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SOME ASPECTS OF VIBRONIC COUPLING IN CIRCULAR DICHROISM[a]

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Abstract—After a review of the quantum mechanical formulation of vibrational-electronic coupling, the adiabatic approximations for ordinary absorption dipole strength and circular dichroic absorption rotatory strength are presented and interpreted. The expressions include the effect of two vibrational quantum changes coupled to electronic excitation in addition to the more familiar concept of coupling by a one quantum change. A polarizability theory of vibronically coupled rotatory strength is presented which is comparable to the polarizability theory of rotatory strength without regard to vibration.

INTRODUCTION

The thrust of most investigations using optical activity has been toward a straightforward appraisal of molecular structure that gives rise to chirality. There has been a growing realization however that such spectral information about the molecule in its stationary equilibrium form is not always readily discerned nor easily separable from dynamic effects in the observed optical activity. Both natural and magnetically induced optical activity, especially in the form of circular dichroism, have been the subject of theoretical and experimental studies along these lines.

The following material summarizes and integrates the prior work on this subject. As well, it introduces the most recent developments of the research group in our laboratory. The reader who is interested in more detail will want to consult the original or, in some cases, forthcoming publications.

QUANTUM-MECHANICAL FOUNDATIONS: THE BORN-OPPENHEIMER SEPARATION†

Born and Oppenheimer showed[1] that in a molecular system, the electronic and nuclear motion operate on such different time scales that, to a certain approximation, they may be regarded as occurring independently. To achieve this result and define its limitations, consider the Schroedinger equation for combined electronic and nuclear motion

$$[\mathcal{H}(q, Q) - E]\Psi(q, Q) = 0 \qquad (1)$$

where q and Q are respectively the electronic and nuclear coordinates. The molecular Hamiltonian $\mathcal{H}$ can be written in two parts:

$$\mathcal{H}(q, Q) = T_n(Q) + \mathcal{H}_e(q, Q) \qquad (2)$$

where $T_n(Q)$ is the kinetic energy operator of the nuclei and $\mathcal{H}_e(q, Q)$ is the electronic Hamiltonian which contains the kinetic energy operator for the electrons, their potential energy in the field of the nuclei, their mutual repulsions energy and the mutual repulsions energy of the nuclei.

$\mathcal{H}_e(q, Q)$ is precisely the Hamiltonian used for ordinary quantum computations of molecular electronic properties. Such computations define an eigenvalue electronic energy V_K (including the coulombic nuclear repulsion) for each set of nuclear positions which may be defined.

On the other hand, the eigenvalue E of Eq 1 gives the combined energy of electronic motion, all coulombic attractions and repulsions, together with the energy of nuclear motion. The corresponding eigenfunction $\Psi(q, Q)$ of Eq 1 gives a probablistic interpretation of where *moving* nuclei, as well as moving electrons, spend their time in the molecule.

For the purpose of solving Eq 1 the electronic Hamiltonian, $\mathcal{H}_e$, can be written as a Taylor series expansion to the quadratic terms in the nuclear normal coordinates about the undistorted molecular configuration; i.e., the nuclear equilibrium position, $Q_r = 0$ for all r.

$$\mathcal{H}_e(q, Q) = \mathcal{H}_e^0 + \sum_r \left(\frac{\partial \mathcal{H}_e}{\partial Q_r}\right)_0 Q_r + \frac{1}{2}\sum_{r,s}\left(\frac{\partial^2 \mathcal{H}_e}{\partial Q_r Q_s}\right)_0 Q_r Q_s. \qquad (3)$$

It is also possible to construct sets of functions $V_K(Q)$ and $P_{LK}(Q)$ which are power series in Q:

$$V_K(Q) = V_K^0 + \sum_r l_K^r Q_r + \frac{1}{2}\sum_{r,s} l_K^{rs} Q_r Q_s \qquad (4)$$

[a]Taken in part from the doctoral dissertation of Edith C. Ong, Tulane University (1973).

†This section draws heavily on the work of W. Moffitt *et al.* See for example, W. Moffitt and A. D. Liehr, *Phys. Rev.* 106, 1195 (1957).

$$P_{LK}(Q) = P^0_{LK} + \sum_r P^r_{LK}Q_r + \frac{1}{2}\sum_{r,s} P^{rs}_{LK}Q_rQ_s. \quad (5)$$

It is further assumed that the eigenfunctions $\psi_K^0(q)$ to the electronic Schroedinger equation for the undistorted molecule:

$$(\mathcal{H}_e^0 - V_K^0)\psi_K^0(q) = 0 \quad (6)$$

form a complete set in the electronic coordinates q, and that the eigenfunction, $\psi_K^0(q)$ can be extended by the usual perturbation method about the nuclear displacement coordinates:

$$\psi_K(q, Q) = \psi_K^0(q) + \sum_{L\neq K} C_{LK}(Q)\psi_L^0(q) \quad (7)$$

where

$$C_{LK}(Q) = \sum_r C^r_{LK}Q_r + \frac{1}{2}\sum_{r,s} C^{rs}_{LK}Q_rQ_s. \quad (8)$$

The coefficients $C_{LK}(Q)$ are chosen in such a way that, for arbitrary displacements Q_r, the $\psi_K(q, Q)$ form a complete orthonormal set with respect to the electronic coordinates q.

Then Eqs 3–5 and 7–8 satisfy the equation

$$[\mathcal{H}_e(q, Q) - V_K(Q)]\psi_K(q, Q) = \sum_L P_{LK}(Q)\psi_L(q, Q). \quad (9)$$

The coefficients l^r_K, l^{rs}_K, P^r_{LK} and P^{rs}_{LK} of Eqs 4 and 5, just like the coefficients C^r_{LK} and C^{rs}_{LK} of Eq 8, are defined by second order perturbation theory and the matrix elements $(\Psi_L^0|(\partial\mathcal{H}_e/\partial Q_r)_0|\Psi_K^0)$ and $(\Psi_L^0|(\partial^2\mathcal{H}_e/\partial Q_r\partial Q_s)_0|\Psi_K^0)$.

The perturbation definition of terms in Eq 5 shows that $P_{LK} = 0$ for any L states that are not degenerate with K. Therefore we see that Eq 9 is the analog of the electronic Schroedinger Eq 6 when ψ_K is non-degenerate. However, Eq 9 is generalized to represent the eigenvalue problem when the molecule is distorted, i.e., when $Q \neq 0$. When ψ_K is one member of a degenerate set, the non-vanishing P_{LK} are responsible for the peculiar phenomena known as Jahn–Teller and Renner effects.

