly affects the polarisations of transitions to the various vibrational levels of the excited state. If the vibrational wavefunctions of quantum number $n$ associated with the ground electronic state and with the electronic functions $|E_x\rangle$, $|E_y\rangle$ are written as $|n_g\rangle$, $|n_x\rangle$, $|n_y\rangle$ respectively we have [11]:

$$\begin{aligned}
|0_g\rangle &= N\exp\left[-\frac{\alpha}{2}Q^2\right]\\
|0_x\rangle &= N\exp\left[-\frac{\alpha}{2}(Q-a)^2\right]\\
|0_y\rangle &= N\exp\left[-\frac{\alpha}{2}(Q+a)^2\right]\\
|1_x\rangle &= N\exp\left[-\frac{\alpha}{2}(Q-a)^2\right]\sqrt{2\alpha}(Q-a)\\
|1_y\rangle &= N\exp\left[-\frac{\alpha}{2}(Q+a)^2\right]\sqrt{2\alpha}(Q+a)
\end{aligned}\tag{4}$$

where

$$\begin{aligned}
N &= (\alpha/\pi)^{1/4},\\
\alpha &= 4\pi^2\mu\omega/\hbar,\\
a &= K/\mu\omega^2.
\end{aligned}$$

The following overlap integrals are then easily calculated:

$$\underline{\langle 0_g|0_y\rangle = \exp\left[-\frac{\alpha a^2}{4}\right]},\tag{5}$$

$$\underline{\langle 0_g|1_y\rangle = a\cdot\left(\frac{\alpha}{2}\right)^{\frac{1}{2}}\exp\left[-\frac{\alpha a^2}{4}\right]},\tag{6}$$

and hence

but

$$\begin{aligned}
\langle 0_g|0_y\rangle &= \langle 0_g|0_x\rangle,\\
\langle 0_g|1_y\rangle &= -\langle 0_g|1_x\rangle.
\end{aligned}\tag{7}$$

This result is also seen to follow from the symmetry of Fig. 1b, which gives the form of relevant vibrational wavefunctions.

It is possible to construct linear combinations of the excited state functions to which transitions are allowed via the absorption of circularly polarised light. These are:

$$|E_{\pm1}(n)\rangle = \frac{1}{\sqrt{2}}|\mp iE_x(n_x) + E_y(n_y)\rangle \tag{8}$$

where

$$|E_x(n_x)\rangle = |E_x\rangle|n_x\rangle \quad \text{etc.}$$

The non-zero electric dipole transition moment integrals from the lowest vibrational level of the ground state to the zeroth and first vibrational levels of the excited state are then given by:

$$\begin{aligned}\langle B_2(0)|m_{\pm 1}|E_{\pm 1}(0)\rangle &= \mp\frac{iM}{2\sqrt{2}}(\langle 0_g|0_x\rangle + \langle 0_g|0_y\rangle)\\ \langle B_2(0)|m_{\mp 1}|E_{\pm 1}(1)\rangle &= \pm\frac{iM}{2\sqrt{2}}(\langle 0_g|1_x\rangle - \langle 0_g|1_y\rangle)\end{aligned} \tag{9}$$

where the upper or lower signs are taken throughout the equations, $m_{+1}$ and $m_{-1}$ refer to r.c.p. and l.c.p. light and $M$ is the reduced matrix element $\langle B_2\|m\|E\rangle$ [12]. A similar consideration of higher vibrational levels of the ground state gives the general result that the polarisations of transitions to the states $|E_{\pm 1}(n)\rangle$ depend upon the vibrational quantum numbers of both the initial and final states.

