range of solvent effects and demonstrate that π back-bonding from ruthenium(II) can indeed increase electron density at remote ligand sites. The protonated species, as well as the Co(III) and Rh(III) complexes, manifest significant charge withdrawal. The γ-carbon resonances are much larger than solvent effects and indicate electron density depletion in the order $H^+ >$ Co(III) $>$ Rh(III) and increase with Ru(II) $>$ Fe(II).

The effect of substituents indicates that the extent of charge delocalization by π back-bonding is greatest for the ligand which is most depleted in electron density. Thus, one expects that *N*-methylpyrazinium and the pyrazinium ion would be more stabilized than pyrazine by the π back-bonding of pentaammineruthenium(II), as found by Malin et al. for the corresponding pentacyanoferrate(II) complexes,[4] supporting an earlier conclusion[2] that the most important factor in causing the increased basicity of pyrazine when it is complexed to Ru(II) is the stabilization of the protonated pyrazine by the ruthenium center.

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Structural–Vibrational Effects in Magnetic Circular Dichroism Spectra[2]

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Abstract: The magnetic circular dichroic intensity of a locally symmetry forbidden transition generated by structural (static) perturbations, vibrational perturbations, and their interactions, is investigated. It is shown that through second order the contributions of such static and vibrational perturbations are additive. The lowest order effects of static–vibrational interactions are first order in the static and second order in the vibrational perturbations.

It is well established that the magnetic circular dichroism (MCD) associated with an electronic transition which is locally symmetry forbidden is sensitive to the molecular environment of the chromophore involved. It is thus potentially possible to obtain information of stereochemical and spectroscopic interest about such systems from MCD data. Studies of this type have been made, for example, on saturated ketones[3-7] and nitroalkanes.[8]

A theorem[9] which is central to the development of some methods of analysis of MCD spectra of forbidden transitions may be stated as follows: The MCD associated with an electric-dipole symmetry-forbidden transition is of second or higher order in the vibrational and structural perturbations through which the transition gains intensity. Also for such transitions, through second order, the contributions to the MCD which arise from perturbations belonging to different irreducible representations of the chromophoric point group are additive.

Although applications of the above theorem to the analysis of MCD data are in principle straightforward, serious practical difficulties are frequently encountered. These difficulties arise from the fact that vibrational and structural (static) perturbations contribute on an equal footing to the MCD. Attempts to separate the effects of the two types of perturbation, and to describe their interactions, have until now been made by applying qualitative physical arguments to the processes involved in the induction of MCD intensity. While this approach has had some success, we found during the course of some recent work[10] on the MCD of saturated ketones that an extension of the analytical protocol was required. It is the purpose of the present paper to consider further the interactions of static and vibrational perturbations and to lay the theoretical groundwork for the analyses which are presented in the following paper.[10]

Theory

The fundamental theoretical quantity which describes the MCD associated with a nondegenerate[11] vibronic transition $|Aa\rangle \rightarrow |Jj\rangle$ is the magneto-optical B term. This quantity is given by[12,13]

$$B(\mathrm{A}a \rightarrow \mathrm{J}j) = \mathrm{Im}\Bigg\{ \sum_{\mathrm{K}k \neq \mathrm{Aa}} (E_{\mathrm{K}k} - E_{\mathrm{A}a})^{-1} \langle \mathrm{K}k | \boldsymbol{\mu} | \mathrm{A}a \rangle \cdot [\langle \mathrm{A}a | \mathbf{m} | \mathrm{J}j \rangle X \langle \mathrm{J}j | \mathbf{m} | \mathrm{K}k \rangle] + \sum_{\mathrm{K}k \neq \mathrm{J}j} (E_{\mathrm{K}k} - E_{\mathrm{J}j})^{-1} \langle \mathrm{J}j | \boldsymbol{\mu} | \mathrm{K}k \rangle \cdot [\langle \mathrm{A}a | \mathbf{m} | \mathrm{J}j \rangle X \langle \mathrm{K}k | \mathbf{m} | \mathrm{A}a \rangle] \Bigg\} \quad (1)$$

where **m** and μ are the electric and magnetic dipole moment operators, respectively. If we ignore hot bands, the B value associated with the entire vibrational envelope of the electronic transition A → J is obtained by summing eq 1 over the vibrational levels of the upper state:

$$B(\mathrm{A} \rightarrow \mathrm{J}) = \sum_j B(\mathrm{A}0 \rightarrow \mathrm{J}j) \quad (2)$$

where $|\mathrm{A}0\rangle$ is the ground vibronic state.