The complete set $\psi_K(q, Q)$ are used to expand the eigenfunction of Eq 1

$$\Psi(q, Q) = \sum_K \psi_K(q, Q)\chi_K(Q) \quad (10)$$

which with Eq 2 allows the equation of combined electronic and nuclear motion Eq 1 to take the form

$$\sum_K (\mathcal{H}_e + T_n(Q) + V_K - V_K - E)\psi_K(q, Q)\chi_K(Q) = 0. \quad (11)$$

After applying the commutation relationship

$$[T_n(Q), \psi_K(q, Q)] = 0 \quad (12)$$

and after making further substitution of Eq 9 into Eq 11, Eq 1 finally takes the form:

$$\sum_K \psi_K(q, Q)\left\{[T_n(Q) + V_K(Q) - E)\chi_K(Q) + \chi_K\sum_L \psi_L(q, Q)P_{LK}(Q)\right\} = 0. \quad (13)$$

Non-degenerate states

Taking a state function ψ_M that is non-degenerate, multiplying it into Eq 13 and integrating gives:

$$[T_n(Q) + V_M(Q) - E]\chi_M = 0 \quad (14)$$

an harmonic oscillator eigenvalue problem. Only one χ_M is defined for an E, therefore an eigenfunction of Eq 1 for a non-degenerate state M = K takes the form

$$\Psi(q, Q) = \psi_K(q, Q)\chi_K(Q) \quad (15)$$

where $\psi_K(q, Q)$ is a solution to the electronic Schroedinger equation at various fixed nuclear configurations, expressed as in Eq 7, and $\chi_K(Q)$ is any one of the harmonic vibrational eigenfunctions for the K electronic state function $V_K(Q)$.

Eq 15 is often expressed in its zeroth-order approximation:

$$\Psi(q, Q) = \psi_K^0(q)\chi_K(Q) \quad (16)$$

where $\psi_K^0(q)$ is the zeroth-order term of the $\psi_K(q, Q)$ expansion in Eq 7. But it is important to note that the Born–Oppenheimer adiabatic approximation, Eq 15, is consistent with the harmonic description of vibration to a level including wave function coefficients C^{rs}_{LK} that depend on $\partial^2\mathcal{H}_e/\partial Q_r\partial Q_s$.

Degenerate states

For an example, we may consider a doubly degenerate state with components ψ_M and $\psi_{M'}$. Multiplying ψ_M and $\psi_{M'}$ in turn into Eq 13 and integrating will give coupled equations for the vibrational eigenvalue problem:

$$\begin{aligned}[T_n(Q) + V_M(Q) - E]\chi_M + P_{MM'}\chi_{M'} &= 0\\ P_{M'M}\chi_M + [T_n(Q) + V_M(Q) - E]\chi_{M'} &= 0\end{aligned} \quad (17)$$

A χ_M and a $\chi_{M'}$ are defined for each value of E.

In such a case the eigenfunctions to Eq 1, defined by specific values for the eigenvalue E, must be expressed by two terms K = M, M' in Eq 10. In addition the vibrational wavefunctions χ_M and $\chi_{M'}$ will reflect the peculiar properties associated with the dynamic Jahn–Teller and Renner effects.

Vibronic coupling

Two limiting cases of vibronic coupling, the interaction of vibrational and electronic motions, are

now readily defined. In the adiabatic approximation, the nuclei move and electronic motion is fully adjusted to each instantaneous nuclear configuration. The vibronic coupling is represented by the Q dependence of $\psi_K(q, Q)$ in Eq 15.

In the non-adiabatic approximation the nuclear motion is modified by the electronic motion. The vibronic coupling can be represented entirely by the vibrational wavefunctions of an expression

$$\Psi(q, Q) = \psi_M{}^0(q)\chi_M(Q) + \psi^0_{M'}(q)\chi_M(Q) \qquad (18)$$

where these vibrational wavefunctions $\chi_M(Q)$ and $\chi_{M'}(Q)$ are given by the coupled Eqs 17.

The most general expressions for vibronic coupling must contain both types of representations. Near degeneracies, rather than exact, may require the general form of Eq 10, giving rise to pseudo-Jahn–Teller effects and the like. On the other hand, exact or essential degeneracies may require nuclear dependence of the electronic wavefunction for a sufficiently precise description, again achieving the general form of Eq 10 in place of the limiting form in Eq 18.

Very little work has appeared on the circular dichroic properties of transitions between electronic states where the non-adiabatic approximation for vibronic coupling is required.[2,3] Much more attention to this area is warranted. It must be considered in a complete theory of natural and magnetically induced circular dichroic absorption of polymers and coordination complexes of metal ions.

ORDINARY ABSORPTION AND CIRCULAR DICHROIC ABSORPTION

For transitions between states that are well separated in energy from others, the adiabatic approximation is generally assumed to give the dominant effects of vibronic coupling. The theory is more complete in this instance.[4-7]

The ordinary absorption and circular dichroic absorption between eigenstates of Eq 1 are then governed respectively by

$$D^{Kk}_{Nn} = |\langle Nn|\boldsymbol{\mu}|Kk\rangle|^2 \qquad (19)$$

the dipole strength, and

$$R^{Kk}_{Nn} = \mathrm{Im}\{\langle Nn|\boldsymbol{\mu}|Kk\rangle \cdot \langle Kk|\mathbf{m}|Nn\rangle\} \qquad (20)$$

the rotatory strength. In this notation for the adiabatic approximation, the $\Psi(q, Q)$ are indexed by K (or N for the ground state) which refers to Eq 9 in its non-degenerate form ($P_{LK} = 0$). It is further indexed by k (or n), referring to Eq 14 M = K (or N). Here k indexes the various vibrational quantum states possible in the given electronic state.

The electric and magnetic dipole transition moments by the use of Eqs 7 and 10 become

$$\langle Nn|\boldsymbol{\mu}|Kk\rangle = \langle N^0|\boldsymbol{\mu}|K^0\rangle\langle n|k\rangle + \sum_r \mathbf{C}_r\langle|Q_r|k\rangle + \frac{1}{2}\sum_{r,s}\mathbf{C}_{rs}\langle n|Q_rQ_s|k\rangle \qquad (21)$$

$$\langle Kk|\mathbf{m}|Nn\rangle = \langle K^0|\mathbf{m}|N^0\rangle\langle k|n\rangle + \sum_r \mathbf{B}_r\langle k|Q_r|n\rangle + \frac{1}{2}\sum_{r\le s}\mathbf{B}_{rs}\langle k|Q_rQ_s|n\rangle \qquad (22)$$

where the nuclear normal coordinate dependent terms are factored off to the right and integrated over normal coordinate space. The left hand factor in each term consists of integrals over the electronic coordinates only. $\langle N^0|\boldsymbol{\mu}|K^0\rangle$ and $\langle K^0|\mathbf{m}|N^0\rangle$ are the transition electric and magnetic dipoles inherent for the undistorted molecule. $\mathbf{C}_r$, $\mathbf{B}_r$, $\mathbf{C}_{rs}$, and $\mathbf{B}_{rs}$ are transition electric and magnetic dipoles created by vibrational distortions.

The vibrational detail implied by Eqs 19 and 20 is not always observable in an electronic spectrum. Thus it is useful to consider the sum over such spectral structure:

$$D_K = \sum_k D^{Kk}_{No} \qquad (23)$$

$$R_K = \sum_k R^{Kk}_{No} \qquad (24)$$

where we have also assumed a low temperature limit. The index No implies that only the zero-point vibrational level is populated in the electronic ground state.

