Anharmonic Effects in Vibrational Circular Dichroism

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Abstract: A formalism has been developed for the evaluation of the rotational strength of a vibrational transition using first-order anharmonic wave functions. This formalism, in contrast to the previous harmonic treatments of the problem, admits circular dichroism in overtone and combination transitions. Explicit expressions have been derived for the rotational strengths of two-quantum vibrational transitions. The possibility of anharmonic contributions to the circular dichroism of vibrational fundamentals is also discussed. It appears that such contributions may arise through anharmonic resonance between a fundamental and an overtone or combination, or through second-order anharmonic effects. These second-order anharmonic effects are shown to be of the same order of magnitude as non-Born–Oppenheimer contributions to the rotational strength.

I. Introduction

Previous calculations[1,2] of the rotational strength associated with a molecular vibrational transition have been based on two assumptions; the first is that the vibrational wave functions are adequately described within the harmonic-oscillator approximation, the second is that the electric and magnetic dipole-moment operators may be approximated by the assumption of a fixed partial charge (fpc) on each atom of the molecule which follows exactly the vibrational motions of that atom.[3] This harmonic-fpc model was first used by Fickett[1a] and later by Cohan and Hameka,[1b] to calculate the rotational strengths of molecules made optically active by isotopic substitution. Deutsche and Moscowitz[1c] used the harmonic-fpc model to calculate the vibrational ORD and CD spectra of several helic polymers. Schellman[2a] has reported harmonic-fpc calculations for some methypyrrolidones and has given a concise development of the basic theory. The harmonic-fpc model was also used by Snir, Frenkel, and Schellman[2b] and by Faulkner et al.[2c]

There have recently been two experimental observations which have led us to consider the extension of the harmonic-fpc model to include anharmonic effects. One observation is the result of studies in our own laboratory in which we have compared the observed rotational strengths associated with a number of CH-stretching vibrations with the rotational strengths calculated on the basis of the harmonic-fpc model, for example, in tartaric acid and 2,2,2-trifluoro-1-phenylethanol. Generally in these investigations we have found that the calculated rotational strengths are an order of magnitude less than the observed ones and, moreover, that the calculated rotational strengths of the CH-stretching vibrations are not very sensitive to the assumed harmonic force field. The fundamental difficulty with the calculations seemed to be that the matrix element of the magnetic dipole-moment operator based on the harmonic-fpc model was much too small, the only contributions being the result of small displacements of the other atoms in the molecule in the CH-stretching normal coordinate. These calculations are discussed in detail in Appendix I of this paper. Accordingly, we sought some other important contribution to the matrix element of the magnetic dipole-moment operator and decided to consider the mixing of the CH-stretching fundamental with the higher vibrational states involving the CH deformations. Such mixing would stem from anharmonic terms in the vibrational Hamiltonian and its consideration would imply an extension of the harmonic-fpc model to include anharmonic effects. The other relevant observation is the report by Keiderling and Stephens[4] of the measurement of vibrational circular dichroism in the overtone and combination-band regions of several organic molecules. In the harmonic-fpc approximation the rotational and dipole strengths of such two-quantum (binary) transitions must vanish, and any theory for such optical activity must necessarily include vibrational anharmonicity.

In this paper we develop the formalism for the calculation of the rotational strengths of vibrational transitions with first-order anharmonic wave functions. The basic theory for the treatment of anharmonicity is established in section II using the contact-transformation approach of Nielsen et al.[5] The fpc model is retained as the basis for the electric and magnetic dipole-moment operators and in this theory all contribution from electrical anharmonicity is ignored. The extended model, which uses anharmonic vibrational wave functions with the fixed partial charge assumption, is conveniently described as the anharmonic-fpc model. From it we have derived explicit expressions for the electric and magnetic dipole transition moments for fundamentals and for binary overtone, combination, and difference bands, and from these the corresponding dipole and rotational strengths may be calculated. The first order anharmonic wave functions give, of course, exactly the same expressions for the rotational strengths of the fundamental transitions as those obtained in the harmonic-fpc approximation.

The contact-transformation approach, which is equivalent to second-order perturbation theory (first-order wave functions), fails in the case of resonance or near resonance. The modification of the anharmonic-fpc model for the treatment of such cases is given in section III. This modification results in anharmonic contributions to the rotational strengths of the fundamentals.

Section IV contains an order-of-magnitude analysis of the anharmonic-fpc rotational and dipole strengths for the vibrational fundamentals and binary overtone, combination, and difference transitions. This analysis shows that, although the rotational and dipole strengths for the two-quantum transitions are expected to be considerably smaller in magnitude than the rotational and dipole strengths of the fundamental, the experimentally important dissymetry factor, G ($=4R/D$), for the binary transitions is expected to be of the same order of magnitude as for a fundamental. This is an important result since state-of-the-art detectors and photoelastic modulators for the near infrared are considerably better than those for the mid- and far-infrared, and consequently it is much easier to measure infrared circular dichroism in the overtone-combination band region. It is also consonant with the experimental observations of Keiderling and Stephens.[4]

Section IV also includes a qualitative discussion of the extension to second-order wave functions of the treatment given in section II. At this level of approximation, the electric and magnetic dipole transition moments for a fundamental differ from those obtained with the harmonic-fpc model even in the absence of a resonance interaction between the fundamental and a binary level. However, it is shown that the correction terms to the harmonic-fpc electric dipole transition moment arising from the second-order treatment are of the same order of magnitude as terms which arise from the breakdown of the Born–Oppenheimer approximation.[6]

The difficulty of using other intensity models instead of the fpc model is addressed in section IV. Using, for example, the bond-moment hypothesis[7] to calculate the electric dipole transition moment while using the fpc model to calculate the magnetic dipole transition moment will lead, in general, to an origin-dependent rotational strength. Further, since most of the infrared absorption-intensity models in use today were developed only as models for the electric dipole-moment operator, the use of these models for the magnetic dipole-moment operator often leads to anbiguous results.

Finally, the problem of calculating the vibrational rotational strength without recourse to explicit models is discussed in section IV. It is shown that, within the Born–Oppenheimer approximation, the electronic contribution to the magnetic dipole transition moment must vanish. Moreover, it is the corrections to the Born–Oppenheimer wave function that produce an electronic contribution to the magnetic dipole transition moment that is of the same order of magnitude as the contributions to the magnetic dipole transition moment arising from nuclear motion within the Born–Oppenheimer approximation. It is also shown that if the rotational strength calculation is carried out within the Born–Oppenheimer approximation (i.e., with no electronic magnetic dipole transition moment) the rotational strength will be origin dependent.

II. Basic Theory

The anharmonic vibrational problem is conveniently handled in the contact-transformation formalism of Nielsen.[5] We consider a purely vibrational Hamiltonian operator of the form $H = H_0 + H_1 + \ldots$ where the harmonic part

$$H_0 = \frac{hc}{2} \sum_s \omega_s [(p_s/\hbar)^2 + q_s{}^2] \tag{1}$$

and the anharmonic part

$$H_1 = hc \sum_{s \leq s' \leq s''} k_{ss's''} q_s q_{s'} q_{s''} + \ldots \tag{2}$$

The normal coordinates, q_s, and conjugate momenta, $p_s/\hbar$, are in dimensionless form. This Hamiltonian is contact transformed by an operator T to yield

$$\tilde{H} = THT^{-1} \tag{3}$$

The condition on T is to require that $\tilde{H}$ be diagonal in the eigenfunctions of H_0, $\psi_n{}^0$. It is then easy to see that the eigenfunctions of H, ψ_n, are given by

$$\psi_n = T^{-1}\psi_n{}^0 \tag{4}$$

The contact transformation, T, is written as

$$T = e^{i\epsilon S} \tag{5}$$

where ϵ is a smallness parameter and S is an Hermitian function of the normal coordinates and their conjugate momenta. The present treatment is restricted to first-order anharmonic wave functions and so only the first contact transformation function is used. The function, S, is given by[5,8]

$$S = \sum_{a \leq b \leq c} S^{abc} p_a p_b p_c + \sum_{a \leq b, c} S_{ab}{}^c \frac{1}{2} (p_c q_a q_b + q_b q_a p_c) \tag{6}$$

Explicit expressions for the numerical coefficients, S^{abc} and $S_{ab}{}^c$, have been given by Amat, Nielsen, and Tarrago.[8]

This form of the S function, which contains no angular-momentum operators, implies that the only additional terms considered in H are those associated with vibrational anharmonicity. The neglect of rotational and rotation–vibration interaction terms is justified since the theory is to be applied to spectra measured in condensed phases.