However, the ordering of excited state Zeeman components in the presence of a magnetic field also depends upon the vibrational level involved. For example:

$$\langle E_{\pm 1}(n)|L_Z|E_{\pm 1}(n)\rangle = \pm i\langle E_x|L_Z|E_y\rangle\langle n_x|n_y\rangle \tag{10}$$

and although the overlap integral $\langle 0_x|0_y\rangle$ is always positive this is not the case for higher vibrational levels. The sign of the integral $\langle n_x|n_y\rangle$ will in general be a function of the parameter $a$, and this effect in the one-dimensional static Jahn-Teller problem represents the quantum mechanical origin of the oscillatory nature of the orbital reduction factor noted earlier. For a given value of $a$, the integral can change in sign as a function of the quantum number $n$.

The dependence of the matrix elements of an electronic operator on the vibrational overlap integrals has been emphasised by Ham [2], and its effect is seen to be four-fold:

1. to reduce the magnitude of diagonal angular momentum matrix elements, i.e. to reduce m.c.d. $A$ terms [13];
2. to affect the sign of the orbital reduction factor;
3. to introduce the possibility of second-order interactions between different vibrational levels since the vibrational functions associated with the electronic functions $|E_x\rangle$ and $|E_y\rangle$ are no longer orthogonal, i.e. to introduce intra-term $B$ terms in m.c.d. [13];
4. to govern the selection rules for absorption of circularly polarised light.

The relative ordering of the Zeeman components and their respective polarisations decide the sign of an $A$ term. The above discussion makes it clear that the signs of $A$ terms associated with particular vibrational components of a progression arising from a Jahn-Teller active mode need not all be the same, and that the observation of such alternation of sign in a progression would constitute proof of Jahn-Teller instability in the excited state. Unfortunately an attempt to observe this phenomenon in the $4K$ spectrum of $VOCl_5^{3-}$ was unsuccessful [1].

## 3. The One-Dimensional Dynamic Jahn-Teller Problem

In order to calculate the dispersion of absorption and m.c.d. spectra in the general case in which the Jahn-Teller and nuclear kinetic energies may be comparable our method is to include all relevant terms in the molecular Hamiltonian which is then diagonalised in the undistorted $^2E$ basis set [9]. This procedure will give the m.c.d. profile without distinguishing between $A$ and $B$ terms, although since the magnetic field energies are so small compared with other terms in the Hamiltonian it would be perfectly valid to introduce the Zeeman operator as a perturbation of the vibronic states in the dynamically distoring molecular system, and hence to evaluate the $A$ and "intra-term" $B$ terms explicitly [14].

The complete Hamiltonian for the species ($VOX_5$) in the presence of a magnetic field may be given as:

$$H = H_e + H_N + H_{\mathrm{J.T.}} + H_{\mathrm{S.O.}} + H_M \tag{11}$$

where $H_e$ = the electronic Hamiltonian for fixed $C_{4v}$ symmetry,
$H_N$ = the harmonic oscillator Hamiltonian,
$H_{\mathrm{J.T.}} = \left(\frac{dH_e}{dQ}\right)_0 \cdot Q$ since only the mode $Q$ is vibronically active,
$H_{\mathrm{S.O.}} = \Sigma\,\zeta(r)\mathbf{1}\cdot \mathbf{s}$
$= 1_z s_z$ in a one-electron system having tetragonal symmetry,
$H_M = +\beta(1_z + 2s_z)H_Z$ in a one-electron tetragonal system and $H_Z$ is the $Z$-component of the magnetic field, applied along the four-fold molecular axis.

As the most convenient basis set for the doubly degenerate state $^2E$ we use the kets:

$$|E^0_{\pm 1}, s, n\rangle = \frac{1}{\sqrt{2}}\left| \mp iE^0_x + E^0_y\rangle |s\rangle |n\rangle$$

where the superscript $^0$ indicates the undistorted configuration $Q^0 = 0$
$|n\rangle$ is a harmonic oscillator function of quantum number $n$, and
$|s\rangle$ represents either $\alpha$ or $\beta$ spin.

By using this basis set we neglect any small interaction between the $^2E$ term and other terms induced by the magnetic field, spin-orbit coupling, or vibronic interaction operators.