Carrying out the required summation with some quantum manipulation yields:[7]

$$\begin{aligned} D_K &= D_{K,A} + D_{K,F} \\ &= |\langle N^0|\boldsymbol{\mu}|K^0\rangle|^2 + \sum_r |\mathbf{C}_r|^2\xi_r \\ &\quad + \langle N^0|\boldsymbol{\mu}|K^0\rangle \cdot \sum_r \mathbf{C}_{rr}\xi_r \\ &\quad + \frac{1}{4}\sum_{r,s}(\mathbf{C}_{rr}\cdot\mathbf{C}_{ss} + 2|\mathbf{C}_{rs}|^2)\xi_r\xi_s \end{aligned} \qquad (25)$$

and

$$\begin{aligned} R_K &= R_{K,A} + R_{K,F} \\ &= \mathrm{Im}\Big\{\langle N^0|\boldsymbol{\mu}|K^0\rangle \cdot \langle K^0|\mathbf{m}|N^0\rangle + \sum_r \mathbf{C}_r\cdot\mathbf{B}_r\xi_r \\ &\quad + \frac{1}{2}\Big[\langle N^0|\boldsymbol{\mu}|K^0\rangle \cdot \sum_r \mathbf{B}_{rr} + \sum_r \mathbf{C}_{rr}\cdot\langle K^0|\mathbf{m}|N^0\rangle\Big]\xi_r \\ &\quad + \frac{1}{8}\Big[\sum_{r,s}\mathbf{C}_{rr}\cdot\mathbf{B}_{ss} + \mathbf{B}_{rr}\cdot\mathbf{C}_{ss})\xi_r\xi_s\Big] \\ &\quad + \frac{1}{2}\sum_{r,s}(\mathbf{C}_{rs}\cdot\mathbf{B}_{rs})\xi_r\xi_s\Big\}. \end{aligned} \qquad (26)$$

The parameter ξ_r is a measure of the extent of molecular distortion by the rth nuclear normal coordinate.

Previous developments of the theory[4-6] suggested that vibronically coupled moments will not combine effectively with moments of the undistorted molecule to contribute to the total electronic rotatory strength. It is apparent from Eq 26 that an important contributing term to the net rotatory strength can be $\frac{1}{2}\sum_r \mathbf{C}_{rr} \cdot \langle K^0|\mathbf{m}|N^0\rangle \xi_r$. This term necessarily applies to molecules where two-quantum vibrational transitions in the electronic transition are responsible for generating electric dipole intensity, i.e., when there is two-quantum vibronic coupling. Such two-quantum vibronic coupling terms are necessarily associated with the vibrational integrals $\langle O_r|Q_r^2|k_r\rangle$ and $\langle O_rO_s|Q_rQ_s|k_rk_s\rangle$ of Eq 21 which in the simplest approximation are nonzero only for $k_r = 0, 2$ and $k_r = k_s = 1$ respectively.

Eqs 25 and 26 each have a first term which can produce absorption in the absence of effective molecule distortion by vibration. Absorption of such origin has been called "allowed character" in contrast to the vibronically coupled absorption of the remaining terms called "forbidden character".[8]

So it would appear that a complete computation of electronic circular dichroic absorption should consider the magnitude of both "characters" as well as their signs, which may or may not differ. It should also be desirable to have some knowledge of how each "character" distributes itself in the spectrum.

Thus it is appropriate to consider computational *models* for the "allowed" and "forbidden characters". While the models to be developed here have an element of naiveness, their simplicity can reveal the essential structure of more complete calculations. The models will apply to inherently symmetric chromophores, where in a zero-order approximation the absorption of energy is limited to a portion of the molecule. That portion taken alone is optically inactive. The chromophore in a dissymmetric molecule develops circular dichroism in its absorption from interaction with the rest of the molecule.

"ALLOWED CHARACTER" ROTATORY STRENGTH*

The "allowed character" rotatory strength of an inherently symmetric chromophore is:

$$R_{K,A} = \mathrm{Im}\{\langle N^0|\boldsymbol{\mu}|K^0\rangle \cdot \langle K^0|\mathbf{m}|N^0\rangle\}$$
$$= -\,i\langle A_oB_o|\boldsymbol{\mu}|A_mB_o\rangle \cdot \langle A_mB_o|\mathbf{m}|A_oB_o\rangle. \quad (27)$$

The correct wavefunctions can be expanded to the first order of perturbation,

$$|A_mB_o\rangle = |A_mB_o\rangle + \sum_{r,s} (E_m - E_r - E_s)^{-1}(A_rB_s|V|A_mB_o)|A_rB_s\rangle \quad (28)$$

with $m = 0$ for the expansion of the gound state wavefunction $|A_0B_0\rangle$. The basis set $|A_rB_s\rangle$ consists of the simple product of spectroscopic state real wavefunctions of chromophore, A_r, and an extrachromophoric perturber, B_s. No electron exchange and negligible differential overlap between the chromophore and perturber are assumed. The perturbation V is the electrostatic energy of interaction between the chromophore and perturber charge distributions.

The transition electric dipole moment for the composite system has the leading terms:

$$\langle A_oB_o|\boldsymbol{\mu}|A_mB_o\rangle = \boldsymbol{\mu}_{om} + \sum_{k\neq m} (E_m - E_k)^{-1}(A_kB_o|V|A_mB_o)\boldsymbol{\mu}_{ok} + \sum_l (E_m - E_l)^{-1}(A_oB_l|V|A_mB_o)\boldsymbol{\mu}_{ol}. \quad (29)$$

Here k indicates that states of the chromophore which combine with the state 0 to give nonzero electric dipole moments. Those states of the perturber system giving nonvanishing electric transition-dipole moments are designated by l. Thus transition dipoles of the chromophore $\boldsymbol{\mu}_{ok}$ and of the perturber $\boldsymbol{\mu}_{ok}$ can be mixed into the zero-order transition dipole $\boldsymbol{\mu}_{om}$. If necessary, the transition magnetic dipole can be expanded in a similar way.

To evaluate the matrix elements of the perturbation V in Eq 29, the coulombic potential of interaction is expanded as shown in Table 1. There R is the distance between the centers of gravity of perturber and chromophore charge distribution; X, Y, and Z are the signed components of that distance. Charge (ϵ), dipole (μ), quadrupole (Θ), and if necessary, higher multipole components of the respective "charge distributions", e.g., $|A_oA_m)$ and $|B_lB_o)$, are required. Their electron coordinates, x, y, and z centered on the respective subsystems, have the same spatial orientation as X, Y, and Z.

*Dynamic coupling**

When a transition of the inherently symmetric chromophore of point group C_{2v} is magnetic dipole allowed and electric dipole forbidden ($\mu_{om} = 0$) the last term of Eq 29 contributes to an expression:

$$R_{om} = -\,15iR^{-7}XYZ\alpha_B\Theta_{om}^{xy}m_{mo}^{z} \quad (30)$$

where

$$\alpha_B = \frac{2}{3}\sum_l E_l(E_l^2 - E_m^2)^{-1}|\boldsymbol{\mu}_{ol}|^2 \quad (31)$$

*"Dynamic" in this context has been used[9] for purely electronic effects, not to be confused with the molecular dynamics accompanying nuclear motion.

for a perturber that is non-polar and has an isotropic polarizability. A remarkable feature of this expression is that the correct absolute signs of the octant rule sectors for optically active ketones can be deduced from the Mulliken–McMurry model for the $n - \pi^*$ (3000 Å) transition of the carbonyl group in ketones. That is, $i\Theta^{xy}_{om}m^z_{mo}$ is real, negative, and large in atomic units. The coordinate system and signed octants are shown in Fig 1. Eq 30 predicts that any substituent perturber placed off the octant nodal planes, thus rendering the molecule optically active, will produce an allowed character rotatory strength and circular dichroic absorption with the sign shown in Fig 1.