From eq 4 the matrix elements of an operator, f, may be written in the first-order anharmonic basis as

$$(\psi_n|f|\psi_m) = (\psi_n{}^0|TfT^{-1}|\psi_m{}^0) \tag{7}$$

and so, to evaluate the anharmonic matrix elements of f, it is sufficient to evaluate the matrix elements of the contact-transformed operator, $\tilde{f} = TfT^{-1}$, in the harmonic-oscillator basis. f and $\tilde{f}$ are written in order-of-magnitude expansions as

$$f = f_0 + \epsilon f_1 + \epsilon^2 f_2 + \ldots$$
$$\tilde{f} = \tilde{f}_0 + \epsilon \tilde{f}_1 + \epsilon^2 \tilde{f}_2 + \ldots$$

and, with the definition of T given in eq 5, it is easily shown that

$$\tilde{f}_0 = f_0,$$
$$\tilde{f}_1 = f_1 + i[S, f_0] \tag{8}$$

and

$$\tilde{f}_2 = f_2 + i[S, f_1] - \frac{1}{2}[S, [S, f_0]]$$

In the fixed partial charge (fpc) model the electric (μ) and magnetic ($\mathbf{m}$) dipole-moment operators are given by[2a]

$$\mu = \sum_A z_A e \mathbf{R}_A \tag{9}$$

$$\mathbf{m} = \sum_A \frac{z_A e}{2m_A c} \mathbf{R}_A \times \mathbf{P}_A \tag{10}$$

Here $\mathbf{R}_A$ and $\mathbf{P}_A$ are the Cartesian position and momentum of the Ath atom which has mass m_A and partial charge $z_A e$. Before proceeding, these expressions must be transformed into dimensionless normal coordinates. The Cartesian position and momentum are linearly related to the dimensionless normal coordinates, $\{q_s\}$, and conjugate momenta, $\{p_s\}$, by

$$\mathbf{R}_A = \mathbf{R}_A{}^0 + \sum_s \mathbf{t}_{As} \frac{1}{\alpha_s} q_s \tag{11}$$

$$\mathbf{P}_A = \sum_s m_A \mathbf{t}_{As} \alpha_s p_s \tag{12}$$

where $\mathbf{R}_A{}^0$ is the equilibrium position of the Ath atom. The vectors $\mathbf{t}_{As}$ are given by

$$t_{As} = \mathbf{l}_{As}/\sqrt{m_A}$$

where $\mathbf{l}_{As}$ is the vector giving the Cartesian displacement of the Ath atom in the sth normal mode and is obtained from the L_x matrix.[9] The constant α_s in eq 11 and 12 arises from the transformation to dimensionless normal coordinates and is given by

$$\alpha_s = [2\pi c \omega_s/\hbar]^{1/2}$$

where ω_s is the harmonic wavenumber of the sth normal mode in cm^{-1}. Equations 11 and 12 are substituted into eq 9 and 10 to yield

$$\mu = \sum_A z_A e \mathbf{R}_A{}^0 + \sum_s \left(\frac{1}{\alpha_s} \sum_A z_A e \mathbf{t}_{As}\right) q_s \tag{13}$$

$$\mathbf{m} = \sum_s \left(\alpha_s \sum_A \frac{z_A e}{2c} \mathbf{R}_A{}^0 \times \mathbf{t}_{As}\right) p_s + \sum_{s,s'} \left(\frac{\alpha_{s'}}{\alpha_s} \sum_A \frac{z_A e}{2c} \mathbf{t}_{As} \times \mathbf{t}_{As'}\right) q_s p_{s'} \tag{14}$$

Since the first term in eq 13 is just the static electric dipole moment at the equilibrium configuration, $\boldsymbol{\mu}_0$, the form of eq 13 may be simplified to

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \sum_s \mathbf{t}_s q_s = \boldsymbol{\mu}_0 + \epsilon \boldsymbol{\mu}_1 \tag{15}$$

where

$$\mathbf{t}_s = \frac{1}{\alpha_s} \sum_A z_A e \mathbf{t}_{As} \tag{16}$$

It is obvious from eq 15 that in the fpc model

$$\mathbf{t}_s = (\partial \boldsymbol{\mu}/\partial q_s)$$

and all higher order derivatives of the dipole moment vanish; one should, however, note that there may be effective contributions to higher derivatives through compensating rotations.[10]

The expression for **m** may also be recast as

$$\mathbf{m} = \sum_s \boldsymbol{\xi}_s p_s + \sum_{s,s'} \boldsymbol{\xi}_{ss'} q_s p_{s'} = \epsilon \mathbf{m}_1 + \epsilon^2 \mathbf{m}_2 \tag{17}$$

where

$$\boldsymbol{\xi}_s = \alpha_s \sum_A \frac{z_A e}{2c} \mathbf{R}_A{}^0 \times \mathbf{t}_{As} \tag{18}$$

$$\boldsymbol{\xi}_{ss'} = \frac{\alpha_{s'}}{\alpha_s} \sum_A \frac{z_A e}{2c} \mathbf{t}_{As} \times \mathbf{t}_{As'} \tag{19}$$

Note that $\boldsymbol{\xi}_{ss'} \neq \boldsymbol{\xi}_{s's}$ and $\boldsymbol{\xi}_{ss} = 0$. The ordering of $\mathbf{m}_1$ in first order and $\mathbf{m}_2$ in second order follows from the inequality

$$|\mathbf{R}_A{}^0| \gg \left| \frac{1}{\alpha_s} \mathbf{t}_{As} q_s \right|$$

The first term in eq 14 may be interpreted as the contribution to the magnetic dipole-moment operator arising from the component of the vibrational motion corresponding to rotation of the partially charged atoms about the overall molecular-coordinate origin. The second term in eq 14 may be interpreted as the contribution to **m** arising from each partially charged atom moving with momentum $p_{s'}$ on a lever arm q_s relative to an origin at the equilibrium position of the atom.

From eq 8 and 15 it is apparent that the terms in the contact-transformed electric dipole-moment operator are given by

$$\tilde{\boldsymbol{\mu}}_0 = \boldsymbol{\mu}_0$$

$$\tilde{\boldsymbol{\mu}}_1 = \boldsymbol{\mu}_1$$

$$\tilde{\boldsymbol{\mu}}_2 = i[S, \boldsymbol{\mu}_1]$$

and thus, to second order,

$$\tilde{\boldsymbol{\mu}} = \boldsymbol{\mu}_0 + \boldsymbol{\mu}_1 + i[S, \boldsymbol{\mu}_1] \tag{20}$$

Similarly, from eq 8 and 17

$$\tilde{\mathbf{m}}_0 = 0$$

$$\tilde{\mathbf{m}}_1 = \mathbf{m}_1$$

$$\tilde{\mathbf{m}}_2 = \mathbf{m}_2 + i[S, \mathbf{m}_1]$$

and the contact-transformed magnetic dipole moment, $\tilde{\mathbf{m}}$, is given to second order by

$$\tilde{\mathbf{m}} = \mathbf{m}_1 + \mathbf{m}_2 + i[S, \mathbf{m}_1] \tag{21}$$

