If the relative energies in Table II are correct, octahedral coordination should contribute negligibly to the liquid structure of $Li^+$ hydrates. The solvation enthalpy for $Li^+$ at 298° is $-227.6$ kcal/mol; one could imagine this is due to tetrahedral first coordination sphere water ($-107$ kcal/mol), second coordination sphere water ($8 \times -10$ kcal/mol), and a substantial contribution from more distant waters. Thus, we conclude that $Li^+$ has an important ordering effect on the water at least through the third coordination sphere.

If one makes the (very drastic) assumption that the $E^{(3)}(Na^+ \cdots (H_2O)_2) = E^{(3)}(Li^+ \cdots (H_2O)_2)$, one finds for $Na^+$ that octahedral coordination is approximately equal energetically to tetrahedral coordination plus two

external waters.[7] Further studies are in progress along these lines.

# A Simple Two-Group Model for Rayleigh and Raman Optical Activity

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**Abstract:** Rayleigh and Raman circular intensity differentials are calculated for a dissymmetric molecule comprised of two neutral optically inactive groups. The dominant mechanism has no counterpart in optical rotation, being of longer range than Kirkwood's dynamic-coupling interaction that leads to optical rotation. Differential scattering increases with increasing separation of the two groups, whereas optical rotation decreases. Predicted magnitudes are of the order of those observed. The signs of the effects give the absolute configuration of the molecule.

R ecent theoretical and experimental work[1-6] has shown that optical activity can be studied through differential Rayleigh and Raman scattering of right and left circularly polarized light. The Raman experiment measures vibrational optical activity and provides information complementary to that obtained from the extension of optical rotatory dispersion and circular dichroism into the infrared, which has recently been observed for the first time in simple molecules.[7,8] Since optical activity increases with the frequency of the exciting light and vibrational frequencies are several orders of magnitude smaller than visible frequencies, vibrational optical activity is barely detectable through infrared rotatory dispersion and circular dichroism; it is accessible through the Raman CID (circular intensity differential) because the Raman effect provides vibrational spectra with visible exciting light. Also the large and interesting effects associated with skeletal vibrations occur at lower frequencies; it has not proved possible to extend infrared rotatory dispersion and circular dichroism into the far infrared, whereas Raman CID can give the entire vibrational optical activity spectrum with a single instrument.

In this article, Rayleigh and Raman CID's generated by a dissymmetric molecule comprised of two neutral optically inactive groups 1 and 2 are calculated. The dominant CID mechanism has no counterpart in optical rotation and circular dichroism, even in an anisotropic sample.[9] In the Kirkwood model the optical rotation generated by a dissymmetrically arranged pair of groups involves dynamic coupling between the groups;[10] only forward-scattered waves that have been deflected from one group to the other have sampled the dissymmetry and can generate optical rotation and circular dichroism on combining with the transmitted wave at the detector[11] (Figure 1). But the transmitted wave is unimportant in Rayleigh and Raman CID, so interference between waves independently scattered from the two groups provides chiral information (Figure 2). Dynamic coupling is not required, although it can make other less important contributions.

The relevant experimental quantity in Rayleigh and Raman optical activity is a dimensionless circular in-

(1) P. W. Atkins and L. D. Barron, *Mol. Phys.*, 16, 453 (1969).
(2) L. D. Barron and A. D. Buckingham, *Mol. Phys.*, 20, 1111 (1971).
(3) L. D. Barron, *J. Chem. Soc. A*, 2899 (1971).
(4) L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *J. Amer. Chem. Soc.*, 95, 603 (1973).
(5) L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *Nature (London)*, 241, 113 (1973).
(6) L. D. Barron and A. D. Buckingham, *Chem. Commun.*, 152 (1973).
(7) G. Holzwarth, E. C. Hsu, H. S. Mosher, T. R. Faulkner, and A. Moscowitz, *J. Amer. Chem. Soc.*, 96, 251 (1974).
(8) T. R. Faulkner, A. Moscowitz, G. Holzwarth, E. C. Hsu, and H. S. Mosher, *J. Amer. Chem. Soc.*, 96, 252 (1974).