The non-zero matrix elements of $H_{\mathrm{J.T.}}$ are given by [7, 11]:

$$\begin{aligned}\langle E^0_{+1}, \alpha, n|H_{\mathrm{J.T.}}|E_{-1}, \beta, m\rangle &= \left\langle E^0_{+1}\left|\frac{dH_e}{dQ}\right|E^0_{-1}\right\rangle \langle n|Q|m\rangle \delta_{\alpha\beta}\\ &= -Km^{\frac{1}{2}}\left(\frac{\hbar\omega}{2\mu\omega^2}\right)^{\frac{1}{2}}\delta_{m(n+1)}\delta_{\alpha\beta} \quad (\text{if } m > n) \qquad (12)\\ &= m^{\frac{1}{2}}\Delta\,\delta_{m(n+1)}\delta_{\alpha\beta}\,,\end{aligned}$$

where $K, \omega, \mu$ are defined in Eqs. (2) and (3). The complex conjugate matrix element to (12) is also non-zero.

The parameter $E_{\mathrm{J.T.}}$ in Fig. 1 is then given by:

$$E_{\mathrm{J.T.}} = \frac{K^2}{2\mu\omega^2} = \frac{\Delta^2}{\hbar\omega}\,. \tag{13}$$

Other necessary matrix elements are diagonal in the basis set and easily calculated in terms of the spin-orbit coupling constant and the magnetic field strength $H_Z$.

Because of the nature of Eq. (12) and the fact that the total Hamiltonian is diagonal in spin co-ordinates the secular matrix factorises to give four submatrices which can be diagonalised by computer. The vibronic eigenfunctions are obtained as linear combinations of the undistorted basis functions:

$$|E_i, s\rangle = \sum_n \left[C_{ni}^{+} |E_{+1}^{0}, s, n\rangle + C_{ni}^{-} |E_{-1}^{0}, s, n\rangle\right] \tag{14}$$

where $s = \alpha$ or $\beta$ throughout.

The non-degenerate ground electronic state is assumed to have the same potential surface as the functions $|E_x^0\rangle$, $|E_y^0\rangle$ with the result that electric dipole transitions are only allowed between ground and undistorted excited states having the same vibrational quantum number. Thus the intensity and polarisation of a transition from the $r^{\text{th}}$ vibrational level of the ground state to the $i^{\text{th}}$ excited state is given by the square of the coefficients $C_{ri}^{+}$ and $C_{ri}^{-}$ in equation (14), and it is then a simple matter to calculate the dispersion of m.c.d. In order to check the convergence of this calculation matrices of dimension (20 × 20) and (30 × 30) were diagonalised; with the highest value of the parameter $\Delta$ used there was no appreciable difference in the results.

The effect of vibronic coupling on the dispersion and polarisation of transitions is demonstrated by Fig. 2, in which a vibrational energy of 300 cm$^{-1}$ for