Since we are interested here only in the *symmetry properties* of $B(\mathrm{A} \rightarrow \mathrm{J})$, a considerable simplification of the expressions which follow is possible if we use the fact that these symmetry properties are the same as those of the corresponding dipole strength $D(\mathrm{A} \rightarrow \mathrm{J})$.[9] Thus we may deal with the less complex quantities

$$D(\mathrm{A} \rightarrow \mathrm{J}) = \sum_j D(\mathrm{A}0 \rightarrow \mathrm{J}j) \quad (3)$$

where

$$D(\mathrm{A}a \rightarrow \mathrm{J}j) = \langle \mathrm{A}a | \mathbf{m} | \mathrm{J}j \rangle \cdot \langle \mathrm{J}j | \mathbf{m} | \mathrm{A}a \rangle \quad (4)$$

If we apply the Born-Oppenheimer adiabatic approximation to the vibronic wave functions, we may write them as products of electronic and vibrational parts. That is,

$$|\mathrm{A}a\rangle = |\mathrm{A}(q,R)\rangle |a(R)\rangle \quad (5)$$

and

$$|\mathrm{J}j\rangle = |\mathrm{J}(q,R)\rangle |j(R)\rangle \quad (6)$$

where the electronic and nuclear coordinates are denoted by q and R, respectively. The vibrational functions $|a\rangle$ and $|j\rangle$ are products of harmonic oscillator wave functions. We proceed in the usual manner[14] and write the molecular electronic Hamiltonian, in the absence of any static perturbations, as

$$H_e(q,Q) = H^{(0)}(q,Q_0) + \sum_r H_r^{(1)} Q_r + \sum_{r,s} H_{rs}^{(2)} Q_r Q_s + \ldots \quad (7)$$

where the $\{Q_r\}$ are the vibrational normal coordinates, and where

$$H_r^{(1)} = (\partial H_e / \partial Q_r)_0 \quad (8)$$

and

$$H_{rs}^{(2)} = \tfrac{1}{2}(\partial^2 H_e / \partial Q_r \partial Q_s)_0 \quad (9)$$

The zero subscripts in eq 7–9 indicate quantities which are evaluated at the equilibrium nuclear configuration ($Q_r = 0$).

We now use second order perturbation theory to express the electronic wave functions $|\mathrm{A}\rangle$ and $|\mathrm{J}\rangle$ in terms of the eigenfunctions of $H^{(0)}$. For example,

$$|\mathrm{A}\rangle = |\mathrm{A}^0\rangle + \sum_r \sum_{\mathrm{K}^0 \neq \mathrm{A}^0} \lambda_{\mathrm{KA}}{}^r Q_r |\mathrm{K}^0\rangle + \frac{1}{2} \sum_{r,s} \sum_{\mathrm{K}^0 \neq \mathrm{A}^0} \lambda_{\mathrm{AK}}{}^r \lambda_{\mathrm{KA}}{}^s Q_r Q_s |\mathrm{A}^0\rangle + \sum_{r,s} \sum_{\mathrm{K}^0 \neq \mathrm{A}^0} \eta_{\mathrm{KA}}{}^{rs} Q_r Q_s |\mathrm{K}^0\rangle \quad (10)$$

where

$$\lambda_{\mathrm{KA}}{}^r = (E_{\mathrm{A}}{}^0 - E_{\mathrm{K}}{}^0)^{-1} \langle \mathrm{K}^0 | H_r^{(1)} | \mathrm{A}^0 \rangle \quad (11)$$