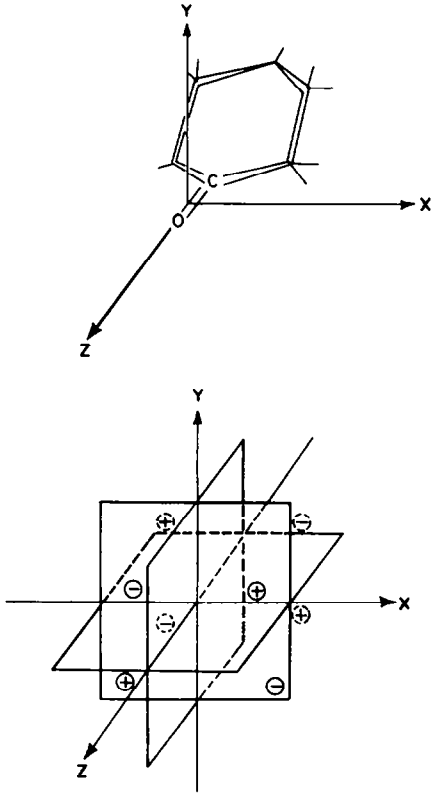

Fig 1A. The molecular co-ordinate system for Table 1. The origin is located at the center of the chromophore. A molecular framework is depicted upon which a dissymmetrically placed pertruber may be substituted. The additive effect, according to Eq 30, of the constituents of the framework gives no contribution to rotatory strength. The (usual) increment in polarizability upon substitution gives a net rotatory strength.

B. The same molecular co-ordinate system with octant rule sectors depicted. The sign of rotatory strength that results from the substituent falling in a given sector is shown for each octant.

When a transition of the inherently symmetric chromophore of any point group is electric dipole allowed ($\mu_{om} \neq 0$) an expansion instead of the magnetic transition dipole is required. The leading term for rotatory strength will depend on anisotropy in the polarizability of the pertuber. It is convenient to represent such anisotropic polarizability by an ellipsoid of revolution.

Orienting the transition electric dipole of the chromophore along the Z coordinate axis with its center at the origin and rotating the molecular system about this axis can bring the perturber polarizability ellipsoid axis parallel to the XZ plane. This is depicted in Fig 2 and defines the angle θ.

The "allowed character" circular dichroism then depends on the sum of two terms. When $\theta = 90°$, an octant rule, as depicted in the upper right of the figure, applies to the sign of circular dichroism that depends on the perturber placement when oriented as described. When the perturber is positioned to lie on the octant nodal surfaces, circular dichroic absorption will still result if $\theta \neq 0, 90°$. The circular dichroism sign then depends on the perturber position according to the conical sectors shown in the lower figure. For more general conditions, both terms will contribute.

Static coupling

The second term of Eq 29 gives rotatory strength that depends on charges in the molecule. For a transition of an inherently symmetric chromophore of point group C_{2v} that is magnetic dipole allowed and electric dipole forbidden, the leading term is:

$$R_{om} = -3iR^{-5}XY\epsilon_B \sum_{k \neq m} (E_m - E_k)^{-1}\Theta^{xy}_{km}\mu^z_{ok}m^z_{mo}. \quad (32)$$

The coordinate system of Fig 1 is applicable. The summation term, like $\Theta^{xy}_{om}m^z_{mo}$ of Eq 30, is a constant of the inherently symmetric chromophore transition. Such static charges ϵ_B can arise from substituent dipoles, incomplete nuclear screening, and the like. According to Eq 32, they should lead to a quadrant rule behavior.

"FORBIDDEN CHARACTER" ROTATORY STRENGTH"*

Instead of a more general development, we will consider that part of the "forbidden character" rotatory strength $R_{K,F}$, Eq 26 that arises from one-quantum vibronic coupling. The perturbation definition of C^r_{LK}, Eq 8 yields:

$$\mathbf{C}_r \cdot \mathbf{B}_r = \sum_{\alpha,\alpha'} (E_m - E_\alpha)^{-1}(E_m - E_{\alpha'})^{-1} \quad (33)$$

$$([AB]_\alpha|H^r|A_mB_o)(A_mB_o|H^r|[AB]_{\alpha'})(A_oB_o|\boldsymbol{\mu}|[AB]_\alpha) \cdot ([AB]_{\alpha'}|\mathbf{m}|A_oB_o)$$

where $[AB]_\alpha$ indicates either A_iB_o or A_oB_i type

*The general structure of theory in this section was presented at the Ann Arbor meeting, National Academy of Sciences (October 1967).

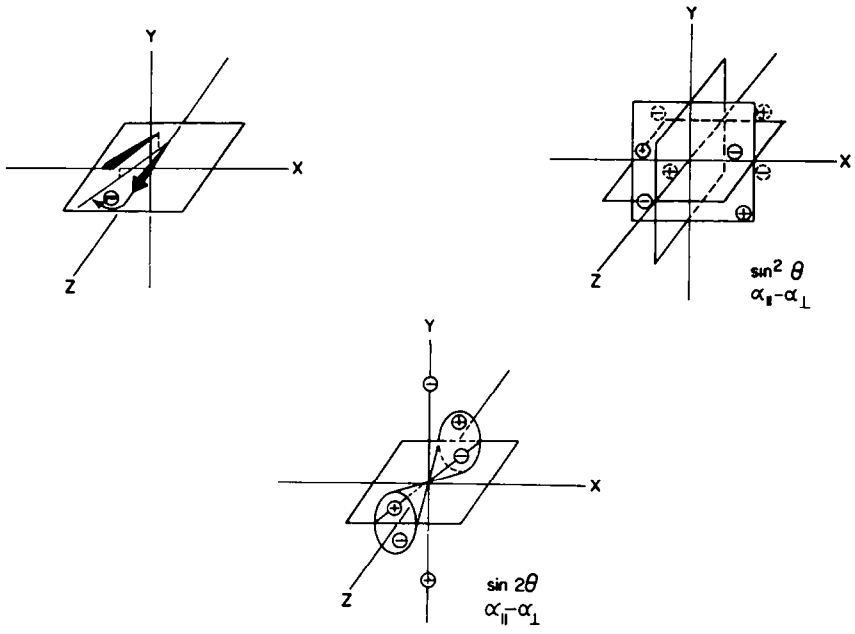

Fig 2. A two-term rotatory strength for the "allowed character" of a dipole allowed transition. The sectors are interpreted as in Fig 1. The trigonometric functions and polarizability anisotropy are additional factors that control the sign of rotatory strength. The signs shown are for perturber anisotropy $(\alpha_\parallel - \alpha_\perp) > 0$ and, for the conical surfaces, $0 < \theta < \pi/2$, where θ is defined as shown in the upper left.

terms and

$$H^r = [\partial(H^A + H^B + V)/\partial Q_r]_0. \tag{34}$$

The matrix elements $H'_{am} = ([AB]_a|H^r|A_mB_o)$ can be expanded by Eq 34. It can be shown that the only important contribution to the transition rotatory strength of a single r mode derives from the perturbation Hamiltonian

$$H^r = [\partial(H^A + V)/\partial Q_r]_0. \tag{35}$$

This is due to the fact that for $H^r = [\partial H^B/\partial Q_r]_0$, the matrix element $H'_{a,m} = (B_0|(\partial H^r/\partial Q_r)_0|B_o)(A_i|A_m)$ or $(B_l|(\partial H^r/\partial Q_r)_0|B_o)(A_o|A_m)$. The terms vanish due to orthogonality of the chromophoric wavefunctions. Therefore, one cannot expect forbidden character to arise from a vibrational dependence of the properties of the perturber itself.