The commutators in eq 20 and 21 may be computed readily with the easily derived relations

$$[S, q_s] = -i\hbar \frac{\partial S}{\partial p_s}$$

$$[S, p_s] = i\hbar \frac{\partial S}{\partial q_s}$$

The results for the first-contact-transformed electric and magnetic dipole-moment operators are

$$\tilde{\boldsymbol{\mu}} = \boldsymbol{\mu}_0 + \sum_j \mathbf{t}_j q_j + \hbar \sum_j \mathbf{t}_j \left\{ \sum_{a \leq b} S^{abj} p_a p_b (1 + \delta_{aj} + \delta_{bj}) + \sum_{a \leq b} S_{ab}{}^j q_a q_b \right\} \tag{22}$$

$$\tilde{\mathbf{m}} = \sum_j \boldsymbol{\xi}_j p_j + \sum_{j,k} \boldsymbol{\xi}_{jk} q_j p_k - \hbar \sum_j \boldsymbol{\xi}_j \left\{ \sum_{a,c} S_{aj}{}^c \frac{1}{2} (p_c q_a + q_a p_c)(1 + \delta_{aj}) \right\} \tag{23}$$

The fundamental and binary transition matrix elements of eq 22 and 23 are easily computed and are

$$(v_s | \tilde{\boldsymbol{\mu}} | v_s + 1) = \left[\frac{v_s + 1}{2} \right]^{1/2} \mathbf{t}_s \tag{24}$$

$$(v_s + 1 | \tilde{\mathbf{m}} | v_s) = i\hbar \left[\frac{v_s + 1}{2} \right] \boldsymbol{\xi}_s \tag{25}$$

$$(v_s | \tilde{\boldsymbol{\mu}} | v_s + 2) = \frac{\hbar}{2} [(v_s + 1) \times (v_s + 2)]^{1/2} \sum_j \mathbf{t}_j \{ -\hbar^2 S^{ssj} (1 + 2\delta_{sj}) + S_{ss}{}^j \} \tag{26}$$

$$(v_s + 2 | \tilde{\mathbf{m}} | v_s) = -i \frac{\hbar^2}{2} [(v_s + 1)(v_s + 2)]^{1/2} \times \sum_j \boldsymbol{\xi}_j \{ S_{js}{}^s (1 + \delta_{sj}) \} \tag{27}$$

$$(v_s, v_{s'} | \tilde{\boldsymbol{\mu}} | v_s + 1, v_{s'} + 1) = \frac{\hbar}{2} [(v_s + l)(v_{s'} + 1)]^{1/2} \times \sum_j \mathbf{t}_j \{ S_{ss'}{}^j - \hbar^2 S^{ss'j} (1 + \delta_{s'j} + \delta_{sj}) \} \tag{28}$$

$$(v_s + 1, v_{s'} + 1 | \tilde{\mathbf{m}} | v_s, v_{s'}) = \frac{i\hbar}{2} [(v_{s'} + 1) \times (v_s + 1)]^{1/2} (\boldsymbol{\xi}_{ss'} + \boldsymbol{\xi}_{s's}) - \frac{i\hbar^2}{2} [(v_{s'} + 1)(v_s + 1)]^{1/2} \sum_j \boldsymbol{\xi}_j \{ S_{s'j}{}^s (1 + \delta_{s'j}) + S_{sj}{}^{s'} (1 + \delta_{sj}) \} \tag{29}$$

$$(v_s + 1, v_{s'} | \tilde{\boldsymbol{\mu}} | v_{s'} + 1, v_s) = \frac{\hbar}{2} [(v_s + 1) \times (v_{s'} + 1)]^{1/2} \sum_j \mathbf{t}_j \{ S_{ss'}{}^j + \hbar^2 S^{ss'j} (1 + \delta_{s'j} + \delta_{sj}) \} \tag{30}$$

$$(v_{s'} + 1, v_s | \tilde{\mathbf{m}} | v_s + 1, v_{s'}) = \frac{i\hbar}{2} [(v_{s'} + 1)(v_s + 1)]^{1/2} \times (\boldsymbol{\xi}_{ss'} - \boldsymbol{\xi}_{s's}) - \frac{i\hbar^2}{2} [(v_{s'} + 1)(v_s + 1)]^{1/2} \times \sum_j \boldsymbol{\xi}_j \{ S_{sj}{}^{s'} (1 + \delta_{sj}) - S_{s'j}{}^s (1 + \delta_{s'j}) \} \tag{31}$$

Secroun, Barbe, and Jouve[11] previously obtained expressions for the electric dipole transition moment which correspond to eq 24, 26, 28, and 30 if the electrical anharmonicity is assumed to be zero and only the first contact transformation of the electric dipole-moment operator is considered. Overend[12] has recently pointed out that the electric-dipole transition moments for combination and difference bands can be quite different and that there is no simple relationship between the absorption intensity for a combination band and the corresponding difference band. From eq 28–31 it is apparent that the same assertions may be made concerning the rotational strengths for combination and difference bands.

The dipole and rotational strengths are computed from eq 24-31 via the expressions

$$D_{v\rightarrow v'} = |(v|\tilde{\mu}|v')|^2 \qquad (32)$$

$$R_{v\rightarrow v'} = \mathrm{Im}\{(v|\tilde{\mu}|v')(v'|\tilde{\mathbf{m}}|v)\} \qquad (33)$$

The validity of eq 24-31 rests on the assumption that the anharmonic wave functions may be adequately approximated through the use of first-order perturbation theory. But it is well known that perturbation theory breaks down in the case of a vibrational resonance,[8,13] and, in the treatment of the first-order vibrational problem, Fermi resonance ($\omega_s \simeq \omega_{s'} + \omega_{s''}$) and Fermi-Dennison resonance ($\omega_s \simeq 2\omega_{s'}$) are the important cases that require consideration. To anticipate the discussion of resonance effects given in the next section, it is possible, in principle, for either a Fermi or a Fermi-Dennison resonance to significantly alter the calculated rotational strength of a fundamental transition. Indeed, in the first-order treatment presented above, a resonance interaction is the only way the calculated rotational strength of a fundamental may differ from that calculated from the harmonic fpc model. This fact is readily ascertained from the expressions for the electric and magnetic dipole transition moments of a fundamental (eq 24 and 25) since they are independent of the vibrational anharmonicity.

The theory developed in this paper ascribes all the anharmonic effects in the CD intensity to the anharmonic motion of the partially charged atoms. One might treat the electrical anharmonicity by using a more sophisticated model for the electric dipole moment such as the polar tensor[14] or electrooptical models[15] which have been used successfully in the explanation of electric-dipole absorption spectra. However, we have found it difficult to define a magnetic dipole-moment operator in terms of these more sophisticated models. Although the fpc model has some shortcomings, it does allow interpretation of the various terms in both the electric and magnetic diople-moment operators. It is our hope that, even though the fpc model cannot give highly reliable numerical estimates of the dipole or rotational strengths, it can provide some useful insights and a conceptual framework for interpreting vibrational circular dichroism data.

It should be noted that, in general, an absorption band in the vibrational spectrum consists of a main transition with a number of superimposed hot bands. In calculating the intensity it is important to sum the transition probabilities for all contributing transitions using the appropriate population weighting factors. This problem has recently been discussed by Yao and Overend.[16] Similar considerations apply in calculating a rotational strength for comparison with an observed CD spectrum. For transitions originating in the ground vibrational state it is probably safe to use the rotational strength of the main transition with unit weight. However, for difference bands this is not acceptable and population weighting must be taken into account.

III. Effects of Resonance

Nielsen[13] has described in detail the way in which the contact-transformation method may be modified to avoid breakdown because of a first-order anharmonic resonance. Briefly the contact-transformation function is modified in such a way that it removes all terms from $\tilde{H}_1$ save the offdiagonal elements giving rise to the resonance. The resulting matrix of $\tilde{H}_1$ is then diagonalized numerically to give the resonance-corrected energies and wave functions. For example, in the case where $\omega_i \simeq \omega_j + \omega_k$, the contact-transformation function, S, is modified by substituting different values for the coefficients, S^{ijk}, $S_{ij}{}^k$, $S_{ik}{}^j$, and $S_{jk}{}^i$. These modified coefficients no longer contain the divergent energy-difference denominator, $\omega_i - \omega_j - \omega_k$. In that case, the matrix of H will have nonvanishing elements, $\langle v_i, v_j, v_k|\tilde{H}_1|v_i \pm 1, v_j \mp 1, v_k \mp 1\rangle$.