and

$$\eta_{\mathrm{KA}}{}^{rs} = (E_{\mathrm{A}}{}^0 - E_{\mathrm{K}}{}^0)^{-1} \langle \mathrm{K}^0 | H_{rs}^{(2)} | \mathrm{A}^0 \rangle - (E_{\mathrm{A}}{}^0 - E_{\mathrm{K}}{}^0)^{-2} \langle \mathrm{K}^0 | H_r^{(1)} | \mathrm{A}^0 \rangle \langle \mathrm{A}^0 | H_s^{(1)} | \mathrm{A}^0 \rangle + (E_{\mathrm{A}}{}^0 - E_{\mathrm{K}}{}^0)^{-1} \sum_{\mathrm{L}^0 \neq \mathrm{A}^0} (E_{\mathrm{A}}{}^0 - E_{\mathrm{L}}{}^0)^{-1} \times \langle \mathrm{K}^0 | H_r^{(1)} | \mathrm{L}^0 \rangle \langle \mathrm{L}^0 | H_s^{(1)} | \mathrm{A}^0 \rangle \quad (12)$$

Upon inserting the expansions for $|\mathrm{A}\rangle$ and $|\mathrm{J}\rangle$ into eq 4, summing over j, and noting that

$$\langle \mathrm{o} | Q_r | \mathrm{o} \rangle = 0 \quad (13)$$

and

$$\langle \mathrm{o} | Q_r Q_s | \mathrm{o} \rangle = \langle \mathrm{o} | Q_r^2 | \mathrm{o} \rangle \delta_{rs} \quad (14)$$

we obtain, through second order,

$$\begin{aligned} D(\mathrm{A} \rightarrow \mathrm{J}) = {} & \langle \mathrm{A}^0 | \mathbf{m} | \mathrm{J}^0 \rangle \cdot \langle \mathrm{J}^0 | \mathbf{m} | \mathrm{A}^0 \rangle \\ & + \langle \mathrm{A}^0 | \mathbf{m} | \mathrm{J}^0 \rangle \cdot \sum_r \Bigg\{ -\langle \mathrm{J}^0 | \mathbf{m} | \mathrm{A}^0 \rangle \times \Bigg(\sum_{\mathrm{K}^0 \neq \mathrm{J}^0} (\lambda_{\mathrm{JK}}{}^r)^2 + \sum_{\mathrm{K}^0 \neq \mathrm{A}^0} (\lambda_{\mathrm{AK}}{}^r)^2 \Bigg) \\ & + 2 \Bigg(\sum_{\mathrm{K}^0 \neq \mathrm{J}^0} \eta_{\mathrm{KJ}}{}^{rr} \langle \mathrm{A}^0 | \mathbf{m} | \mathrm{K}^0 \rangle + \sum_{\mathrm{K}^0 \neq \mathrm{A}^0} \eta_{\mathrm{KA}}{}^{rr} \langle \mathrm{J}^0 | \mathbf{m} | \mathrm{K}^0 \rangle \Bigg) \\ & + 2 \sum_{\mathrm{K}^0 \neq \mathrm{A}^0} \sum_{\mathrm{L}^0 \neq \mathrm{J}^0} \lambda_{\mathrm{KA}}{}^r \lambda_{\mathrm{LJ}}{}^r \langle \mathrm{K}^0 | \mathbf{m} | \mathrm{L}^0 \rangle \Bigg\} \langle \mathrm{o} | Q_r^2 | \mathrm{o} \rangle \\ & + \sum_r \Bigg\{ \sum_{\mathrm{K}^0 \neq \mathrm{J}^0} \sum_{\mathrm{L}^0 \neq \mathrm{J}^0} \lambda_{\mathrm{KJ}}{}^r \lambda_{\mathrm{LJ}}{}^r \langle \mathrm{A}^0 | \mathbf{m} | \mathrm{K}^0 \rangle \cdot \langle \mathrm{L}^0 | \mathbf{m} | \mathrm{A}^0 \rangle \\ & + 2 \sum_{\mathrm{K}^0 \neq \mathrm{J}^0} \sum_{\mathrm{L}^0 \neq \mathrm{A}^0} \lambda_{\mathrm{KJ}}{}^r \lambda_{\mathrm{LA}}{}^r \langle \mathrm{A}^0 | \mathbf{m} | \mathrm{K}^0 \rangle \cdot \langle \mathrm{L}^0 | \mathbf{m} | \mathrm{J}^0 \rangle \\ & + \sum_{\mathrm{K}^0 \neq \mathrm{A}^0} \sum_{\mathrm{L}^0 \neq \mathrm{A}^0} \lambda_{\mathrm{KA}}{}^r \lambda_{\mathrm{LA}}{}^r \langle \mathrm{K}^0 | \mathbf{m} | \mathrm{J}^0 \rangle \cdot \langle \mathrm{L}^0 | \mathbf{m} | \mathrm{J}^0 \rangle \Bigg\} \langle \mathrm{o} | Q_r^2 | \mathrm{o} \rangle \end{aligned} \quad (15)$$