(9) A. D. Buckingham and M. B. Dunn, *J. Chem. Soc. A*, 1988 (1971).
(10) J. G. Kirkwood, *J. Chem. Phys.*, 5, 479 (1937).
(11) P. W. Atkins and R. G. Woolley, *Proc. Roy. Soc., Ser. A*, 314, 251 (1970).
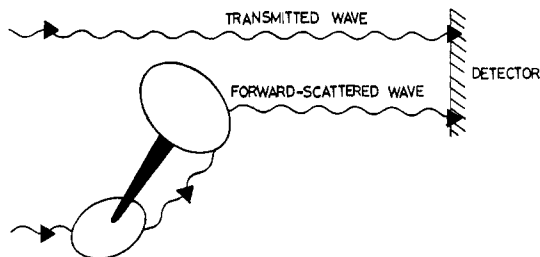
**Figure 1.** In the Kirkwood model, optical rotation is generated through interference between transmitted and forward-scattered waves that have sampled the dissymmetry of the two groups.

tensity differential

$$\Delta = (I^R - I^L)/(I^R + I^L) \quad (1)$$

where $I^R$ and $I^L$ are the scattered intensities in right and left circularly polarized incident light (right circular polarization involves a clockwise rotation of the electric vector when viewed toward the source of the light). Expressions for the components of $\Delta$ for scattered radiation polarized parallel ($\Delta_z$) and perpendicular ($\Delta_x$) to the scattering plane $yz$ are derived for the two-group model from a consideration of the origin dependence of the optical activity tensors.

## Rayleigh CID

According to Barron and Buckingham,[2] the components of the Rayleigh CID for radiation scattered in the $y$ direction are

$$\Delta_z = \frac{4(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{2c(3\alpha_{\gamma\delta}\alpha_{\gamma\delta} - \alpha_{\gamma\gamma}\alpha_{\delta\delta})} \quad (2a)$$

$$\Delta_x = \frac{2(7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} + \frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\gamma\delta}\alpha_{\gamma\delta} + \alpha_{\gamma\gamma}\alpha_{\delta\delta})} \quad (2b)$$

where $\omega$ is the angular frequency, $\alpha_{\alpha\beta}$ is the polarizability tensor, $G'_{\alpha\beta}$ is the electric dipole–magnetic dipole distortion tensor, and $A_{\alpha\beta\gamma}$ is the electric dipole–electric quadrupole distortion tensor; as is usual in tensor notation, a repeated Greek suffix denotes a summation over the three Cartesian components. Time-dependent perturbation theory provides the following quantum mechanical expressions for the distortion tensors at transparent frequencies[12]

$$\alpha_{\alpha\beta} = 2\hbar^{-1}\sum_j(\omega_{jn}^2 - \omega^2)^{-1} \times$$

$$\omega_{jn}Re(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle) = \alpha_{\beta\alpha} \quad (3a)$$

$$G'_{\alpha\beta} = -2\hbar^{-1}\omega\sum_j(\omega_{jn}^2 - \omega^2)^{-1}Im(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle) \quad (3b)$$

$$A_{\alpha\beta\gamma} = 2\hbar^{-1}\sum_j(\omega_{jn}^2 - \omega^2)^{-1} \times$$

$$\omega_{jn}Re(\langle n|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle) = A_{\alpha\gamma\beta} \quad (3c)$$

where $|n\rangle$ and $|j\rangle$ are the ground and excited molecular electronic states, and $\mu_\alpha$, $m_\alpha$, and $\Theta_{\alpha\beta}$ are the electric dipole, magnetic dipole, and electric quadrupole moment operators defined by

$$\mu_\alpha = \sum_i e_i r_{i\alpha} \quad (4a)$$

$$m_\alpha = \sum_i \frac{e_i}{2m_i}\epsilon_{\alpha\beta\gamma}r_{i\beta}p_{i\gamma} \quad (4b)$$

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_i e_i(3r_{i\alpha}r_{i\beta} - r_i^2\delta_{\alpha\beta}) \quad (4c)$$

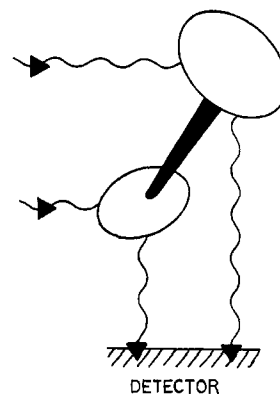(12) A. D. Buckingham, *Advan. Chem. Phys.*, **12**, 107 (1967).



**Figure 2.** Rayleigh and Raman CID can be generated through interference between waves independently scattered from the two groups.