If the orthogonal transformation that diagonalizes the matrix of $\tilde{H}_1$ is denoted as U and the resonance-corrected contact transformation as T_{F}, the new transformed Hamiltonian is given by

$$UT_{\mathrm{F}}HT_{\mathrm{F}}{}^{-1}U^{-1}$$

In matrix terms the rows of U are the eigenvectors of the matrix of $\tilde{H}_1$. Since the new anharmonic wave functions are given by

$$\psi_n = T_{\mathrm{F}}{}^{-1}U^{-1}\psi_n{}^0$$

the matrix elements of an operator, f, are given by

$$\begin{aligned}(\psi_n|f|\psi_m) &= (T_F{}^{-1}U^{-1}\psi_n{}^0|f|T_F{}^{-1}U^{-1}\psi_m{}^0)\\ &= (U^{-1}\psi_n{}^0|T_FfT_F{}^{-1}|U^{-1}\psi_m{}^0) \qquad (34)\end{aligned}$$

Note that for a wave function, $\psi_n{}^0$, not involved in the resonance, U^{-1} acts as the identity operator, viz.,

$$U^{-1}\psi_n{}^0 = \psi_n{}^0 \qquad (35)$$

In the example cited above in which $\omega_i \simeq \omega_j + \omega_k$, the electric dipole transition moment for a fundamental transition in the *i*th normal mode is

$$(U^{-1}\psi_0{}^0|T_{\mathrm{F}}\mu T_{\mathrm{F}}{}^{-1}|U^{-1}\psi_i{}^0)$$

where $\psi_0{}^0$ represents the vibrational ground state and $\psi_i{}^0$ the state with one quantum of excitation in the *i*th normal mode. From eq 35

$$U^{-1}\psi_0{}^0 = \psi_0{}^0$$

and

$$U^{-1}\psi_i{}^0 = (\psi_i{}^0|U^{-1}|\psi_i{}^0)\psi_i{}^0 + (\psi_{jk}{}^0|U^{-1}|\psi_i{}^0)\psi_{jk}{}^0 \qquad (36)$$

where $\psi_{jk}{}^0$ represents the state with one quantum of vibrational energy in each of the normal modes j and k. The two matrix elements in eq 36 are easily recognized as the two elements of the eigenvector of the resonance dyad derived from $\psi_i{}^0$ and $\psi_{jk}{}^0$. Because of the orthogonality of U, we have

$$U_{i,i} = (\psi_i{}^0|U^{-1}|\psi_i{}^0) = (\psi_i{}^0|U|\psi_i{}^0)$$

and

$$U_{i,jk} = (\psi_{jk}{}^0|U^{-1}|\psi_i{}^0) = (\psi_i{}^0|U|\psi_{jk}{}^0)$$

The electric dipole transition moment then becomes

$$\begin{aligned}(\psi_0{}^0|T_{\mathrm{F}}\mu T_{\mathrm{F}}{}^{-1}|U^{-1}\psi_i{}^0) &= U_{i,i}(\psi_0{}^0|T_{\mathrm{F}}\mu T_{\mathrm{F}}{}^{-1}|\psi_i{}^0)\\ &\quad + U_{i,jk}(\psi_0{}^0|T_{\mathrm{F}}\mu T_{\mathrm{F}}{}^{-1}|\psi_{jk}{}^0) \qquad (37)\end{aligned}$$

Thus the calculation of the electric dipole transition moment for a vibrational transition, the upper state of which is involved in a resonance, would proceed in two steps. First, the harmonic-oscillator matrix elements of the electric dipole moment operator transformed with the resonance-corrected contact transformation would be calculated for all the states in the resonance polyad. The final electric dipole moment matrix elements would then be constructed using the eigenvectors of the resonance polyad along the lines of eq 37. Such a resonance interaction may make significant contribution to the optical activity in a CH-stretching fundamental through resonance with the overtones and combinations of the CH deformation modes. The CH-stretching fundamental usually occurs near 2900 cm^{-1} and the two bending fundamentals near 1350 cm^{-1}.[17] The overtones and combination band of the CH-bending modes should occur near 2700 cm^{-1}. Thus the energy separation between the CH-stretching fundamental and the bending overtone is of the order of 200 cm^{-1}. Because of the low relative mass of the hydrogen atom, the bending and stretching vibrations have large amplitude and are therefore more sensitive to anharmonicity in the molecular force field. As a consequence, the off-diagonal matrix element coupling the CH-stretching fundamental with the binary overtones and combination of the CH bending modes is typically quite large (100-150 cm^{-1})[18] and so can lead to significant mixing of the stretching fundamental with the bending overtones and combination.

IV. Discussion

The theory developed in the previous sections rests on two basic assumptions. The first of these is that the perturbation treatment is adequate to describe the anharmonic vibrational wave functions. This is most certainly an acceptable assumption and in those cases in which the perturbation theory breaks down (i.e., in the case of resonance) it is possible to make the necessary corrections to the wave functions. The second, and probably the more serious, assumption is that the fpc model may be used to represent the electric and magnetic dipole moment operators. Although more sophisticated models for the electric dipole moment operator are currently available,[7,14,15] their use in formulating the magnetic dipole moment operator is equivocal. Moreover, the use of, say, a polar-tensor model for the electric dipole moment operator and the fpc model for the magnetic dipole moment operator would, in general, lead to a rotational strength that was origin dependent. To establish this assertion, consider the rotational strength given by

$$R_{0k} \sim \langle 0|\mathbf{R}|k\rangle\langle k|\mathbf{R}\times\mathbf{P}|0\rangle \tag{38}$$

Letting $\mathbf{R} \rightarrow \mathbf{R} + \mathbf{Y}$ yields a new rotational strength, R_{0k}', given by

$$\begin{aligned} R_{0k}' \sim {} & \langle 0|\mathbf{R}|k\rangle\langle k|\mathbf{R}\times\mathbf{P}|0\rangle \\ & + \langle 0|\mathbf{R}|k\rangle \mathbf{Y}\times\langle k|\mathbf{P}|0\rangle \end{aligned} \tag{39}$$

The first term in eq 39 is equal to R_{0k}; the second term in eq 39 will vanish whenever the vectors $\langle 0|\mathbf{R}|k\rangle$ and $\langle k|\mathbf{P}|0\rangle$ are parallel. When this happens the rotational strength will be independent of the choice of molecular origin. But if there are no symmetry restrictions on the directions of $\langle 0|\mathbf{R}|k\rangle$ and $\langle k|\mathbf{P}|0\rangle$, as is usually the case in a chiral molecule, it cannot be assumed that these two matrix elements will always be parallel.

In the theory of the vibrational rotational strength developed in this paper, the fpc model has been used for both the electric and magnetic dipole moment operators. Although this is not a guarantee that the rotational strength will be origin dependent, it can be shown that the rotational strengths calculated from eq 24-31 are, indeed, origin independent.