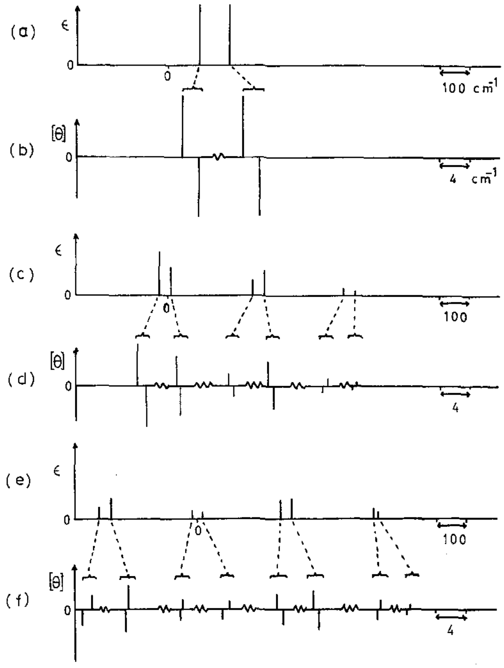

Fig. 2a–f. Schematic representation of the effect of dynamic Jahn-Teller instability in the $^2E$ state on the vibrational fine structure of absorption and m.c.d. spectra. Pairs of Zeeman components are bracketed, $\Delta$ is the Jahn-Teller parameter defined in the text. a absorption spectrum, $\Delta = 0$; b m.c.d. spectrum, $\Delta = 0$; c absorption spectrum, $\Delta = 213$ cm$^{-1}$; d m.c.d. spectrum, $\Delta = 213$ cm$^{-1}$, transitions from zeroth ground state vibrational level; e absorption spectrum, $\Delta = 213$ cm$^{-1}$; f m.c.d. spectrum $\Delta = 213$ cm$^{-1}$, transition from first excited vibrational level of ground state

the active $b_1$ mode, a value of 100 $\mathrm{cm}^{-1}$ for $\zeta$ and a Zeeman splitting of 2 $\mathrm{cm}^{-1}$ in the $^2B_2$ ground state have been assumed. In order to emphasise the effects of the Jahn-Teller interaction on the Zeeman splittings of the excited state when drawing Fig. 2 we have neglected any population difference between the Zeeman components of each ground state vibrational level; i.e. we have assumed a sufficiently high temperature that $C$-terms [13] are unimportant in the spectra. Such temperature dependent effects will be discussed below. The diagrams representing each absorption "spectrum" are drawn to scale, but in the corresponding m.c.d. "spectrum" immediately below the energy scale has been expanded in order to illustrate the Zeeman splitting. Figures 2a, b and 2c, d show the dispersion of the absorption and m.c.d. for transitions from the lowest vibrational level of the ground state when the Jahn-Teller parameter $\Delta$ has the value 0 and 213 $\mathrm{cm}^{-1}$ respectively. Figures 2e and 2f show the dispersion of absorption and m.c.d. when $\Delta = 213\ \mathrm{cm}^{-1}$, but in this case for transitions from the first excited vibrational level of the ground state i.e. for vibrational hot bands.

This diagram serves to emphasise the earlier point that the form of the m.c.d. spectrum depends in complicated fashion on the initial and final vibrational states. However the ordinate scales are too small to demonstrate that there is asymmetry in the intensities of a pair of Zeeman components which results from the presence of $A$ terms (symmetrical in intensity) and intra-term $B$ terms (unsymmetrical in intensity). If the spectral lines are broad compared with the Zeeman splitting the m.c.d. spectrum may be dominated by $B$-terms, and these may be

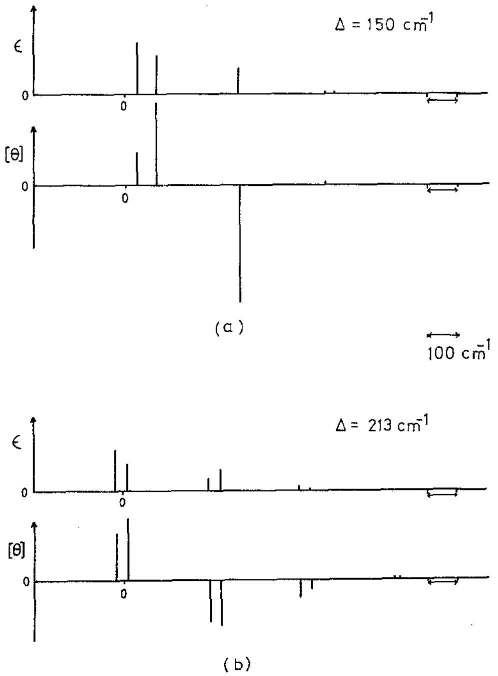

Fig. 3a and b. Absorption spectra and $B$-term dispersion in m.c.d. at $T = OK$ in the presence of Jahn-Teller interaction. a $\Delta = 150\ \mathrm{cm}^{-1}$; b $\Delta = 213\ \mathrm{cm}^{-1}$

calculated from the eigenfunctions (14) as the difference in intensity of any pair of Zeeman components. The $B$-term dispersion is also sensitive to the degree of vibronic interaction, as shown in Fig. 3 for the cases $\Delta = 150\,\mathrm{cm}^{-1}$ and $213\,\mathrm{cm}^{-1}$. Here the Zeeman splitting has been neglected, and the dichroism scale $[\theta]_M$ is arbitrarily expanded in relation to Fig. 2.