In writing eq 15 we have assumed that the eigenfunctions of $H^{(0)}$ are real.

If the $|\mathrm{A}^0\rangle \rightarrow |\mathrm{J}^0\rangle$ transition is symmetry forbidden, only the last three terms in eq 15 survive, and we may write

$$D^{\mathrm{V}}(\mathrm{A} \rightarrow \mathrm{J}) = \sum_r D_r{}^{\mathrm{V}}(\mathrm{A} \rightarrow \mathrm{J}) \quad (16)$$

where $D_r{}^{\mathrm{V}}(\mathrm{A} \rightarrow \mathrm{J})$, the vibrational contribution to the dipole strength which arises from the rth normal mode, is of second order in Q_r.

We now wish to investigate the effect of adding a static perturbation $U(q,Q_0)$ to the Hamiltonian. The operator U may be decomposed into components which form bases for the irreducible representations of the point group of the unperturbed molecule, so we write

$$U = \sum_\Gamma U(\Gamma) \quad (17)$$

where $U(\Gamma)$ forms a basis for the Γth irreducible representation of the molecular point group. (For simplicity we assume that all group representations are one-dimensional. Extension of the following arguments to include multidimensional representations is straightforward.) We now apply the perturbation U to the electronic states which appear in eq 15.

The only purely static contributions to the dipole strength arise from the first term of eq 15. Since $\langle \mathrm{A}^0 | \mathbf{m} | \mathrm{J}^0 \rangle$ vanishes for an electric dipole forbidden transition, it is clear that such contributions are of at least second order in the static perturbation, and to that order we may write

$$D^{\mathrm{S}}(\mathrm{A}\rightarrow\mathrm{J}) = \sum_{\Gamma} D_{\Gamma}{}^{\mathrm{S}}(\mathrm{A}\rightarrow\mathrm{J}) \qquad (18)$$

where $D_{\Gamma}{}^{\mathrm{S}}(\mathrm{A}\rightarrow\mathrm{J})$ is the partial dipole strength induced by the perturbation $U(\Gamma)$.

Finally, we consider contributions to $D(\mathrm{A}\rightarrow\mathrm{J})$ which result from the interaction of static and vibrational perturbations. In order to do this we must first demonstrate some symmetry properties of the expansion coefficients λ and η. To begin with, since $H_{rr}{}^{(2)}$ is totally symmetric, the matrix element $\langle \mathrm{K}^0|H_{rr}{}^{(2)}|\mathrm{A}^0\rangle$ can be nonzero only if $|\mathrm{K}^0\rangle$ and $|\mathrm{A}^0\rangle$ belong to the same irreducible representation of the molecular point group. This condition must also be met if the products $\langle \mathrm{K}^0|H_r{}^{(1)}|\mathrm{A}^0\rangle\langle \mathrm{A}_0|H_r{}^{(1)}|\mathrm{A}^0\rangle$ and $\langle \mathrm{K}^0|H_r{}^{(1)}|\mathrm{L}^0\rangle\langle \mathrm{L}^0|H_r{}^{(1)}|\mathrm{A}^0\rangle$ are not to vanish. Therefore, it follows from eq 12 that $\eta_{\mathrm{KA}}{}^{rr} = 0$ unless $\Gamma(\mathrm{K}^0) = \Gamma(\mathrm{A}^0)$. In a similar fashion it can be shown that $\lambda_{\mathrm{KL}}{}^{r}\lambda_{\mathrm{MN}}{}^{r}$ can be nonzero only if the direct product $\Gamma(\mathrm{K}^0) \otimes \Gamma(\mathrm{L}^0)$ is equal to $\Gamma(\mathrm{M}^0) \otimes \Gamma(\mathrm{N}^0)$.