It is interesting to use the electric and magnetic dipole transition moments, eq 24-31, to evaluate the order of magnitude of the rotational strength for one- and two-quantum transitions. For this analysis it is convenient to go over to the units ($\hbar = c = 1$) and the notation of Mead and Moscowitz.[19] In their notation, the characteristic lengths of electronic motion a_{e} and nuclear motion a_{N} are given by

$$a_{\text{e}} \sim 1/me^2 \qquad a_{\text{N}} \sim \kappa/me^2 \tag{40}$$

Here m is the electronic mass and κ is the usual Born-Oppenheimer expansion parameter, $\kappa \sim [m/M]^{1/4}$, with M denoting a typical nuclear mass. Characteristic electronic and nuclear energies are given by

$$E_{\text{e}} \sim me^4 \qquad E_{\text{N}} \sim me^4\kappa^2 \tag{41}$$

Using these results it may be shown that eq 24 and 25 become

$$|(v_s|\tilde{\boldsymbol{\mu}}|v_s + 1)| \sim |\mathbf{t}_s| \sim \kappa e a_{\text{e}} \tag{42}$$

$$|(v_s + 1|\tilde{\mathbf{m}}|v_s)| \sim |\boldsymbol{\xi}_s| \sim \kappa^3 e/m \tag{43}$$

As is shown in Appendix II the constants in the contact-transformation function (6) are of the order of

$$|S^{abc}| \sim |S_{ab}{}^{c}| \sim \kappa$$

The electric and magnetic dipole transition moments for an overtone transition, eq 26 and 27, become

$$|(v_s|\tilde{\boldsymbol{\mu}}|v_s + 2)| \sim \left|\sum_j \mathbf{t}_j(S^{ssj}(1 + 2\delta_{sj}) + S_{ss}{}^{j})\right| \sim \kappa^2 e a_{\text{e}} \tag{44}$$

$$|(v_s + 2|\tilde{\mathbf{m}}|v_s)| \sim \left|\sum_j \boldsymbol{\xi}_j\, S_{js}{}^{s}(1 + \delta_{sj})\right| \sim \kappa^4 e/m \tag{45}$$

Hence the overtone rotational strength is of order

$$R_{v\rightarrow v+2} \sim \frac{e^2 a_{\text{e}}}{m}\,\kappa^6$$

Comparing this result to the fundamental rotational strength eq 42, 43, 24, and 25 given by

$$R_{v\rightarrow v+1} \sim \frac{e^2 a_{\text{e}}}{m}\,\kappa^4 \tag{46}$$

it is evident that the overtone rotational strength is about two orders of κ smaller than the rotational strength of the fundamental. Similar results may be derived for the rotational strength of the binary combination and difference bands.

The small magnitude of the rotational strength of a binary transition relative to the rotational strength of a fundamental does not necessarily imply that the measurement of overtone optical activity will be any more difficult than the measurement of a vibrational fundamental. The experimentally important parameter is the dissymmetry factor, G, given by

$$G = 4R/D$$

For the fundamental,

$$G \sim \left(\frac{e^2 a_{\text{e}}\kappa^4}{m}\right) \Big/ (e a_{\text{e}}\kappa)^2 \sim e^2\kappa^2$$

for the overtone,

$$G \sim \left(\frac{e^2 a_{\text{e}}\kappa^6}{m}\right) \Big/ (e a_{\text{e}}\kappa^2)^2 \sim e^2\kappa^2$$

The conclusion is that the optical activity of a binary overtone, combination, or difference band should be about as easy to measure as that of a fundamental. This is an important conclusion because, for technological reasons, it is presently easier to measure infrared circular dichrosim in the near-infrared region (1-3 μm) than it is in the mid-infrared region (3-20 μm).

Another interesting order of magnitude comparison is that of the terms, $\boldsymbol{\xi}_j$ and $\boldsymbol{\xi}_{jk}$, that appear in eq 29 and 31. Since $|\mathbf{t}_{Aj}| \sim 1/\sqrt{m_A}$, then

$$|\boldsymbol{\xi}_{jk}| \sim \frac{e}{M} \sim \frac{e}{m}\,\kappa^4$$

From eq 29 the contribution due to the $\boldsymbol{\xi}_j$ terms is given by

$$\left|\sum_j \boldsymbol{\xi}_j\{S_{s'j}{}^{s}(1 + \delta_{s'j}) + S_{sj}{}^{s'}(1 + \delta_{sj})\}\right| \sim \frac{e}{m}\,\kappa^4$$

Clearly the $\boldsymbol{\xi}_j$ term in eq 31 is of the same order of magnitude. Thus the contributions of the $\boldsymbol{\xi}_j$ and $\boldsymbol{\xi}_{jk}$ terms to the overall magnetic dipole transition moment are of the same order of magnitude.

The extension of the anharmonic-fpc model to include higher order effects is straightforward. Both the first and second contact transformations, described by Amat, Nielsen, and

Tarrago,[8] are required. It is straightforward, though tedious, to evaluate the twice-transformed electric and magnetic dipole moment operators. Although the complete expressions are not given here, it is of some interest to consider the form of the results that emerge from the second-order treatment. The second-order expression for the electric dipole transition moment of a fundamental transition is given by[20]

$$\begin{aligned}(v_s|\tilde{\boldsymbol{\mu}}|v_s+1) &= (1/\sqrt{2})\mathbf{t}_s \\ &+ (1/2\sqrt{2})\sum_j \mathrm{t}_j\left\{\sum_a S_s{}^{aaj}(1+2\delta_{aj}) + 3\sum_a S_{aas}{}^j\right\} \\ &-(1/4\sqrt{2})\sum_j \mathrm{t}_j\left\{\sum_{a\le b} S^{abj}(1+\delta_{aj}+\delta_{bj})\right. \\ &\times[S_{sb}{}^a(1+\delta_{bs}) + S_{sa}{}^b)1+\delta_{as})] \\ &- \sum_{a\le b} S_{ab}{}^j\Bigg[S_{bs}{}^a + S_{as}{}^b + \delta_{as}\sum_d (S_{dd}{}^b \\ &\left.+ S^{ddb}(1+2\delta_{bd})) + \delta_{bs}\sum_d (S_{dd}{}^a + S^{dda}(1+2\delta_{ad}))\Bigg]\right\}\end{aligned} \tag{47}$$

On the right hand side of eq 47, v_s is set to zero to simplify the expressions. For the purposes of the present discussion it is sufficient to observe that in eq 47 there are contributions to the electric dipole transition moment of a fundamental which arise from vibrational anharmonicity. Moreover, these contributions are not due to resonance interaction of the fundamental with a nearby overtone or combination level. An order of magnitude analysis, similar to that described above, may be used to show that the additional terms in eq 47 are two orders of κ smaller than the leading $\mathbf{t}_s$ term. This implies that the anharmonic corrections to the rotational strength of a fundamental are two orders of κ smaller than the leading $\mathbf{t}_s\xi_s$ term. This may be compared to the situation of a resonance interaction between the fundamental and, for example, a binary overtone. In that case, the resonance corrections to the electric dipole transition moment and to the rotational strength of the fundamental are only one order of κ smaller than the leading terms.

It appears that the additional anharmonic correction terms in eq 47 are of the same order of smallness in κ as terms that arise from the breakdown of the Born-Oppenheimer approximation. It is therefore appropriate to consider the contributions to the rotational strength which might result from such a breakdown.

In the following discussion, a crucial role is played by the electronic component of the electric-dipole transition moment. Such a consideration will result in direct contributions to electrical anharmonicity and, accordingly, it is appropriate to consider the relative contributions of electrical and mechanical anharmonicity to the rotational strength.

The usual expansion of the electric dipole moment is given by[7]

$$\mu = \mu(0) + \sum_i\left(\frac{\partial\mu}{\partial R_i}\right)R_i + \sum_{i,j}\left(\frac{\partial^2\mu}{\partial R_i\partial R_j}\right)R_iR_j + \sum_{i,j,k}\left(\frac{\partial^3\mu}{\partial R_i\partial R_j\partial R_k}\right)R_iR_jR_k$$

In terms of the Born-Oppenheimer vibrational-electronic wave function, $\Psi_{0\alpha}(\mathbf{r},\mathbf{R})$,[19] the function μ is given by

$$\mu = (\Psi_{0\alpha}(\mathbf{r},\mathbf{R})|e(\mathbf{r}+\mathbf{R})|\Psi_{0\alpha}(\mathbf{r},\mathbf{R}))$$

Here $\mathbf{r}$ and $\mathbf{R}$ denote the electronic and nuclear coordinates, respectively, and 0 and α denote the electronic and vibrational ground states, respectively. The function μ may be decomposed as

$$\mu = \mu_e + \mu_N$$

where

$$\mu_e = (\psi_0(\mathbf{r},\mathbf{R})|e\mathbf{r}|\psi_0(\mathbf{r},\mathbf{R}))$$

$$\mu_N = (\phi_\alpha(\mathbf{R})|e\mathbf{R}|\phi_\alpha(\mathbf{R}))$$

Here ψ_0 and ϕ_α represent the electronic and nuclear wave functions whose product is $\Psi_{0\alpha}(\mathbf{r},\mathbf{R})$, i.e.,

$$\Psi_{0\alpha}(\mathbf{r},\mathbf{R}) = \psi_0(\mathbf{r},\mathbf{R})\phi_\alpha(\mathbf{R})$$