The subsequent development requires a knowledge of the origin dependence of the optical activity tensors $G'$ and $A$. If the origin is moved from $O$ to a point $O + a$, where $a$ is some constant vector, the position vector $r_i$ in the old coordinate system becomes $r_i - a$ in the new. For a neutral collection of charges the moments change to

$$\mu_\alpha \longrightarrow \mu_\alpha \quad (5a)$$

$$m_\alpha \longrightarrow m_\alpha - \frac{1}{2}\epsilon_{\alpha\beta\gamma}a_\beta\mu_\gamma \quad (5b)$$

$$\Theta_{\alpha\beta} \longrightarrow \Theta_{\alpha\beta} - \frac{3}{2}\mu_\alpha a_\beta - \frac{3}{2}\mu_\beta a_\alpha + \mu_\gamma a_\gamma\delta_{\alpha\beta} \quad (5c)$$

Using the operator equivalents of these changed moments in the tensors (eq 3) it is found that[13]

$$\alpha_{\alpha\beta} \longrightarrow \alpha_{\alpha\beta} \quad (6a)$$

$$G'_{\alpha\beta} \longrightarrow G'_{\alpha\beta} + \frac{1}{2}\omega\epsilon_{\beta\gamma\delta}a_\gamma\alpha_{\alpha\delta} \quad (6b)$$

$$A_{\alpha\beta\gamma} \longrightarrow A_{\alpha\beta\gamma} - \frac{3}{2}a_\beta\alpha_{\alpha\gamma} - \frac{3}{2}a_\gamma\alpha_{\alpha\beta} + a_\delta\alpha_{\alpha\delta}\delta_{\beta\gamma} \quad (6c)$$

We assume no electron exchange between the two groups and write the distortion tensors of the pair as the sum of the corresponding group tensors. The group tensors must be referred to a fixed origin within the molecule, which we choose to be the local origin in group 1.

$$\alpha_{\alpha\beta} = \alpha_{1\alpha\beta} + \alpha_{2\alpha\beta} +$$

static and dynamic coupling terms (7a)

$$G'_{\alpha\beta} = G_1'_{\alpha\beta} + G_2'_{\alpha\beta} - \frac{1}{2}\omega\epsilon_{\beta\gamma\delta}R_{21\gamma}\alpha_{2\alpha\delta} +$$

static and dynamic coupling terms (7b)

$$A_{\alpha\beta\gamma} = A_{1\alpha\beta\gamma} + A_{2\alpha\beta\gamma} + \frac{3}{2}R_{21\beta}\alpha_{2\alpha\gamma} +$$

$$\frac{3}{2}R_{21\gamma}\alpha_{2\alpha\beta} - R_{21\delta}\alpha_{2\alpha\delta}\delta_{\beta\gamma} +$$

static and dynamic coupling terms (7c)

where $\alpha_{i\alpha\beta}$, $G_i'_{\alpha\beta}$, and $A_{i\alpha\beta\gamma}$ are tensors referred to a local origin in the $i$th group, and $R_{21} = R_2 - R_1$ is the vector from the origin in 1 to that in 2. Even though all components of $G_i'_{\alpha\beta}$ and $A_{i\alpha\beta\gamma}$ may be zero when referred to local group origins, the origin-dependent parts may not be. Also, although the groups are assumed to be intrinsically optically inactive in the usual sense, for certain symmetries (*e.g.*, $C_{2v}$) there are nonzero components of the optical activity tensors that can contribute to Rayleigh and Raman CID.

(13) A. D. Buckingham and H. C. Longuet-Higgins, *Mol. Phys.*, **14**, 63 (1968).

Using eq 7, the relevant polarizability–optical activity products in the CID components (eq 2) can be approximated by

$$\alpha_{\alpha\beta}G'_{\alpha\beta} = -\,^1\!/_2\omega\epsilon_{\beta\gamma\delta}R_{21\gamma}\alpha_{1\alpha\beta}\alpha_{2\delta\alpha} \,+$$

$$\alpha_{1\alpha\beta}G_2'_{\alpha\beta} + \alpha_{2\alpha\beta}G_1'_{\alpha\beta} \quad (8a)$$

$$^1\!/_3\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} = -\,^1\!/_2\omega\epsilon_{\beta\gamma\delta}R_{21\gamma}\alpha_{1\alpha\beta}\alpha_{2\delta\alpha} \,+$$

$$^1\!/_3\omega\alpha_{1\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{2\gamma\delta\beta} + \,^1\!/_3\omega\alpha_{2\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{1\gamma\delta\beta} \quad (8b)$$

$$\alpha_{\alpha\alpha}G'_{\beta\beta} = 0 \quad (8c)$$

where the higher order coupling terms have been omitted. Notice that each of these equations is independent of the choice of local origins in 1 and 2, as may be verified by the replacements $R_{1\alpha} \rightarrow R_{1\alpha} + \Delta r_{1\alpha}$, $R_{2\alpha} \rightarrow R_{2\alpha} + \Delta r_{2\alpha}$, $R_{21\alpha} \rightarrow R_{21\alpha} - \Delta r_{1\alpha} + \Delta r_{2\alpha}$ where $\Delta r_1$ and $\Delta r_2$ are shifts of the local origins within 1 and 2.