The nuclear normal coordinate Q_r associated with the distortions represented in Eq 33 gives an in-phase movement to every nucleus in the molecule. On the other hand the familiar concepts of group vibrations and the existance of functional group frequencies illustrate the fact that certain nuclei of a molecule usually carry out more motion than others for a given mode of vibration. It is helpful to define certain limiting conditions for the distribution of vibrational motion in the total molecular system.

The normal coordinate Q_r can be expanded:

$$\begin{aligned} Q_r &= \bar{Q}_r^A + \bar{Q}_r^B \\ &= \sum_s l_s^A Q_s^A + \bar{Q}_r^B \end{aligned} \tag{36}$$

where Q_s^A is a symmetry coordinate of the subsystem A. $\bar{Q}_r^A$ and $\bar{Q}_r^B$ are the parts of the normal coordinate located in A and B. Then for one of the terms in $([AB]_a|H^r|A_mB_o)$

$$\left(A_i\left|\left(\frac{\partial H^A}{\partial Q_r}\right)_0\right|A_m\right) = \sum_s l_s^A \left(A_i\left|\left(\frac{\partial H^A}{\partial Q_s^A}\right)_0\right|A_m\right) \tag{37}$$

one may apply symmetry arguments to determine the states α (or more specifically i) of Eq 33 which will have non-vanishing $(A_i|(\partial H^A/\partial Q_s^A)_0|A_m)$.

Case III A will be defined as the limiting case where l_s^A are non-zero for symmetry coordinates of more than one irreducible representation of the symmetric chromophore.

Then "forbidden character" rotatory strength, Eq 33, contains terms

$$\begin{aligned} \mathbf{C}_r \cdot \mathbf{B}_r = \sum_{i,k} \sum_{s,s'} (E_m - E_i)^{-1}(E_m - E_k)^{-1} \\ l_s^A l_{s'}^A \left(A_i\left|\left(\frac{\partial H^A}{\partial Q_s^A}\right)_0\right|A_m\right)\left(A_m\left|\left(\frac{\partial H^A}{\partial Q_{s'}^A}\right)_0\right|A_k\right)\boldsymbol{\mu}_{oi} \cdot \mathbf{m}_{ko}. \end{aligned} \tag{38}$$

Note that both transition dipoles are of the inherently symmetric chromophore.

For an inherently symmetric chromophore, the scalar product $\mu_{oi} \cdot m_{ko}$ must vanish by symmetry whenever Q_s^{Λ} and Q_t^{Λ} belong to the same representations of the chromophore point group. The scalar product need not vanish, however, when the representations are different. Fig 3 details an example of such ketone activity.

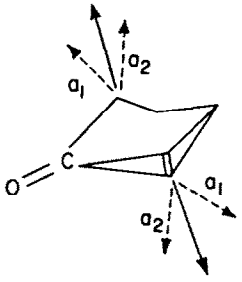

Fig 3. A dissymmetric vibration Q, resolved into components that transform as a_1 and a_2 of the C_{2v} point group. According to Eq 38 and assuming the transition is the n-π^*, a vibronic electric transition dipole parallel to the C=O axis will be created by the a_2 component. A vibronic magnetic transition dipole also along the C=O axis will be created by the a_1 component.

The limiting case represented by Eq 38 does not depend at all on V, the perturbation required in the formulations of allowed character rotatory strength. The forbidden character rotatory strength is that of a chromophore (or an even greater portion of the molecular system) which remains *electronically* symmetric in its vibrational equilibrium position, but undergoes *dissymmetric vibration.* A calculation with Eq 38 requires a complete normal coordinate analysis of the total molecular system to obtain the terms l_r^{Λ} and l_s^{Λ}. Klingbiel and Eyring[10] have carried out calculations of this type for bicycloheptanone systems.

The calculation of matrix elements such as $(A_i|(\partial H^{\Lambda}/\partial Q_s^{\Lambda})_0|A_m)$ has been critically reviewed in the work of Liehr.[11] The definition of coefficients C_{LK} in Eq 8 calls for wavefunctions in the matrix element that are exact for the undistorted ($Q_r = 0$) molecule together with an infinite summation over states i and k in Eq 38.

Liehr's work shows that with the usual limited computational basis set of states, it is more exact to replace $(A_i|(\partial H^{\Lambda}/\partial Q_s)_0|A_m)$ by $[\partial(A_i|H^{\Lambda}|A_m)/\partial Q_s^{\Lambda}]_0$ while "floating" the atomic orbital basis set along with the moving nuclei. In such a scheme, the important contributions of electrons adiabatically following nuclei, in addition to the contributions of the moving nuclei themselves,[10,12] are preserved in computing the vibronic coupling.[13]

Case III B will be defined as the limiting case where all $l_s^{\Lambda} = 0$ except for one well chosen symmetry coordinate Q_t^{Λ}. The lowest order terms for "forbidden character" rotatory strength in Eq 33 arises from

$$\mathbf{C}_r \cdot \mathbf{B}_t = \sum_{k,l} (E_m - E_k)^{-1}(E_m - E_l)^{-1} \qquad (39)$$

$$l_t^{\Lambda}\left(A_k\left|\left(\frac{\partial H^{\Lambda}}{\partial Q_t^{\Lambda}}\right)\right|A_m\right)\left(A_m B_o\left|\left(\frac{\partial V}{\partial Q_r}\right)_0\right|A_o B_l\right)$$

$$(\mu_{ok} \cdot m_{lo} + \mu_{ol} \cdot m_{ko})$$

where for the dynamic coupling matrix element:

$$\left(A_m B_o\left|\left(\frac{\partial V}{\partial Q_r}\right)\right|A_o B_l\right) = l_r^x\left(A_m B_o\left|\left(\frac{\partial V}{\partial X}\right)_0\right|A_o B_l\right) + l_r^y\left(A_m B_o\left|\left(\frac{\partial V}{\partial Y}\right)_0\right|A_o B_l\right) + l_r^z\left(A_m B_o\left|\left(\frac{\partial V}{\partial Z}\right)_0\right|A_o B_l\right). \qquad (40)$$

Note that in Eq 39 one transition dipole is of the chromophore, the other of the perturber.

The term l_r^x for example is related* to the coefficient of the X displacement coordinate (mass weighted) of B in the *rth* normal coordinate.