Focusing on μ_e, the first derivative may be written as

$$\left|\left(\frac{\partial\mu_e}{\partial R_i}\right)\right| \sim e\left|\left(\frac{\partial\psi_0(\mathbf{r},\mathbf{R})}{\partial R_i}|\mathbf{r}|\psi_0(\mathbf{r},\mathbf{R})\right)\right| \sim e\left|\sum_j\left(\frac{\partial\psi_0}{\partial R_i}\middle|\psi_j\right)(\psi_j|\mathbf{r}|\psi_0)\right| \sim \left(\frac{1}{a_e}\right)(ea_e) \sim e$$

The above result makes use of the estimates

$$\left(\frac{\partial\psi_0}{\partial R_i}\middle|\psi_j\right) \sim \frac{1}{a_e}$$

$$(\psi_j|\mathbf{r}|\psi_0) \sim a_e$$

as given by Mead and Moscowitz.[19]

The second derivative of μ_e with respect to the nuclear coordinates is treated similarly:

$$\begin{aligned}\left|\left(\frac{\partial^2\mu_e}{\partial R_i\partial R_j}\right)\right| &\sim e\left|\left(\frac{\partial^2\psi_0}{\partial R_i\partial R_j}|\mathbf{r}|\psi_0\right)\right| \\ &+ e\left|\left(\frac{\partial\psi_0}{\partial R_i}|\mathbf{r}|\frac{\partial\psi_0}{\partial R_j}\right)\right| \sim e\left|\sum_j\left(\frac{\partial^2\psi_0}{\partial R_i\partial R_j}\middle|\psi_j\right)(\psi_j|\mathbf{r}|\psi_0)\right| \\ &+ e\left|\sum_{j,k}\left(\frac{\partial\psi_0}{\partial R_i}\middle|\psi_j\right)(\psi_j|\mathbf{r}|\psi_k)\left(\psi_k\middle|\frac{\partial\psi_0}{\partial R_i}\right)\right| \\ &\sim e\left(\frac{1}{a_e{}^2}\right)(a_e) + e\left(\frac{1}{a_e}\right)(a_e)\left(\frac{1}{a_e}\right) \sim \frac{e}{a_e}\end{aligned}$$

This result makes use of the additional relationship

$$\left|\left(\frac{\partial^2\psi_0}{\partial R_i\partial R_j}\middle|\psi_j\right)\right| \sim \frac{1}{a_e{}^2}$$

which may also be found in ref 19. In a similar way, the third derivative of μ_e with respect to the nuclear coordinates may be shown to be of order

$$\left|\left(\frac{\partial^3\mu_e}{\partial R_i\partial R_j\partial R_k}\right)\right| \sim \frac{e}{a_e{}^2}$$

These derivatives may be introduced into the electric dipole-moment expansion to obtain an order of magnitude relation for the electric dipole-transition moment for the vibrational transition $\phi_\alpha \rightarrow \phi_\beta$:

$$|(\phi_\alpha|\mu_e|\phi_\beta)| \sim e|(\phi_\alpha|R|\phi_\beta)| + \frac{e}{a_e}|(\phi_\alpha|R^2|\phi_\beta)| + \frac{e}{a_e{}^2}|(\phi_\alpha|R^3|\phi_\beta)|$$

It is easily shown that

$$|(\phi_\alpha|R^l|\phi_\beta)| \sim (a_N)^l \sim \kappa^la_e{}^l$$

and therefore

$$|(\phi_\alpha|\mu_e|\phi_\beta)| \sim ea_e\kappa + ea_e\kappa^2 + ea_e\kappa^3 + \ldots \tag{48}$$

The term proportional to κ^3 in eq 48 represents the electrical anharmonicity that will make a contribution to the electric dipole transition moment of a forbidden transition, $\alpha \rightarrow \beta$. This term is of the same order in κ as the correction terms arising from mechanical anharmonicity in eq 47.

Up to this point Born-Oppenheimer wave functions have been used. However, in the notation of ref 19, the exact molecular wave functions may be approximated by

$$\Psi_{0\alpha} \simeq \psi_0\phi_\alpha + \sum_{j\gamma} a_{j\gamma}\psi_j\phi_{j\gamma}$$

$$\Psi_{0\beta} \simeq \psi_0\phi_{0\beta} + \sum_{j\gamma} b_{j\gamma}\psi_j\phi_{j\gamma}$$

Note that a 0 subscript has been added to the electronic ground state vibrational wave functions. Thus,

$$\begin{aligned}|(\Psi_{0\alpha}|e\mathbf{r}|\Psi_{0\beta})| \sim |(\phi_{0\alpha}|\boldsymbol{\mu}_{\mathrm{e}}|\phi_{0\beta})| \\ + \left|\sum_{j\gamma} b_{j\gamma}(\psi_0|e\mathbf{r}|\psi_j)(\phi_{0\alpha}|\phi_{j\gamma})\right| \\ + \left|\sum_{j\gamma} a_{j\gamma}{}^*(\psi_{j\gamma}|e\mathbf{r}|\psi_0)(\phi_{j\gamma}|\phi_{0\beta})\right| \quad (49)\end{aligned}$$

The mixing coefficients are[19]

$$|a_{j\gamma}| \sim |b_{j\gamma}| \sim \kappa^3$$

If the Franck-Condon factors $(\phi_{0\alpha}|\phi_{j\gamma})$ and $(\phi_{j\gamma}|\phi_{0\beta})$ are assumed to be of order unity, the correction terms in eq 49 are of the order

$$\begin{aligned}\left|\sum_{j\gamma} b_{j\gamma}(\psi_0|er|\psi_j)(\phi_{0\alpha}|\phi_{j\gamma})\right| \\ + \left|\sum_{j\gamma} a_{j\gamma}{}^*(\psi_j|er|\psi_0)(\phi_{j\gamma}|\phi_{0\beta})\right| \sim ea_{\mathrm{e}}\kappa^3\end{aligned}$$

Thus the corrections to the electric dipole transition moment resulting from breakdown of the Born-Oppenheimer approximation are of the same order in κ as those that arise from both mechanical and electrical anharmonicity. Also, it should be noted that the mechanical and electrical corrections are calculated within the Born-Oppenheimer approximation. Thus the calculation of any electric dipole transition moment that requires inclusion of these third-order terms must, as shown above, include consideration of non-Born-Oppenheimer effects.

The electronic portion of the magnetic dipole transition moment cannot be treated in a manner analogous to that used for the electric dipole transition moment because, in the case of a molecule with a nondegenerate singlet ground state, the electronic contribution to the vibrational magnetic dipole transition moment must vanish when calculated with Born-Oppenheimer wave functions. This result is easily seen if one considers the magnetic dipole analogue of $\boldsymbol{\mu}_{\mathrm{e}}$ given by

$$\int \phi_\alpha{}^*(\mathbf{R})\left[\int \psi_0{}^*(\mathbf{r},\mathbf{R})\mathbf{m}_{\mathrm{el}}\psi_0(\mathbf{r},\mathbf{R})\mathrm{d}\mathbf{r}\right]\phi_\beta(\mathbf{R})\mathrm{d}\mathbf{R} \quad (50)$$

Here $\mathbf{m}_{\mathrm{el}}$ is the conventional electronic magnetic dipole-moment operator

$$\mathbf{m}_{\mathrm{el}} = \frac{-e}{2mc}\sum_i \mathbf{r}_i \times \mathbf{p}_i$$

If ψ_0 is a wave function for a singlet nondegenerate electronic ground state, the integral in brackets in eq 50 must vanish since the diagonal elements of a purely imaginary operator expressed in a purely real basis vanish. In this approximation only the nuclei, through the nuclear magnetic dipole-moment operator, will contribute to the magnetic dipole transition moment.[1b]

Should the rotational-strength calculation be carried out within the Born-Oppenheimer approximation, the rotational strength will be origin dependent. The reason for this origin dependence is as follows: the electric dipole transition moment will have both electronic and nuclear contributions, but the magnetic dipole transition moment will have only terms arising from nuclear magnetic dipole operator. Hence, the additional term in the origin-shifted rotational strength (see previous discussion) is given by

$$(0|R|k)\mathbf{Y} \times (k|\mathbf{P}|0)$$

and, in general, will not vanish.