If both groups have threefold or higher rotation axes (which we take to be the 3 axis) eq 8 can be given a tractable form. If the groups are optically inactive, they cannot be pure rotation groups, and for the remaining groups the components of the second-rank axial tensors $G'_{\alpha\beta}$ and $\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta}$ are either zero or have $G'_{12} = -G'_{21}$ and $\epsilon_{1\gamma\delta}A_{\gamma\delta2} = -\epsilon_{2\gamma\delta}A_{\gamma\delta1}$.[12,14] The terms $\alpha_{i\alpha\beta}G_j'_{\alpha\beta}$ and $\alpha_{i\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{j\gamma\delta\beta}$ in (8) are then zero because $\alpha_{\alpha\beta} = \alpha_{\beta\alpha}$. If the principal axes 1, 2, and 3 of the $i$th group are associated with unit vectors $s_i$, $t_i$, and $u_i$, its polarizability tensor may be written

$$\alpha_{i\alpha\beta} = \alpha_i(1 - \kappa_i)\delta_{\alpha\beta} + 3\alpha_i\kappa_iu_{i\alpha}u_{i\beta} \quad (9)$$

where

$$\kappa = (\alpha_{33} - \alpha_{11})/3\alpha \quad (9a)$$

$$\alpha = \,^1\!/_3(\alpha_{11} + \alpha_{22} + \alpha_{33}) \quad (9b)$$

Then

$$\epsilon_{\beta\gamma\delta}R_{21\gamma}\alpha_{1\alpha\beta}\alpha_{2\delta\alpha} = 9\epsilon_{\beta\gamma\delta}R_{21\gamma}\alpha_1\alpha_2\kappa_1\kappa_2u_{1\alpha}u_{2\alpha}u_{1\beta}u_{2\delta} \quad (10)$$

We consider the simplest dissymmetric pair where the principal axes of the two monomers are in parallel planes (Figure 3). For this structure

$$\epsilon_{\beta\gamma\delta}R_{21\gamma}\alpha_{1\alpha\beta}\alpha_{2\delta\alpha} = -\,^9\!/_2R_{21}\alpha_1\alpha_2\kappa_1\kappa_2 \sin 2\theta \quad (11)$$

From (8) and (11) the polarizability–optical activity products required in the CID components (2) are

$$3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta} - \,^1\!/_3\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} =$$

$$^9\!/_2\omega R_{21}\alpha_1\alpha_2\kappa_1\kappa_2 \sin 2\theta \quad (12a)$$

$$7\alpha_{\alpha\beta}G'_{\alpha\beta} + \alpha_{\alpha\alpha}G'_{\beta\beta} + \,^1\!/_3\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} =$$

$$18\omega R_{21}\alpha_1\alpha_2\kappa_1\kappa_2 \sin 2\theta \quad (12b)$$

We also require certain polarizability–polarizability products. From (7a)

$$\alpha_{\alpha\beta}\alpha_{\alpha\beta} = \alpha_{1\alpha\beta}\alpha_{1\alpha\beta} + \alpha_{2\alpha\beta}\alpha_{2\alpha\beta} + 2\alpha_{1\alpha\beta}\alpha_{2\alpha\beta} \quad (13)$$

and from (9) we can write, for axially symmetric groups

$$\alpha_{i\alpha\beta}\alpha_{j\alpha\beta} = 3\alpha_i\alpha_j + 3\alpha_i\alpha_j\kappa_i\kappa_j(3u_{i\alpha}u_{j\alpha}u_{i\beta}u_{j\beta} - 1) =$$

$$3\alpha_i\alpha_j + \,^3\!/_2\alpha_i\alpha_j\kappa_i\kappa_j(1 + 3\cos 2\theta_{ij}) \quad (14a)$$

$$\alpha_{i\alpha\alpha}\alpha_{j\beta\beta} = 9\alpha_i\alpha_j \quad (14b)$$

Consequently

$$3\alpha_{i\alpha\beta}\alpha_{j\alpha\beta} - \alpha_{i\alpha\alpha}\alpha_{j\beta\beta} = \,^9\!/_2\alpha_i\alpha_j\kappa_i\kappa_j(1 + 3\cos 2\theta_{ij}) \quad (15a)$$

(14) R. R. Birss, "Symmetry and Magnetism," North-Holland Publishing Co., Amsterdam, 1966.
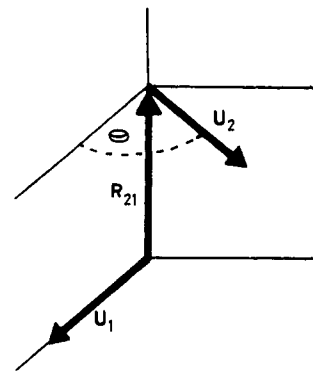


Figure 3. The geometry of a dissymmetric dimer where the symmetry axes $u_1$ and $u_2$ of the monomers are in parallel planes.