Hence when the vibronic transitions are broadened by rotational and librational motion the actual form of the m.c.d. dispersion for each Zeeman pair will depend upon the relative magnitudes of Zeeman splitting and bandwidth. It should also be noted that a relatively short progression in the Jahn-Teller mode of the kind shown in Fig. 2 could be built on successive members of a longer progression in a higher energy totally symmetric mode, leading to a more complex vibrational envelope in which progressions overlap. In fact such a situation has recently been shown to occur in the $^1T_2(t_1^5 e)$ excited state of the permanganate ion [14].

The dispersion of m.c.d. shown in Fig. 2 is best understood by consideration of the vibronic selection rules for the transitions. For a non-degenerate $b_1$ mode the symmetries of the vibrational wavefunctions are respectively $a_1$ and $b_1$, for even and odd numbers of vibrational quanta. Hence the vibronic symmetries are:

1) for the $E$ excited state

$$E^0_{\pm1} \times a_1 \rightarrow e_{\pm1} \qquad (n \text{ even}),$$
$$E^0_{\pm1} \times b_1 \rightarrow e_{\mp1} \qquad (n \text{ odd}).$$

2) for the $B_2$ ground state

$$B^0_2 \times a_1 \rightarrow b_2 \qquad (n \text{ even}),$$
$$B^0_2 \times b_1 \rightarrow a_2 \qquad (n \text{ odd}).$$

The optical selection rules are then:

$$\langle b_2 | m_{\pm1} | e_{\pm1} \rangle = \mp \frac{iM'}{\sqrt{2}}$$
$$\langle a_2 | m_{\pm1} | e_{\mp1} \rangle = \pm \frac{iM''}{\sqrt{2}}$$

where $M'$, $M''$ are reduced matrix elements.

These selection rules explain the opposite $A$-terms dispersion observed for the cold and hot bands in Fig. 2d and 2f associated with transitions to any Zeeman pair of the excited vibronic states.

If the effective orbital $g$-value of the $i^{\text{th}}$ vibronic state is now defined, including sign, by $2\langle e^i_{+1} | L_z | e^i_{+1} \rangle$, the orbital reduction factor $k_i$ is defined as the ratio of this $g$-value to that predicted in the absence of Jahn-Teller coupling. The latter is given by $(-1)^i \cdot 2 \cdot \langle E^0_{+1} | L_z | E^0_{+1} \rangle$. Using our calculated Zeeman splittings the orbital reduction factor is shown as a function of excitation energy in Fig. 4 for one of the Kramers doublets arising from the $^2E$ state, and for two values of the Jahn-Teller parameter $\Delta$. Almost identical results are obtained for the second