The only other electronic contributions to the magnetic dipole transition moment are those due to the Born-Oppenheimer corrections

$$\begin{aligned}(\Psi_{0\alpha}|\mathbf{m}_{\mathrm{el}}|\Psi_{0\beta}) = \sum_{j\gamma} b_{j\gamma}(\psi_0\phi_{0\alpha}|\mathbf{m}_{\mathrm{el}}|\psi_j\phi_{j\gamma}) \\ + \sum_{j\gamma} a_{j\gamma}{}^*(\psi_j\phi_{j\gamma}|\mathbf{m}_{\mathrm{el}}|\psi_0\phi_{0\beta}) \quad (51)\end{aligned}$$

The matrix elements on the right-hand side of eq 51 are of the order of magnitude of the Bohr magneton which, in our units, is e/m. Since the perturbation coefficients in eq 51 are of order κ^3, it follows that the first nonzero electronic contributions to the magnetic dipole transition moment are of order $\kappa^3 e/m$. This is of the same order of magnitude as the magnetic dipole transition moment calculated in the fpc approximation. Accordingly, it appears that, if a more sophisticated treatment than the fpc model is to be used to estimate the magnetic dipole transition moment, it would also be proper to include consideration of the corrections to the Born-Oppenheimer wave function.

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Appendix I

In this appendix we set out the results of a number of harmonic-fpc model calculations and compare them with experimental results. The purpose is to point out some of the shortcomings of the harmonic-fpc model. In particular, we discuss the C*-H and O-H stretching modes in 2,2,2-trifluorophenylethanol (TFPE) and the C*-H stretching modes in tartaric acid. Complete details of the harmonic-fpc calculations, i.e., the force constants, partial charges, and molecular geometries, have been given by Faulkner.[21]

The only previous comparison between harmonic-fpc calculations and experimental results was given by Faulkner et al.[2c] for the C*-D stretching mode in neopentyl-*1-d* chloride and the C*-H stretching mode of TFPE. In the case of TFPE the calculated rotational strength has the same sign as the observed one but is one order of magnitude lower. The relevant results are summarized in Table I.

There is one difficulty in that, subsequent to the determination of the experimental rotational rotational strength quoted by Faulkner, which was observed for pure liquid TFPE, Nafie et al.[22] obtained the IRCD spectrum of TFPE in *dilute solution* and found that the rotational strength of the C*-H stretching mode was opposite in sign to that in the pure liquid. The magnitude of the rotational strength in dilute solution is roughly comparable with that of the pure liquid. It is relatively easy to calculate a C*-H rotational strength of different sign by assuming a different O-H conformer but, even in that case, the calculated rotational strength is still an order of magnitude less than the experimental value.

Nafie et al.[22] have also determined the rotational strengths in the O-H stretching region of TFPE in dilute solution. Since the rotational strengths associated with the O-H and C*-H stretching modes are opposite in sign and of roughly equal magnitude, the possibility exists that the optical activity in these two modes arises from a coupled oscillator mechanism.[23] To test this hypothesis TFPE was deuterated at the hydroxyl position (TFPE-d_1).[24] The harmonic-fpc calculation was carried through for TFPE-d_1 using the same force constants and partial charges as for TFPE; it was found that the rotational strength of the C*-H stretching mode was reversed in sign (see Table I). Also there was a decrease in magnitude of the rotational strength of the C*-H stretching mode by about a factor of 2.5. This result conflicts with experimental observation. Both the magnitude and sign of the rotational strength of the C*-H stretching mode in TFPE-d_1 are the same as in

Table I. Rotational and Dipole Strengths for (*S*)-D-2,2,2-Trifluoro-1-phenylethanol[a,b]

	Wavenumber, cm^{-1}	R, (esu cm)^2	D, (esu cm)^2
TFPE			
C*-H stretch	2910	-2×10^{-44}	1.6×10^{-39}
	(2921)	(2×10^{-45})	(1.5×10^{-39})
O-H stretch	3620	2×10^{-44}	6.8×10^{-39}
	(3680)	(2×10^{-46})	(1.3×10^{-38})
TFPE-d_1			
C*-H stretch	2910	-2×10^{-44}	1.8×10^{39}
		(0.7×10^{-45})	(1.5×10^{-39})
O-D stretch	2670	Positive	3.2×10^{-39}

[a] All experimental data are for dilute CCl_4 solution spectra. The experimental O-H rotational strength is derived from the CD spectrum of Figure 5, ref 22. All other experimental values obtained from the following samples: TFPE, C*-H stretch, 0.070 M, 5.9 mm path length; O-H stretch, 0.35 M, 0.244 mm path length; TFPE-*d*, C*-H stretch, 0.070 M, 5.9 mm path length; O-D stretch, 0.070 M, 1.04 mm path length. [b] Results in parentheses are calculated values using the harmonic-fpc model.

TFPE. This result appears to preclude the possibility that the optical activity of the C*-H stretching mode in TFPE has its origin in a coupled oscillator mechanism involving the O-H stretching mode.

In their original interpretation of the rotational strength of the C*-H stretching fundamental of TFPE, Faulkner et al.[2c] assumed that the C*-H bond stretch was admixed with the C*-O-H deformation and that the electric-dipole transition moment was due primarily to the C*-H stretching motion and the magnetic-dipole transition moment to the C*-O-H deformation motion. They found later[21] that is was possible to obtain a calculated value of the rotational strength close to the experimental one if they introduced an interaction force constant, $f_{r\delta} = -0.24$ mdyn, coupling the C*-H stretch and C*-O-H deformation in the valence force field. However, in the original valence force field on which their calculations were based, it was assumed that $f_{r\delta}$ was 0. It may well be that the rotational strength is more sensitive to this force constant than any other spectroscopic quantity, but there is, in fact, no real evidence that $f_{r\delta}$ should be so large.

If anharmonic effects are considered there is a possibility that the overtone of the C*-H deformation or the combination of the two C*-H deformation modes might mix significantly with the C*-H stretch; we expect these overtone and combination states to lie near 2700 cm^{-1} and in our trial anharmonic fpc calculations it appears that the cubic normal-coordinate force constants connecting the C*-H stretching fundamental with these overtones and combinations seemed to be of the order of 100 cm^{-1}. Hence a considerable anharmonic mixing of the fundamental and the overtone and combination states is to be expected.

The other molecule in which we are able to compare calculated and experimental values of the rotational strength is tartaric acid. Sugeta et al.[25] measured the circular dichroism associated with the two C*-H stretching fundamentals of tartaric acid and found a monosignate CD spectrum with an overall rotational strength of about 8×10^{-44} (esu cm)^2 in magnitude. A number of harmonic-fpc calculations[21] were carried out based on the Urey-Bradley force field for ethylene glycol determined by Matsuura and Miyazawa.[26]

In the first set of harmonic fpc calculations it was assumed that the two C*-H bonds in tartaric acid are coplanar in either a cis or trans arrangement. In that case it was found that the calculated rotational strengths are about one order of magnitude less than the experimental ones and, moreover, that the rotational strengths for the two C*-H stretching modes are generally of opposite sign and so should give rise to a bisignate CD spectrum.