$$7\alpha_{i\alpha\beta}\alpha_{j\alpha\beta} + \alpha_{i\alpha\alpha}\alpha_{j\beta\beta} =$$

$$30\alpha_i\alpha_j + \,^{21}\!/_2\alpha_i\alpha_j\kappa_i\kappa_j(1 + 3\cos 2\theta_{ij}) \quad (15b)$$

Using (15) in (13), the polarizability–polarizability products required in the CID components in (2) are

$$3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta} = 18(\alpha_1^2\kappa_1^2 + \alpha_2^2\kappa_2^2) \,+$$

$$9\alpha_1\alpha_2\kappa_1\kappa_2(1 + 3\cos 2\theta) \quad (16a)$$

$$7\alpha_{\alpha\beta}\alpha_{\alpha\beta} + \alpha_{\alpha\alpha}\alpha_{\beta\beta} = 30(\alpha_1^2 + \alpha_2^2 + 2\alpha_1\alpha_2) \,+$$

$$42(\alpha_1^2\kappa_1^2 + \alpha_2^2\kappa_2^2) + 21\alpha_1\alpha_2\kappa_1\kappa_2(1 + 3\cos 2\theta) \quad (16b)$$

If groups 1 and 2 are identical, (16) and (12) in (2) give the following Rayleigh CID components generated by a dissymmetric dimer

$$\Delta_z = \frac{2\pi R_{21} \sin 2\theta}{\lambda(5 + 3\cos 2\theta)} \quad (17a)$$

$$\Delta_x = \frac{24\pi R_{21}\kappa^2 \sin 2\theta}{\lambda[40 + 7\kappa^2(5 + 3\cos 2\theta)]} \quad (17b)$$

where $\kappa$ is the group anisotropy. Notice that no knowledge of the polarizabilities of the two groups is required to calculate $\Delta_z$.

It is instructive to compare the expressions in (17) for Rayleigh CID with the Kirkwood expression for the optical rotation generated by an isotropic sample of the same dissymmetric pairs

$$\theta = -\frac{1}{3}\omega\mu_0lNG'_{\alpha\alpha} \approx \frac{3\omega^2\mu_0lN}{16\pi\epsilon_0R_{21}^2}\alpha^2\kappa^2 \sin 2\theta \quad (18)$$

where $l$ is the path length and $N$ is the number density of molecules.[10] The Rayleigh CID increases with increasing separation of the monomers, whereas optical rotation decreases since it is generated through dynamic coupling. Also, the absolute configuration of Figure 3 leads to positive Rayleigh CID's and a positive optical rotation (a clockwise rotation when viewed toward the source of the light) at the same transparent wavelength. The CID's (17) are valid only for $R_{21} \ll \lambda$.

If the dimer is a twisted biphenyl, the symmetry axes $u_1$ and $u_2$ are along the sixfold rotation axes of the aromatic rings (for simplicity we disregard the fact that the ring substituents required to constrain the biphenyl to a dissymmetric conformation destroy the axial symmetry of the aromatic rings). With $R_{21} \sim 5$ Å, $\theta = \pi/4$, and $\lambda$ 5000 Å, (17a) gives $\Delta_z \sim 1.3 \times 10^{-3}$. Taking $|\kappa| = 0.18$ for benzene,[15] $\Delta_x \sim 0.6 \times 10^{-4}$. Thus

(15) N. J. Bridge and A. D. Buckingham, *Proc. Roy. Soc., Ser. A*, **295**, 334 (1966).

we expect $\Delta_z$ to be at least an order of magnitude larger than $\Delta_x$. These estimates only apply to gaseous samples; in liquids a significant reduction in Rayleigh scattering occurs through interference, the isotropic contribution being suppressed much more than the anisotropic contribution.[16]

## Raman CID

The CID's in (2) apply to vibrational Raman scattering if the polarizability and optical activity tensors are replaced by transition tensors $\langle f | \alpha_{\alpha\beta} | i \rangle$, etc., between initial and final vibrational states $i$ and $f$. We consider the Raman CID associated with coupled vibrations of two *identical* monomers, not vibrations of the dimer skeleton. The ground vibrational state $|0\rangle$ of the dimer is the direct product of the ground vibrational states $|0_1\rangle$ and $|0_2\rangle$ of groups 1 and 2,

$$|0\rangle = |0_1 0_2\rangle \tag{19a}$$

and the first excited vibrational state $|1_\pm\rangle$ involves symmetric and antisymmetric combinations of singly excited monomer states

$$|1_\pm\rangle = 2^{-1/2}(|1_1 0_2\rangle \pm |0_1 1_2\rangle) \tag{19b}$$

Interaction between the two singly excited monomer states results in a "phonon splitting" of their degeneracy.