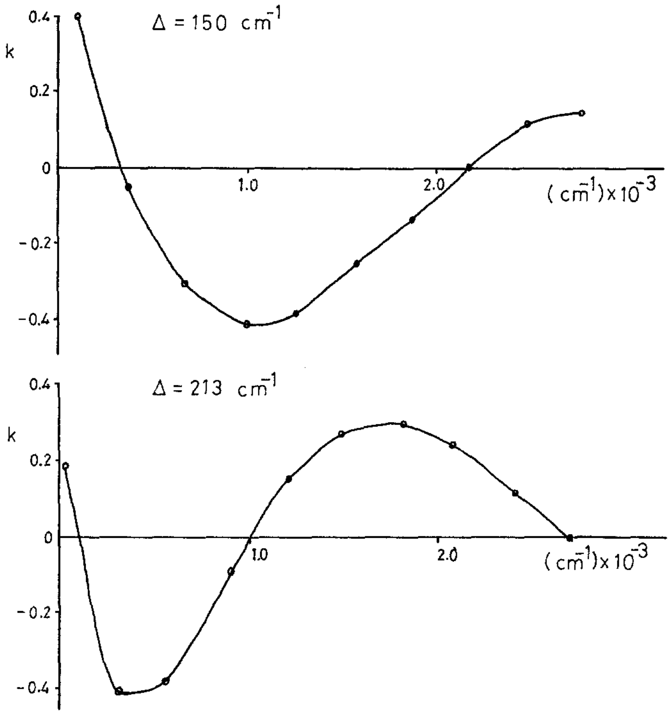

Fig. 4a and b. Orbital reduction factor $k$ as a function of excitation energy in the presence of Jahn-Teller interaction. a $\Delta = 150\,\mathrm{cm}^{-1}$; b $\Delta = 213\,\mathrm{cm}^{-1}$

Kramers doublet. As can be seen from Fig. 4, the orbital reduction factor is oscillatory as a function of excitation energy, as found by Washimiya for trigonal molecular systems [9]. The period of oscillation is similarly found to be approximately proportional to $1/\Delta$.

Finally it was pointed out above that even when fine structure is absent from an experimental spectrum it may still be possible to study vibronic interactions by measurement of the moments of the band envelopes [3, 4]. The first moments of both absorption and m.c.d. are independent of any vibronic interaction in the excited state, but while the second moment of absorption does contain information about such interaction the fact that m.c.d. reflects the difference in absorption of right and left circularly polarised light means that only the third and higher moments are functions of electron lattice coupling.

As illustration the moments of our simulated m.c.d. spectrum may be evaluated as a function of the Jahn-Teller parameter $\Delta$ using the eigenfunctions obtained above. Moments higher than the first are calculated about the mean absorption frequency. Temperature-dependent effects are easily introduced since the $^2B_2$ electronic ground state is orbitally non-degenerate and each ground state vibrational level may be treated independently. Each pair of Zeeman components arising from spin-degeneracy of the single $d$-electron is simply weighted according to the Boltzmann distribution, introducing spin-dependent $C$-terms into the model and making the moments temperature-dependent.

The zeroth, first and second moments of m.c.d. calculated from this model are, as expected, independent of the Jahn-Teller parameter $\Delta$. The zeroth and second moments are identically zero, and the temperature dependence of the first moment is shown in Fig. 5 to be the same for various values of $\Delta$. However the third moment of m.c.d. is not independent of the vibronic coupling, and in fact for any value of $\Delta$ it is a function of the ground state vibrational level from which the transition occurs. Assuming that only the lowest and first excited vibrational levels of the ground state are populated and weighted according to the Boltzmann distribution, and a vibrational frequency of 300 cm$^{-1}$, the temperature dependence of the third moment is shown in Fig. 5 for various values of the parameter $\Delta$. It is evident that the Jahn-Teller interaction has two major effects on such a plot:

1. at low temperature the plot is linear, but with a slope depending upon the strength of the vibronic coupling;