The matrix element operator $(\partial V/\partial X)_0$ can be found in Table 1. For example, when V is the charge–dipole term, the terms of $(\partial V/\partial X)_0$ consists of the dipole–dipole terms for V that contain μ_x (B), but with ϵ (B) replacing μ_x (B). Similarly when V is the dipole–dipole term, the terms of $(\partial V/\partial Z)_0$ consist of the dipole–quadrupole terms for V that contain $\Theta_{zz}(A)$, $\Theta_{yz}(A)$ and $\Theta_{yz}(A)$ but with μ_z (A) replacing Θ_{zz} (A), μ_x (A) replacing Θ_{yz} (A) and μ_y (A) replacing Θ_{yz} (A). Such an evaluation of the matrix element satisfies the criticisms put forward by Liehr[11] for the computation of vibronic coupling. With these observations the same techniques which yield models for allowed character rotatory strength such as Eqs 30 and 32 will yield models for forbidden character rotatory strength.

Assume now that the forbidden character is associated with the $^1A_2 \leftarrow {}^1A_1$ n-π^* transition of a C_{2v} symmetric carbonyl function (A) of an optically active ketone. The ketone activity is assumed to arise from one substituent (B) creating dissymmetry, as in a mono-substituted adamantanone. The four vibration symmetries of the C_{2v} point group give the following "forbidden character" rotatory strengths†

*More precisely, the term measures the motion of perturber B *relative* to the chromophore A. Pople and Sidman[12] give examples of the rotational and translational transformations that derives the term from the normal coordinate.

†The relation of normal modes a_1, etc. to coefficients l_r^z, etc. has been made ideally simple. Actually, an a_1 mode, for example, may have non-vanishing l_r^x as well as l_r^z.

Table 1. Expanded terms of coulombic potential between two nonoverlapping charge distributions A and B

Charge–dipole

$$V = \epsilon(B)R^{-3}(X\mu_x(A) + Y\mu_y(A) + Z\mu_z(A)]$$

Charge–quadrupole

$$V = \epsilon(B)R^{-5}[(1/2)(3X^2 - R^2)\theta_{xx}(A) + (1/2)(3Y^2 - R^2)\theta_{yy}(A) + (1/2)(3Z^2 - R^2)\theta_{zz}(A) + 3XY\theta_{xy}(A) + 3XZ\theta_{xz}(A) + 3YZ\theta_{yz}(A)]$$

Dipole–dipole

$$V = R^{-5}\{[(R^2 - 3X^2)\mu_x(B) - 3XY\mu_y(B) - 3XZ\mu_z(B)]\mu_x(A) + [-3XY\mu_x(B) + (R^2 - 3Y^2)\mu_y(B) - 3YZ\mu_z(B)]\mu_y(A) + [-3XZ\mu_x(B) - 3YZ\mu_y(B) + (R^2 - 3Z^2)\mu_z(B)]\mu_z(A)\}$$

Dipole–quadrupole

$$V = (3/2)R^{-7}\{[(3R^2X - 5X^3)\mu_x(B) + (R^2Y - 5X^2Y)\mu_y(B) + (R^2Z - 5X^2Z)\mu_z(B)]\theta_{xx}(A) + [(R^2X - 5XY^2)\mu_x(B) + (3R^2Y - 5Y^3)\mu_y(B) + (R^2Z - 5Y^2Z)\mu_z(B)]\theta_{yy}(A) + [(R^2X - 5XZ^2)\mu_x(B) + (R^2Y - 5YZ^2)\mu_y(B) + (3R^2Z - 5Z^3)\mu_z(B)]\theta_{zz}(A) + 2[(R^2Y - 5X^2Y)\mu_x(B) + (R^2X - 5XY^2)\mu_y(B) - 5XYZ\mu_z(B)]\theta_{xy}(A) + 2[(R^2Z - 5X^2Z)\mu_x(B) - 5XYZ\mu_y(B) + (R^2X - 5XZ^2)\mu_z(B)]\theta_{xz}(A) + 2[-5XYZ\mu_x(B) + (R^2Z - 5Y^2Z)\mu_y(B) + (R^2Y - 5YZ^2)\mu_z(B)]\theta_{yz}(A)\}$$

$$R^{a_1}_{K,F} = -15iXY(R^2 - 7Z^2)R^{-9}\alpha_B\Theta^{xy}_{o,n\pi}l_r^z M^{a_1} \quad (41)$$

$$R^{b_2}_{K,F} = \tfrac{1}{2}Y(R^2 + 10X^2 - 5Y^2)R^{-7}\alpha_B\Theta^{xy}_{o,n\pi}E_{n\pi}\frac{2\pi}{hc}l_r^y M^{a_2} \quad (42)$$

$$R^{b_1}_{K,F} = 15XYZR^{-7}\alpha_B\Theta^{xy}_{o,n\pi}E_{n\pi}\frac{2\pi}{hc}l_r^y M^{b_1} \quad (43)$$

$$R^{b_2}_{K,R} = -15XYZR^{-7}\alpha_B\Theta^{xy}_{o,n\pi}E_{n\pi}\frac{2\pi}{hc}l_r^y M^{b_2} \quad (44)$$

where

$$M^{b_2} = \sum_i (E_{n\pi} - E_i)^{-1}\left(A_i\left|\left(\frac{\partial H^A}{\partial Q^A_{t(r)}}\right)_0\right|A_{n\pi}\right)l^A_{t(r)}\mu^x_{oi}\xi_r \quad (45)$$

M^{b_2} is essentially a constant of the inherently symmetric chromophore for a given vibrational mode of the given symmetry. M^{b_1} is obtained by replacing μ^y_{oi} by μ^y_{oi}. For M^{a_2} and M^{a_1}, μ^z_{oi} and m^r_{io} respectively replace μ^x_{oi}.

One must keep in mind that Eqs 41–44, like the equations for "allowed character" rotatory strength, are based on leading terms. Successive terms and other terms depending on anisotropy of polarizability, for example, are not given and might contribute significantly in more complete calculations.

Eq 44 for $R^{b_2}_{K,F}$ closely resembles the "allowed character" expression, Eq 30, even predicting an octant rule. The term im_{no} of Eq 30 is replaced by $E_{n\pi}(2\pi/hc)l_r^y M^{b_2}$. By some rearrangement

$$E_{n\pi}\frac{2\pi}{hc}l_r^y M^{b_2} = \sum_i\left[(E_{n\pi} - E_i)^{-1}\left(A_i\left|\left(\frac{\partial H^A}{\partial Q_t^A}\right)_0\right|A_{n\pi}\right) \times l^A_{t(r)}\xi_r^{1/2}\right]\frac{e}{2m_ec}\left(l_r^y\xi_r^{1/2} \times \frac{2m_eE_{n\pi}}{e\hbar}\mu^x_{oi}\right). \quad (46)$$

The term in brackets is a dimensionless quantity that governs ordinary absorption vibronically coupled dipole strength. We may compare the remaining term to a magnetic transition dipole $im^z_{n\mu,o}$. Since $e/2m_ec$ is the gyromagnetic ratio, $l_r^y\xi_r^{1/2}$ takes the place of a radial distance and $2m_eE_{n\pi}\mu^x_{oi}/2\hbar$ is a momentum perpendicular to the radial vector. Eq 42 for $R^{b_2}_{K,F}$, having a sector rule other than octant-like, could yield "forbidden character" rotatory strength where the "allowed character" according to Eq 30 is minimal.