The required transition polarizability–transition optical activity products are now, for the $1_\pm \leftarrow 0$ transitions of the dimer

$$\langle 0 | \alpha_{\alpha\beta} | 1_\pm \rangle \langle 1_\pm | G'_{\alpha\beta} | 0 \rangle =$$
$$\mp \tfrac{1}{4} \omega \epsilon_{\beta\gamma\delta} R_{21\gamma} \langle 0_1 | \alpha_{1\alpha\beta} | 1_1 \rangle \langle 1_2 | \alpha_{2\delta\alpha} | 0_2 \rangle \pm$$
$$\tfrac{1}{2} \langle 0_1 | \alpha_{1\alpha\beta} | 1_1 \rangle \langle 1_2 | G_2'_{\alpha\beta} | 0_2 \rangle \pm$$
$$\tfrac{1}{2} \langle 0_2 | \alpha_{2\alpha\beta} | 1_2 \rangle \langle 1_1 | G_1'_{\alpha\beta} | 0_1 \rangle \tag{20a}$$

$$\tfrac{1}{3} \omega \langle 0 | \alpha_{\alpha\beta} | 1_\pm \rangle \langle 1_\pm | \epsilon_{\alpha\gamma\delta} A_{\gamma\delta\beta} | 0 \rangle =$$
$$\mp \tfrac{1}{4} \omega \epsilon_{\beta\gamma\delta} R_{21\gamma} \langle 0_1 | \alpha_{1\alpha\beta} | 1_1 \rangle \langle 1_2 | \alpha_{2\delta\alpha} | 0_2 \rangle \pm$$
$$\tfrac{1}{6} \omega \langle 0_1 | \alpha_{1\alpha\beta} | 1_1 \rangle \langle 1_2 | \epsilon_{\alpha\gamma\delta} A_{2\gamma\delta\beta} | 0_2 \rangle \pm$$
$$\tfrac{1}{6} \omega \langle 0_2 | \alpha_{2\alpha\beta} | 1_2 \rangle \langle 1_1 | \epsilon_{\alpha\gamma\delta} A_{1\gamma\delta\beta} | 0_1 \rangle \tag{20b}$$

$$\langle 0 | \alpha_{\alpha\alpha} | 1_\pm \rangle \langle 1_\pm | G'_{\beta\beta} | 0 \rangle = 0 \tag{20c}$$

If the two groups have threefold or higher rotation axes, $\langle 0_i | \alpha_{i\alpha\beta} | 1_i \rangle \langle 1_j | G_j'_{\alpha\beta} | 0_j \rangle$ and $\langle 0_i | \alpha_{i\alpha\beta} | 1_i \rangle \langle 1_j | \epsilon_{\alpha\gamma\delta} A_{j\gamma\delta\beta} | 0_j \rangle$ in (20) are zero, and the transition polarizabilities can be written in a form analogous to (9); we then obtain equations analogous to (12) but incorporating a factor of $\pm \tfrac{1}{2}$.

Also

$$\langle 0 | \alpha_{\alpha\beta} | 1_\pm \rangle \langle 1_\pm | \alpha_{\alpha\beta} | 0 \rangle = \tfrac{1}{2} \langle 0_1 | \alpha_{1\alpha\beta} | 1_1 \rangle \langle 1_1 | \alpha_{1\alpha\beta} | 0_1 \rangle +$$
$$\tfrac{1}{2} \langle 0_2 | \alpha_{2\alpha\beta} | 1_2 \rangle \langle 1_2 | \alpha_{2\alpha\beta} | 0_2 \rangle \pm \langle 0_1 | \alpha_{1\alpha\beta} | 1_1 \rangle \langle 1_2 | \alpha_{2\alpha\beta} | 0_2 \rangle \tag{20d}$$

so that

$$3 \langle 0 | \alpha_{\alpha\beta} | 1_+ \rangle \langle 1_+ | \alpha_{\alpha\beta} | 0 \rangle - \langle 0 | \alpha_{\alpha\alpha} | 1_+ \rangle \langle 1_+ | \alpha_{\beta\beta} | 0 \rangle =$$
$$\tfrac{9}{2} |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (5 + 3 \cos 2\theta) \tag{21a}$$

$$3 \langle 0 | \alpha_{\alpha\beta} | 1_- \rangle \langle 1_- | \alpha_{\alpha\beta} | 0 \rangle - \langle 0 | \alpha_{\alpha\alpha} | 1_- \rangle \langle 1_- | \alpha_{\beta\beta} | 0 \rangle =$$
$$\tfrac{27}{2} |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (1 - \cos 2\theta) \tag{21b}$$