A second series of calculations was made for assumed configurations in which the two C*-H bonds are staggered with respect to each other. In that case the the coupled oscillator mechanism comes into play and it was found that the rotational strengths of the individual symmetric and antisymmetric modes involving the C*-H bonds are much larger than for the planar cases and are of the same order of magnitude as the experimental values. However, the calculated rotational strengths of the two C*-H stretching modes are opposite in sign and one would predict the CD spectrum to be bisignate in character, contrary to experiment.[25]

It is interesting to note that, in the planar conformations, the dominant contributions to the rotational strength of the staggered conformers cancel out. In the planar case the optical activity may be viewed as arising from the electric dipole transition moments due primarily to the C*-H bond stretches and small magnetic dipole transition moments arising from the motion of atoms outside the two C*-H bonds.

The interpretation of the experimental results suggested by Sugeta et al.[25] is that the rotational strength is primarily due to separate local contributions from each of the two C*-H bonds. Each asymmetric center in, for example, *l*-tartaric acid is of the *S* configuration and so the individual contributions to the rotational strength from each C*-H bond stretch should be of the same sign and the CD spectrum should be monosignate in agreement with experiment. Unfortunately, the harmonic-fpc calculations show no evidence of such contributions to the rotational strength from the individual local C*-H oscillators. However, if the suggested interpretation of Sugeta et al.[25] is correct, a similar model might also explain the TFPE results where a dominant local C*-H bond stretch contribution would be consistent with the experimental observation that the C*-H stretch rotational strength is insensitive to deuteration of the alcohol moiety.

One final observation about the harmonic-fpc calculation should be made. It is possible to construct to construct a band shape that would approximate a monosignate band in the CD spectrum by superimposing two bisignate bands which might arise from roughly equal populations of two of the staggered conformers. We have explored this possibility but, if we accept the calculated frequency splittings, which seem to match those experimentally observed,[25] it does not seem possible to superimpose bisignate curves to synthesize a CD spectrum at all similar to that seen experimentally.

Appendix II

Amat, Nielsen, and Tarrago[8] give the following expressions for the quantities S^{abc} and $S_{ab}{}^{c}$:

$$S_{ab}{}^{c} = -\frac{2\pi c}{\hbar}(1 + \delta_{ac} + \delta_{bc})\lambda_c{}^{1/2}(\lambda_c - \lambda_a - \lambda_b)D_{abc}k_{abc}$$

$$S^{abc} = \frac{4\pi c}{\hbar^3}k_{abc}(\lambda_a\lambda_b\lambda_c)^{1/2}D_{abc} \tag{A1}$$

Here k_{abc} is a cubic normal coordinate force constant and

$$\lambda_a{}^{1/2} = 2\pi c\omega_a$$

where ω_a is the harmonic frequency of the *a*th normal mode, expressed in cm^{-1}. The quantity D_{abc} is given by

$$D_{abc} = [(\lambda_a{}^{1/2} + \lambda_b{}^{1/2} + \lambda_c{}^{1/2})(\lambda_a{}^{1/2} - \lambda_b{}^{1/2} - \lambda_c{}^{1/2}) \times (\lambda_a{}^{1/2} - \lambda_b{}^{1/2} + \lambda_c{}^{1/2})(\lambda_a{}^{1/2} + \lambda_b{}^{1/2} - \lambda_c{}^{1/2})]^{-1} \tag{A2}$$

To prove that S^{abc} and $S_{ab}{}^{c}$ are both of order κ in magnitude it is necessary to establish the order of magnitude of k_{abc}. By definition

$$k_{abc} = \frac{\partial^3 V}{\partial q_a \partial q_b \partial q_c}$$

where V is the intramolecular potential function which within the Born-Oppenheimer approximation can be written as

$$V = (\psi_0 | T_e + V_{ee} + V_{Ne} + V_{NN} | \psi_0) \tag{A3}$$

Here T_e is the electronic kinetic energy operator, V_{ee} is the interelectronic Coulomb potential, V_{Ne} is the nuclear-electronic Coulomb potential, and V_{NN} is the nuclear-nuclear Coulomb potential. Since the potential energy is expanded in dimensionless coordinates, the order of magnitude of k_{abc} may be expressed as

$$|k_{abc}| \sim \left| \frac{\partial^3 V}{\partial R_N{}^3} a_N{}^3 \right| \tag{A4}$$

Consider first the electron-electron terms; the first derivative may be expressed as

$$\left| \frac{\partial}{\partial R_N} (\psi_0 | T_e + V_{ee} | \psi_0) \right| \sim \left| \left(\frac{\partial \psi_0}{\partial R_N} \middle| T_e + V_{ee} \middle| \psi_0 \right) \right|$$
$$\sim \left| \sum_j \left(\frac{\partial \psi_0}{\partial R_N} \middle| \psi_j \right) (\psi_j | T_e + V_{ee} | \psi_0) \right| \sim E_e / a_e$$

and the second derivative as

$$\left| \frac{\partial^2}{\partial R_N{}^2} (\psi_0 | T_e + V_{ee} | \psi_0) \right| \sim \left| \left(\frac{\partial^2 \psi_0}{\partial R_N{}^2} \middle| T_e + V_{ee} \middle| \psi_0 \right) + \left(\frac{\partial \psi_0}{\partial R_N} \middle| T_e + V_{ee} \middle| \frac{\partial \psi_0}{\partial R_N} \right) \right|$$
$$\sim \left| \sum_j \left(\frac{\partial^2 \psi_0}{\partial R_N{}^2} \middle| \psi_0 \right) (\psi_j | T_e + V_{ee} | \psi_0) + \sum_{j,k} \left(\frac{\partial \psi_0}{\partial R_N} \middle| \psi_j \right) (\psi_j | T_e + V_{ee} | \psi_k) \left(\psi_k \middle| \frac{\partial \psi_0}{\partial R_N} \right) \right|$$
$$\sim \frac{1}{a_e{}^2} E_e + \frac{1}{a_e} E_e \frac{1}{a_e} \sim E_e / a_e{}^2$$

Similarly the third derivative may be expressed as

$$\left| \frac{\partial^3}{\partial R_N{}^3} (\psi_0 | T_e + V_{ee} | \psi_0) \right| \sim \frac{E_e}{a_e{}^3} \tag{A5}$$

Since V_{Ne} depends on the nuclear coordinates, the derivatives of the potential term containing V_{Ne} will contain

$$\left| \left(\frac{\partial}{\partial R_N} \right)^m \frac{e^2}{|\mathbf{r} - \mathbf{R}|} \right| \sim \left| \frac{e^2}{|\mathbf{r} - \mathbf{R}|^{(m+1)}} \right|$$

and hence

$$\left(\psi_i \middle| \frac{\partial^m V_{Ne}}{\partial R_N{}^m} \middle| \psi_j \right) \sim \frac{E_e}{a_e{}^m}$$

The expansion technique used for the electron-electron terms together with the above result yields

$$\left| \frac{\partial^3}{\partial R_N{}^3} (\psi_0 | V_{Ne} | \psi_0) \right| \sim \frac{E_e}{a_e{}^3} \tag{A6}$$

Finally, the contribution from the nuclear-nuclear potential is

$$\left| \frac{\partial^3}{\partial R_N{}^3} (\psi_0 | V_{NN} | \psi_0) \right| = \left| \frac{\partial^3 V_{NN}}{\partial R_N{}^3} \right| \sim \frac{e^2}{a_e{}^4} \sim \frac{E_e}{a_e{}^3} \tag{A7}$$

Inserting eq A5-A7 into eq A4 yields

$$k_{abc} \sim \frac{E_e}{a_e{}^3} a_N{}^3 \sim \kappa^3 E_e \tag{A8}$$

This result, when used in eq A1, gives

$$|S_{ab}{}^c| \sim \kappa^3 E_e \frac{E_N{}^3}{E_N{}^4} \sim \kappa^3 E_e \left(\frac{1}{\kappa^2 E_e} \right) \sim \kappa$$

$$|S^{abc}| \sim \kappa^3 E_e \frac{E_N{}^3}{E_N{}^4} \sim \kappa$$

The quartic transformation constants, $S_d{}^{abc}$ and $S_{abc}{}^d$, may be shown, by methods similar to the above, to be of order

$$|S_{abc}{}^d| \sim |S_d{}^{abc}| \sim \kappa^2$$

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