The β-axial substituted adamantanones synthesized by Snatzke *et al.*[14] should follow closely the assumptions of the model. Their circular dichroisms show anomolies that are readily accomodated as "forbidden character".

THE DISTRIBUTION OF "ALLOWED" AND "FORBIDDEN CHARACTER"[4,7]

When considering for example the $n - \pi^*$ transition of a ketone, Eq 30 defines the integrated total "allowed character" rotatory strength $R_{K,A}$. As Eq 24 implies, this integrated total represents the sum over such detailed structure in the electronic UV-visible spectrum as can be ascribed to the "allowed character" mechanism.

In a similar way Eq 44, for example, represents the integrated total "forbidden character" $R_{K,F}$ arising from a b_2 chromophore vibration. While Eq 44 is limited to "one quantum" vibronic coupling, "forbidden character" will also obtain from the "two quantum" coupling mechanisms involving C_π and B_π terms of Eq 26.

Where do the "allowed character" and "forbidden character" R^{Kk}_{No} fall in a spectrum? It is possible to define such things as the center of gravity and the

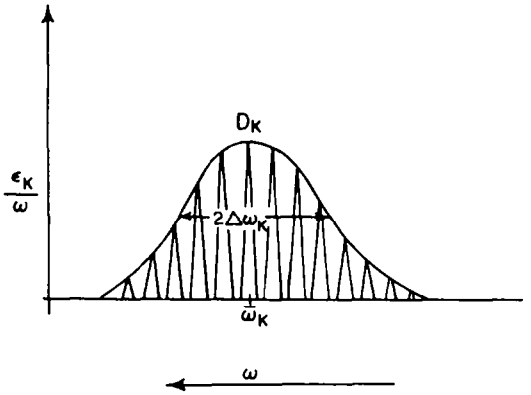

Fig 4. A schematic distribution of K←N absorption band "spikes" and the parameters for characterization of the distribution. Each spike has the area D_{Nn}^{Kk} and is centered at the frequency ω_{Nn}^{Kk}. D_K is the total area under the spikes. The mean frequency $\bar{\omega}_K$ is the center of gravity of such a distribution. The width $\Delta\omega_K$ is a measure of the spread of the distribution. If the distribution is Gaussian, the width is one half of the frequency interval between the two points where the intensity falls to 1/e of the maximum. In many cases, the conditions of observation yield a smooth curve for the distribution.

spread or width of their distribution. (See Fig 4.) While this still avoids an answer feature for feature, it is advantageous for a number of reasons. As already mentioned, the vibrational detail represented by a discrete peak for each R_{No}^{Kk} may not be discernible in a spectrum broadened by solvent effects or extensive overlap of peaks. Secondly, even if a given detail R_{No}^{Kk} is discernible, part of its intensity may be "allowed character" and part "forbidden character". Finally, it seems likely that such expressions can be used to analyse in a broad sense a broad curve of solution circular dichroism, somewhat as detailed vibrational analyses are made of discrete ordinary absorption spectra recorded from the vapor phase.

The spectral distribution of "allowed character", as given by its center of gravity and its width, is the same for circular dichroic absorption as it is for ordinary absorption. Moreover the peaks R_{No}^{Kk} and D_{No}^{Kk} for each k (Fig 5), if discernible, will have the same relative intensity as well as position in frequency.

The center of gravity or mean frequency is given by:

$$\bar{\omega}_{K,A} = \hbar^{-1}V_K^{00} + \frac{1}{2}\left(\sum_\tau \omega_\tau - \sum_\tau \omega_\tau\right) + (2\hbar)^{-1}\sum_\tau l_K^{\tau\tau}\delta_\tau^2 + \frac{1}{4}\sum_\tau (\omega_\tau - \omega_{r(\tau)})^2/\omega_{r(\tau)}. \quad (48)$$

The first two terms define ω_{No}^{Ko} the position of the 0–0 vibrational band. The last two terms move the center of gravity to higher values. They reflect the

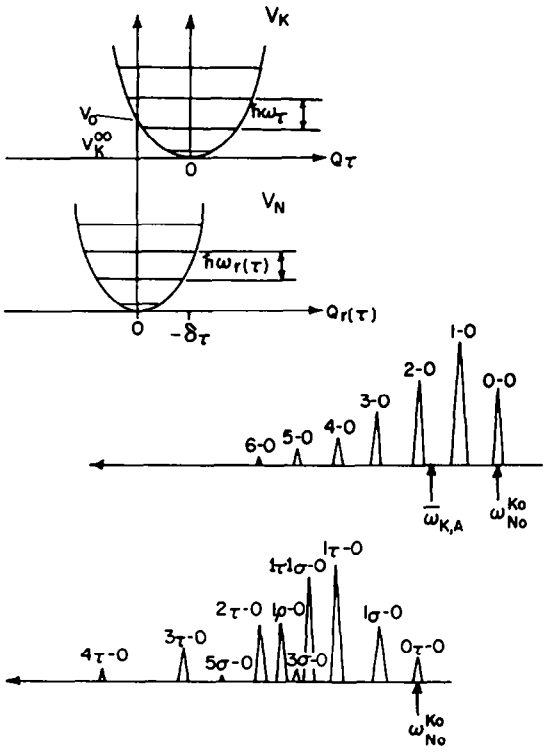

Fig 5. Upper panel: The nuclear potential surfaces V_K and V_N (cf. Eqs 9 and 14) for a molecular system as a function of one normal co-ordinate $Q_{r(\tau)}$. The origins of the potential surfaces are separated by the energy V_K^{00}. The levels contained in the parabolas correspond to eigenvalues of Eqs 1 and 14. In this case the normal mode coordinate in the upper state is given by $Q_\tau = Q_{r(\tau)} + \delta_\tau$ indicating a change in molecular size or shape accompanying electronic excitation. Normal mode frequencies are $\omega_\tau = \omega_{r(\tau)}$. These conditions correspond to no mixing of modes accompanying electronic excitation.

Middle Panel: The "allowed character" spectrum that arises from the set of potential surfaces. Several sets may contribute in a spectrum. For both ordinary and circular dichroic absorption, all such features will have the same sign. When $\delta_\tau = 0$, only *very* small portions of the 2–0, 4–0, 6–0, etc. bands will appear in addition to the 0–0 band if $\omega_\tau \neq \omega_{r(\tau)}$. The "allowed character" distribution has some mean frequency $\bar{\omega}_{K,A}$. The frequency ω_{No}^{Ko} designates the location of the real origin, the 0–0 band.