$$7 \langle 0 | \alpha_{\alpha\beta} | 1_+ \rangle \langle 1_+ | \alpha_{\alpha\beta} | 0 \rangle + \langle 0 | \alpha_{\alpha\alpha} | 1_+ \rangle \langle 1_+ | \alpha_{\beta\beta} | 0 \rangle =$$
$$\tfrac{3}{2} [40 |\langle 1_i | \alpha_i | 0_i \rangle|^2 + 7 |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (5 + 3 \cos 2\theta)] \tag{21c}$$

$$7 \langle 0 | \alpha_{\alpha\beta} | 1_- \rangle \langle 1_- | \alpha_{\alpha\beta} | 0 \rangle + \langle 0 | \alpha_{\alpha\alpha} | 1_- \rangle \langle 1_- | \alpha_{\beta\beta} | 0 \rangle =$$
$$\tfrac{63}{2} |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (1 - \cos 2\theta) \tag{21d}$$

The relative intensities of the two bands in circularly polarized incident light are then

$$\frac{I_z^-}{I_z^+} = \frac{3(1 - \cos 2\theta)}{5 + 3 \cos 2\theta} \tag{22a}$$

$$\frac{I_x^-}{I_x^+} = \frac{21 |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (1 - \cos 2\theta)}{40 |\langle 1_i | \alpha_i | 0_i \rangle|^2 + 7 |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (5 + 3\cos 2\theta)} \tag{22b}$$

These expressions indicate that, if the two identical groups are parallel ($\theta = 0$), all the Raman intensity goes into the $1_+ \leftarrow 0$ transition; this would appear as a frequency shift on going from monomer to dimer, with the band intensity for a single dimer equal to that for two monomers. The direction of the shift depends on the sign of the coupling energy; if positive, the $1_+ \leftarrow 0$ transition shifts to higher frequency. As the groups move out of parallel, a doublet appears as intensity shifts from the $1_+ \leftarrow 0$ transition into the $1_- \leftarrow 0$ transition, although the coupling energy probably decreases with a consequent decrease in the resolution of the two bands. A similar situation is encountered in electronic spectra.[17] The depolarization ratios of the two bands in circularly polarized incident light are

$$\rho^+ = \frac{I_z^+}{I_x^+} =$$
$$\frac{6 |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (5 + 3 \cos 2\theta)}{40 |\langle 1_i | \alpha_i | 0_i \rangle|^2 + 7 |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (5 + 3 \cos 2\theta)} \tag{23a}$$

$$\rho^- = I_z^- / I_x^- = \tfrac{6}{7} \tag{23b}$$

Thus $\rho^-$ is $\tfrac{6}{7}$ for all values of $\theta$ and all allowed species of monomer vibrations; whereas $\rho^+$ has a maximum value of $\tfrac{6}{7}$, being less for totally symmetric monomer vibrations since $\langle 1_i | \alpha_i | 0_i \rangle$ is then nonzero. If the dimer is part of a larger asymmetric structure, all vibrations are totally symmetric to some degree, so the symmetric band should be polarized more than the antisymmetric band.

The Raman CID components associated with the two bands are

$$\Delta_z^+ = \frac{2\pi R_{21} \sin 2\theta}{\lambda(5 + 3 \cos 2\theta)} \tag{24a}$$

$$\Delta_z^- = -\frac{2\pi R_{21} \sin 2\theta}{3\lambda(1 - \cos 2\theta)} = -\frac{2\pi R_{21} \cot \theta}{3\lambda} \tag{24b}$$

$$\Delta_x^+ =$$
$$\frac{24\pi R_{21} |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 \sin 2\theta}{\lambda[40 |\langle 1_i | \alpha_i | 0_i \rangle|^2 + 7 |\langle 1_i | \alpha_{i\kappa_i} | 0_i \rangle|^2 (5 + 3 \cos 2\theta)]} \tag{24c}$$

$$\Delta_x^- = -\frac{8\pi R_{21} \sin 2\theta}{7\lambda(1 - \cos 2\theta)} = -\frac{8\pi R_{21} \cot \theta}{7\lambda} \tag{24d}$$

The divergence of (24b) and (24d) at $\theta = 0$ is not meaningful since there is no scattered radiation in this approximation and the higher order terms remove the singularity. Notice that $\Delta_z^+$ and $\Delta_z^-$ are independent of the symmetry species of the monomer vibrations and are of opposite sign. $\Delta_x^+$ and $\Delta_x^-$ are also of opposite sign, and it is remarkable that only $\Delta_x^+$ depends on the

(16) I. L. Fabelinskii, "Molecular Scattering of Light," Plenum Press, New York, N. Y., 1968, Section 19.