We will now use the above-derived symmetry properties of the expansion coefficients to demonstrate that only the last three terms of eq 15 can contain contributions which are of first order in the static perturbations. We have already mentioned that the first term in that equation can contain no such contributions, and for the same reasons neither can other terms which contain the scalar product $\langle \mathrm{A}^0|\mathbf{m}|\mathrm{J}^0\rangle \cdot \langle \mathrm{J}^0|\mathbf{m}|\mathrm{A}^0\rangle$. Also, since the $|\mathrm{A}^0\rangle \rightarrow |\mathrm{J}^0\rangle$ transition is symmetry forbidden, and since $\eta_{\mathrm{KJ}}{}^{rr}$ can be nonzero only if $\Gamma(\mathrm{K}^0) = \Gamma(\mathrm{J}^0)$, $\eta_{\mathrm{KA}}{}^{rr}$ can be nonzero only if $\Gamma(\mathrm{K}^0) = \Gamma(\mathrm{A}^0)$, and $\lambda_{\mathrm{KA}}{}^{r}\lambda_{\mathrm{LJ}}{}^{r}$ can be nonzero only if $\Gamma(\mathrm{K}^0) \otimes \Gamma(\mathrm{L}^0) = \Gamma(\mathrm{A}^0) \otimes \Gamma(\mathrm{J}^0)$, it follows that the products $\eta_{\mathrm{KJ}}{}^{rr}\langle \mathrm{A}^0|\mathbf{m}|\mathrm{K}^0\rangle$, $\eta_{\mathrm{KA}}{}^{rr}\langle \mathrm{J}^0|\mathbf{m}|\mathrm{K}^0\rangle$, and $\lambda_{\mathrm{KA}}{}^{r}\lambda_{\mathrm{LJ}}{}^{r}\langle \mathrm{K}^0|\mathbf{m}|\mathrm{L}^0\rangle$ all vanish on symmetry grounds. These products appear in eq 15 only multiplicatively with the transition moment $\langle \mathrm{A}^0|\mathbf{m}|\mathrm{J}^0\rangle$, and therefore no first-order static contribution can arise from them. The lowest order interaction terms, those which are of first order in the static perturbations and second order in the vibrational ones, can come then only from the last three terms of eq 15.

For the sake of clarity, we write again the terms of eq 15 which can exhibit the lowest order effects of static–vibrational interactions:

$$\begin{aligned} D^{\mathrm{V}}(\mathrm{A}\rightarrow\mathrm{J}) = \sum_{r} \Bigg\{ & \sum_{\mathrm{K}^0\neq\mathrm{J}^0}\sum_{\mathrm{L}^0\neq\mathrm{J}^0} \lambda_{\mathrm{KJ}}{}^{r}\lambda_{\mathrm{LJ}}{}^{r}\langle \mathrm{A}^0|\mathbf{m}|\mathrm{K}^0\rangle \\ & \cdot \langle \mathrm{L}^0|\mathbf{m}|\mathrm{A}^0\rangle + 2\sum_{\mathrm{K}^0\neq\mathrm{J}^0}\sum_{\mathrm{L}^0\neq\mathrm{A}^0} \lambda_{\mathrm{KJ}}{}^{r}\lambda_{\mathrm{LA}}{}^{r}\langle \mathrm{A}^0|\mathbf{m}|\mathrm{K}^0\rangle \\ & \cdot \langle \mathrm{L}^0|\mathbf{m}|\mathrm{J}^0\rangle + \sum_{\mathrm{K}^0\neq\mathrm{A}^0}\sum_{\mathrm{L}^0\neq\mathrm{A}^0} \lambda_{\mathrm{KA}}{}^{r}\lambda_{\mathrm{LA}}{}^{\mathrm{r}}\langle \mathrm{K}^0|\mathbf{m}|\mathrm{J}^0\rangle \\ & \cdot \langle \mathrm{L}^0|\mathbf{m}|\mathrm{J}^0\rangle \Bigg\} \langle \mathrm{o}|Q_r{}^2|\mathrm{o}\rangle \qquad (19) \end{aligned}$$