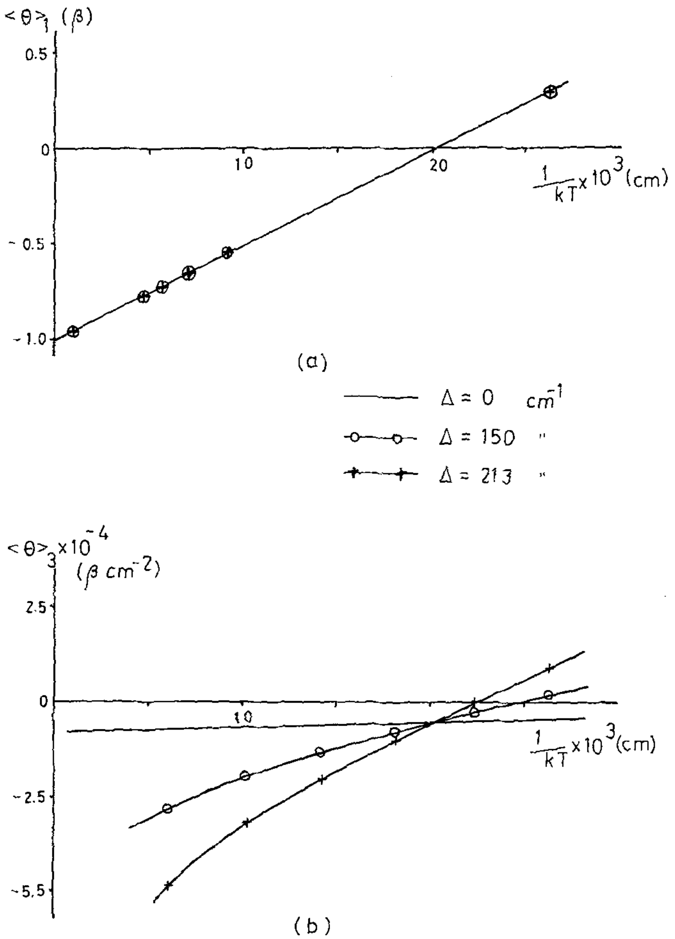

Fig. 5. Temperature dependence of first (a) and third (b) moments of m.c.d. in the presence of Jahn-Teller interaction. $\zeta = 100$ cm$^{-1}$. M.c.d. moments are divided by the total dipole strength

2. at higher temperatures the plot becomes non-linear as the first excited vibrational level of the ground state is populated and hot bands appear in the spectrum.

In the absence of vibronic coupling, the plot should remain linear with temperature.

The third moment derived experimentally will be rather sensitive to the "wings" of the m.c.d. band. However in favourable cases it may be possible to determine whether the temperature dependence departs from linearity at higher temperatures and hence to study the Jahn-Teller interaction in the absence of resolved fine structure.

*Acknowledgements.* This work was largely carried out at the University of East Anglia. The author is grateful to both Dr. A. J. Thomson, who originally suggested the project, and Dr. P. A. Cox for helpful discussions, and to S.R.C. for support in the form of a studentship and subsequent fellowship.

## References

1. Robbins, D. J., Stillman, M. J., Thomson, A. J.: To be published
2. Ham, F. S.: Phys. Rev. A **138**, 1727 (1965)
3. Henry, C. H., Schnatterly, S. E., Slichter, C. P.: Phys. Rev. A **137**, 583 (1965)
4. Stephens, P. J.: J. Chem. Phys. **52**, 3489 (1970)
5. Child, M. S.: Mol. Phys. **3**, 601 (1960)
6. Hougen, J. T.: J. Mol. Spectry. **13**, 149 (1964)
7. Ballhausen, C. J.: Theoret. Chim. Acta (Berl.) **3**, 368 (1965)
8. Nakamoto, K.: Infrared spectra of inorganic and co-ordination compounds. Wiley & Sons Inc. (1970)
9. Washimiya, S.: Phys. Rev. Letters **28**, 556 (1972)
10. Longuet-Higgins, H. C.: Advan. Spectry. **2**, 429 (1961)
11. Pauling, L., Wilson, E.: Introduction to quantum mechanics. McGraw-Hill Book Co. (1935)
12. Griffith, J. S.: The irreducible tensor method for molecular symmetry groups. Prentice Hall Inc. (1962)
13. Schatz, P. N., McCaffery, A. J.: Quart. Rev. **23**, 552 (1969)
14. Cox, P. A., Robbins, D. J., Day, P., Denning, R. G.: To be published

Dr. D. J. Robbins
Royal Radar Establishment
St. Andrews Road
Gt. Malvern
Worcs., England