(17) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Chapman and Hall, London, 1963, p 137.

symmetry species of the monomer vibrations. If the sign of the coupling energy is known, the symmetric and antisymmetric bands can be identified. This identification could also follow from the polarization characteristics of the two bands, in which case the sign of the coupling energy could be deduced. The sign of the two Raman CID bands then gives the absolute configuration of the dimer; that of Figure 3 leads to a positive CID in the symmetric band.

The extension of this theory to a dimer consisting of two lower-symmetry groups in an arbitrary dissymmetric relative orientation is complicated. Extra terms involving components of intrinsic optical activity tensors of the monomers must be included to maintain origin invariance (for example, $G'_{12} \neq -G'_{21}$ in $C_{2v}$), and the polarizability tensors cannot be reduced to the simple form of (9). Nonetheless, some of the general features of the simple dimer treatment may extend to more complicated situations. In fact, Raman CID bands have been observed[6] which could originate in this mechanism. In $\alpha$-pinene, a large $\Delta_z$ couplet exists in two barely resolved bands centered at $\sim 780$ cm$^{-1}$. The relative intensities, depolarization ratios, and CID's of the two bands are of the orders deduced above. Since the bands fall in the $CH_2$ rocking region, these CID's could originate in coupling between $CH_2$ rocking vibrations on the two starred groups, which together constitute a rigid, highly dissymmetric structure.



Unfortunately, a detailed analysis of this situation is subject to all the fearful complexities mentioned above.

# A Study of the Distances Obtained from Nuclear Magnetic Resonance Nuclear Overhauser Effect and Relaxation Time Measurements in Organic Structure Determination. Distances Involving Internally Rotating Methyl Groups. Application to cis- and trans-Crotonaldehyde

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**Abstract:** Absolute internuclear distances between all of the protons of cis- and trans-crotonaldehyde in solution have been obtained by measuring the $^1$H{$^1$H} nuclear Overhauser enhancements between all of the spins and the $^1$H and $^{13}$C nuclear spin–lattice relaxation times for all of the spins. The results are compared with the reported microwave structure for trans-crotonaldehyde and a theoretically optimized structure (starting from the X-ray structure) for cis-crotonaldehyde. The internuclear distances involving the methyl protons are used to test two models for the effective position of the methyl protons when internal motions are considered.

The potential of the nuclear Overhauser effect[1] for providing information on the conformation of molecules in solution was first demonstrated by Anet and Bourn.[2a] The widespread chemical applications of the NOE which followed this initial report have recently been reviewed in detail by Noggle and Schirmer.[2b] Of particular interest are the paper of Bell and Saunders,[3] reporting a direct correlation of NOE enhancements with internuclear distance, and a series of papers by Noggle and coworkers,[4] demonstrating how relative internuclear distances can be quantitatively determined on systems of three or more spins from the NOE

measurements. Noggle and Schirmer[2b] have also stressed the value of an understanding of the nuclear spin–lattice relaxation.

We have been interested in the application of the NOE to the determination of the conformation in solution of the visual chromophore, 11-cis-retinal.[5,6] As a model system to test the quantitative aspects of the NOE approach, we have studied the molecules cis- and trans-crotonaldehyde, I and II below, respectively. The cis-



(I)      (II)
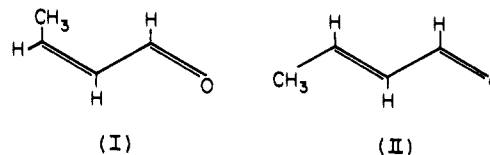
crotonaldehyde is analogous to the terminal fragment (C13–C15) of retinal. One question in particular which arose in the NOE studies of the retinals[5,6] was what

(1) (a) Abbreviations used: nuclear Overhauser effect, NOE; nuclear magnetic resonance, nmr; nuclear spin–lattice relaxation time, $T_1$. (b) In this paper unless stated otherwise NOE enhancements will refer to $^1$H{$^1$H} double resonance experiments.

(2) (a) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965); (b) J. H. Noggle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971.

(3) R. A. Bell and J. K. Saunders, *Can. J. Chem.*, **48**, 1114 (1970).

(4) (a) R. E. Schirmer, J. H. Noggle, J. P. Davis, and P. A. Hart, *J. Amer. Chem. Soc.*, **92**, 3266 (1970); (b) *ibid.*, **92**, 7239 (1970); (c) R. E. Schirmer, J. P. Davis, J. H. Noggle, and P. A. Hart, *ibid.*, **94**, 2561 (1972); (d) R. E. Schirmer and J. H. Noggle, *ibid.*, **94**, 2947 (1972).

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(6) R. Rowan, A. Warshel, B. D. Sykes, and M. Karplus, *Biochemistry*, **13**, 970 (1974).