Lower Panel: A schematic "forbidden character" spectrum that arises in part from the potential surfaces shown. The progression 0_τ-0, 1_τ-0, 2_τ-0, 3_τ-0, 4_τ-0, etc. represents one- and two-quantum coupling when $\delta_\tau \neq 0$. The appearance would be similar but not identical if only one-quantum coupling were important. The progression 1_σ-0, 3_σ-0, 5_σ-0, etc. represents one-quantum coupling with $\delta_\sigma = 0$, $\omega_\sigma \neq \omega_{r(\sigma)}$. The feature $1_\rho 1_\sigma$-0 arises from two-quantum coupling. The sign in circular dichroism for the one-quantum coupled component and the two-quantum coupled component, like the sign for the "allowed character", are given by the respective terms in Eq 26. Each feature could serve as a "false" origin, its intensity being distributed in the progression that gives rise to the "allowed character" distribution.

influence that vibrational progressions obviously will have in locating the distribution center of gravity. As one might expect, the same parameters that define the contribution of vibrational progressions to mean frequency define also a width:

$$\Delta\omega_{K,A} = \left[(2\hbar)^{-1}\sum_{\tau} I_K^{\infty}\delta_\tau^2\omega_\tau^2/\omega_{r(\tau)} + \frac{1}{8}\sum_{\tau}(\omega_\tau^2 - \omega_{r(\tau)}^2)/\omega_{r(\tau)}^2\right]^{1/2}. \quad (49)$$

"Forbidden character" has a width and center of gravity that differs from that for the allowed character. Indeed the two-quantum coupled "forbidden character" has a width and center of gravity that differs from that for the one-quantum coupled "forbidden character". Furthermore, one can expect that these differences are not exactly the same in circular dichroic absorption as they are in ordinary absorption.

The difference in circular dichroism between the mean frequency for the one-quantum coupling and the "allowed character" is:

$$\omega_{K,F(\tau)}^0 - \bar{\omega}_{K,A}^0 = \omega_\tau + \tfrac{1}{2}(\omega_\tau - \omega_{r(\tau)})^2/\omega_{r(\tau)} + \Delta^0 \quad (50)$$

The difference for ordinary absorption is the same except that Δ replaces Δ^0. Without Δ or Δ^0, the one-quantum coupled "forbidden character" will be at higher frequencies almost exactly as expected from its displacement of false origin by ω_τ from the true origin, the 0–0 vibration band (Fig 6). The second term depending on frequency difference is comparatively small.

The terms Δ and Δ^0 depend in a complex way on the change in size or shape of a molecule that can accompany the electronic excitation of the transition. The circular dichroism term Δ^0 depends in part on the factor $C_r\langle K^0|\mathbf{m}|N^0\rangle\delta_r$. Thus if the reshaping indicated by δ_r corresponds in motion to a vibronically coupled vibrational mode, it can influence the distribution of one-quantum coupled rotatory strength. Δ and Δ^0 are not equal and can be separately positive, negative, or zero.

Ignoring relatively small frequency difference terms that arise from $\omega_\tau \neq \omega_{r(\tau)}$, the difference between "forbidden character" and "allowed character" width of distribution can approximately vanish. But in case one encounters molecular reshaping such as contributes to the Δ^0 of Eq 50, the width of one-quantum coupled "forbidden character" can be up to half again as large as that of the allowed character. More exactly, if there is only one vibrational mode involved in the molecular reshaping, and if that vibrational mode is also vibronically coupled

$$(\Delta\omega_{K,F(\tau)}^0) = 3(\Delta\omega_{K,A}^0)^2 + \Gamma^0 \quad (51)$$

Γ^0 depends on the same parameters that defined Δ^0.

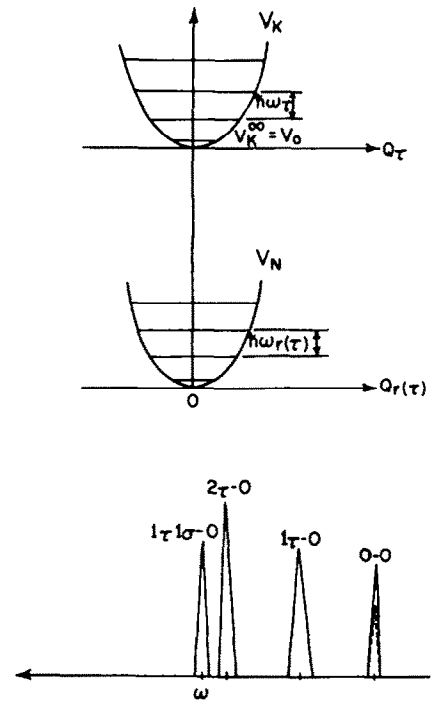

Fig 6. Upper Panel: Potential surfaces as in figure 5 but with $Q_\tau = Q_{r(\tau)}$.

Lower Panel: A schematic electronic spectrum which may arise from the potential surfaces. The "allowed character" spectrum consists of the dashed portion of the 0–0 band. The one-quantum coupled "forbidden character" spectrum consists of the 1_τ–0 band. The two-quantum coupled "forbidden character" spectrum consists of the 2_τ–0 band and upper portion of the 0–0 band or the $1_\tau 1_\sigma$–0 band alone ($\omega_\sigma > \omega_\tau$) where Q_σ is the normal mode coordinate of another set of potential surfaces. Again each signed feature could serve as a "false" origin, its intensity being distributed in the progression that gives rise to an "allowed character" distribution like that shown in Fig 5.

The width for ordinary absorption is the same except Γ replaces Γ^0.

The two-quantum coupling contributions to mean frequency and width of "forbidden character" are all the more complex. In the case of mean frequency, when there is only one coupled mode and it is *not* related to molecular reshaping on electronic excitation, the two-quantum component is centered at a frequency higher than the "allowed character" by approximately 4/3 ω_τ. The corresponding value for one-quantum coupling was approximately ω_τ (*cf* Eq 50). These mean frequency characteristics for two-quantum coupling are illustrated in Fig 7.

It would appear that the identification of "characters" by the uniquely different properties of their spectral distributions may well be feasible. Comparable data on a closely related set of molecular systems would aid such "spectral analyses".

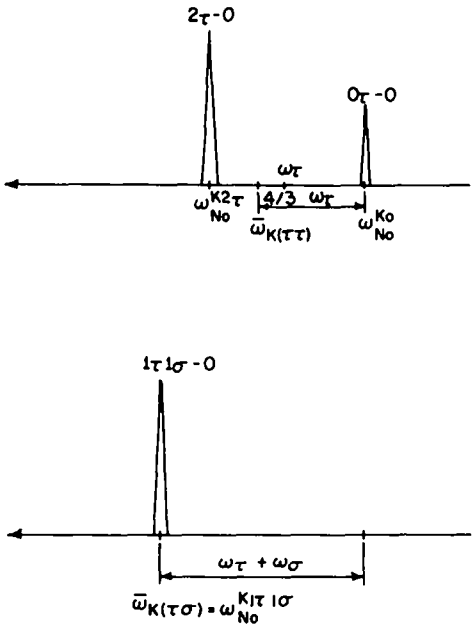

Fig 7. The two-quantum coupling bands (cf. Fig 6) and their mean frequencies $\bar{\omega}_{K(\tau,\tau)}$ and $\bar{\omega}_{K(\tau,\sigma)}$. The two-quantum vibrational integrals of Eqs 21 and 22 show that the intensity of the 2τ–0 band is twice that of the vibronically coupled part of the 0_τ–0 band.

The distribution of intensity in magnetically induced circular dichroism of non-degenerate states should lend itself to similar treatment.[15] Except for terms that will be the analogs of Δ^0 and Γ^0, it is clear that similar effects should be observed. And moreover, the intensity of ketone $n-\pi^*$ "forbidden character" should be more prominent than in natural circular dichroism.[15,16]

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