Consider now the first term in eq 19. If it is to be nonvanishing, the symmetries of the electronic states must be such that

$$\langle \mathrm{K}^0|H_r{}^{(1)}|\mathrm{J}^0\rangle\langle \mathrm{L}^0|H_r{}^{(1)}|\mathrm{J}^0\rangle\langle \mathrm{A}^0|m_i|\mathrm{K}^0\rangle\langle \mathrm{L}^0|m_i|\mathrm{A}^0\rangle \neq 0 \qquad (20)$$

where the subscript i denotes the Cartesian components of **m**. If a static perturbation is applied, a nonzero first-order contribution can result only if the perturbation forms a basis for the irreducible representation given by the direct product of the irreducible representations to which belong all of the wave functions and operators which appear in eq 20. Since all of these wave functions and operators appear twice, it follows that this representation is the totally symmetric one, i.e., only the component $U(\Gamma_{\mathrm{tot.sym.}})$ contributes to the dipole strength in first order.

The same arguments apply to the other two terms which appear in eq 19, and so to lowest nonvanishing order we may write the contribution to the dipole strength which arises from static–vibrational interactions as

$$D^{\mathrm{VS}}(\mathrm{A}\rightarrow\mathrm{J}) = \sum_{r} D_r{}^{\mathrm{VS}}(\mathrm{A}\rightarrow\mathrm{J}) \qquad (21)$$

Note that the additivity properties with respect to the vibrational perturbations are preserved in eq 21.

Since the magneto-optical B term has the same symmetry properties as the dipole strength, we may write $B(\mathrm{A}\rightarrow\mathrm{J})$ as

$$\begin{aligned} B(\mathrm{A}\rightarrow\mathrm{J}) &= B^{\mathrm{V}}(\mathrm{A}\rightarrow\mathrm{J}) + B^{\mathrm{S}}(\mathrm{A}\rightarrow\mathrm{J}) + B^{\mathrm{VS}}(\mathrm{A}\rightarrow\mathrm{J}) \\ &\quad + \text{higher-order terms} \\ &= \sum_{r} B_r{}^{\mathrm{V}}(\mathrm{A}\rightarrow\mathrm{J}) + \sum_{\Gamma} B_{\Gamma}{}^{\mathrm{S}}(\mathrm{A}\rightarrow\mathrm{J}) \\ &\quad + \sum_{r} B_r{}^{\mathrm{VS}}(\mathrm{A}\rightarrow\mathrm{J}) + \text{higher-order terms} \qquad (22) \end{aligned}$$

Here $B_r{}^{\mathrm{V}}$ is the purely vibrational contribution of the nontotally symmetric normal mode Q_r to the B term associated with the $|\mathrm{A}\rangle \rightarrow |\mathrm{J}\rangle$ transition, $B_{\Gamma}{}^{\mathrm{S}}$ is the purely static contribution of $U(\Gamma)$, and $B_r{}^{\mathrm{VS}}$ is the contribution of static–vibrational interactions. $B_r{}^{\mathrm{VS}}$ is of second order in the normal coordinate Q_r and first order in the totally symmetric component of the static perturbation.

Summary

It has been shown above that the lowest order contribution of static–vibrational interactions to the B term associated with a symmetry-forbidden transition involves only the totally symmetric component of the static perturbation. At this order, the physical mechanism involved is an alteration by the static perturbation of the efficacy of the vibronic coupling through which the transition gains magnetic circular dichroic intensity.

Applications

In the accompanying paper,[10] we shall have occasion to use eq 22 in structural interpretations of MCD data. The type of situation we shall encounter involves, for example, the substitution of a methyl group for a hydrogen atom. In certain instances, a substitution of this sort can make significant contributions to the MCD intensity through the $B_r{}^{\mathrm{VS}}$ terms of eq 22, terms which implicate the totally symmetric part of a structural perturbation. Explicit recognition of the potential importance of such terms has been absent in the past.

Obviously, the perturbations wrought by the substitution of a methyl group for a hydrogen atom cannot be classified as purely structural. The mere fact that the number of atoms is different in the parent and daughter compounds means that the basic set of normal coordinates has been affected by the perturbation. Nevertheless, we shall at times, as a first approximation, treat the perturbations accompanying substitution as if they were of the purely structural (static) kind assumed in the derivation of eq 22. That is, we shall assume that differences between normal modes in parent and daughter compounds are unimportant for purposes of estimating the $B_r{}^{\mathrm{VS}}$ terms. Such an assumption makes no provision for any "conformational stabilization" effects (ref 7, section II.B.3.e). These will have to be considered additionally.

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An Expiscation of Structural–Vibrational Effects in Magnetic Circular Dichroism Spectra of Saturated Ketones[2]

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Abstract: It is now known (preceding paper in this issue) that totally symmetric static structural perturbations can alter the MCD intensity borrowed by nontotally symmetric vibrations in a forbidden transition. The effect is examined numerically with the aid of molecular orbital theory. A simple semiempirical stereochemical model is developed that handles the vibrational–structural interaction associated with substituent atoms at the α carbons in saturated ketones. The model is tested against the experimental MCD data (B values) for a wide variety of alkyl substituted saturated ketones (*trans*-2-decalones, cyclobutanones, acyclic ketones, cyclopentanones, bicyclo[2.2.2]octan-2-ones, cyclohexanones, and certain bridged ketones) and is found to work satisfactorily. The model also provides a useful extension of our earlier analysis of MCD-structural relationships. The revised protocol, within stated limitations, accounts reasonably well for the variation in MCD intensity with variation in structure.

While the keto group is one of the most widely studied chromophores, the diversity of structures to which it may be attached and the effects of substituents on its electronic structure continue to challenge chemists and spectroscopists. Since the near ultraviolet electronic transition, $n \rightarrow \pi^*$, is locally electric dipole forbidden but magnetic dipole allowed, chiroptical methods have been extensively used to gain structural information about both ground and excited states.[3-6] More recently, magnetic circular dichroism (MCD) spectra have been shown to be sensitive to the stereochemistry of ketones,[7] and certain aspects of the mechanisms involved have been investigated.[8-12] Here, and in the preceding paper,[2a] we recognize the importance of and investigate a previously neglected effect: the effect that totally symmetric structural perturbations have on the MCD intensity generated by nontotally symmetric vibrational perturbations. In the preceding paper we examined the general theory; here we continue with specific applications to the $n \rightarrow \pi^*$ (${}^1A_1 \rightarrow {}^1A_2$) excitation in saturated ketones.

Theory

(A) **Background.** We rely heavily in this work on three earlier studies, two of which[9,12] concern the group theoretical interpretation of the MCD spectra of saturated ketones; the other[10] is an investigation of the vibronic coupling mechanism in formaldehyde.

Since the $n \rightarrow \pi^*$ excitation in ketones is locally symmetry forbidden, the intensity of the MCD spectrum associated with the transition is of second or higher order in perturbations that are nontotally symmetric in C_{2v}. Furthermore, the partial B values which result from perturbations belonging to different irreducible representations of C_{2v} are additive through second order.[12] In ref 9, we classified such perturbations as either structural (static) or vibrational. Physical arguments were presented which related the signs of the partial B values associated with the static and vibrational perturbations, and the signs of the vibrational contributions were determined from the MCD spectra of C_{2v} molecules such as formaldehyde and cyclobutanone. It was also shown that the then available data were in the large consistent with these arguments and inferences, provided that due consideration be given to possible changes in the vibrational contributions upon substitution.

Generally, we wished to focus attention on the static (structural) perturbations and we tended to make our detailed comparisons only on compounds which could reasonably be expected to have a constant vibrational contribution. Subsequently,[10] we presented the geometric perturbation (GP) method for the calculation of vibrational contributions to the B values of formaldehyde. With this tool, we have now reexamined some of our previous assumptions and find that revisions are needed. This reexamination was made necessary by the generation of new experimental data[13,14] that indicate that our previous analyses[9] failed to recognize the importance of a contribution associated with *totally symmetric* static perturbations.

The rationale for the subordination of totally symmetric structural perturbations in ketones (except for conformational stabilization effects) lay in the fact that nontotally symmetric perturbations are required for the generation of MCD intensity in a forbidden transition. However, as shown in the accom-