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Vibrational Analysis by Electron Paramagnetic Resonance Spectroscopy. The Isopropyl Radical[1]

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Abstract: The isotropic hyperfine interactions of the protons and the α carbon atom of the isopropyl radical have been measured by EPR spectroscopy over the temperature range 130–350 K in liquid isooctane or propane. The data fit extremely well to a hypercotangent function of temperature derived on the assumption that a single, simple harmonic oscillator, the out of plane vibration of the radical, modulates the isotropic coupling constants. A vibration frequency of 380 ± 12 cm^{-1} deduced from the results is in excellent accord with the infrared spectroscopic value. INDO molecular orbital calculations predict hyperfine interactions and their dependences on the out of plane angle which are in fair agreement with the experimental observations.

Introduction

Modern experimental EPR techniques permit the observation of practically any thermodynamically stable radical even though it is kinetically transient,[2] and yield isotropic coupling constants which lead directly to structural information on free radicals. By contrast, gas-phase ultraviolet, photoelectron spectroscopic, and matrix isolation infrared methods provide detailed information about the vibrational behavior of radicals. They generally provide less structural information and are often limited experimentally because of the difficulties associated with radical generation.

It would clearly be advantageous, for experimental reasons, if the EPR technique could be used to provide vibrational information. This is possible, in principle, for a mode in which the isotropic coupling constants are strongly dependent on vibrational energy. Measurement of the temperature dependence of the coupling constants over a temperature range appropriate to the vibrational frequency in such a case should yield information about that particular mode, such as the frequency and the EPR parameters for radicals in vibrationally excited states.[3]

Such possibilities for the application of EPR have been recognized for some time.[4] For example, methyl has been studied to a limited extent[5] experimentally[7,8] while *tert*-butyl,[9] 7-norbornenyl,[10] some aromatic anions and cations,[11] and

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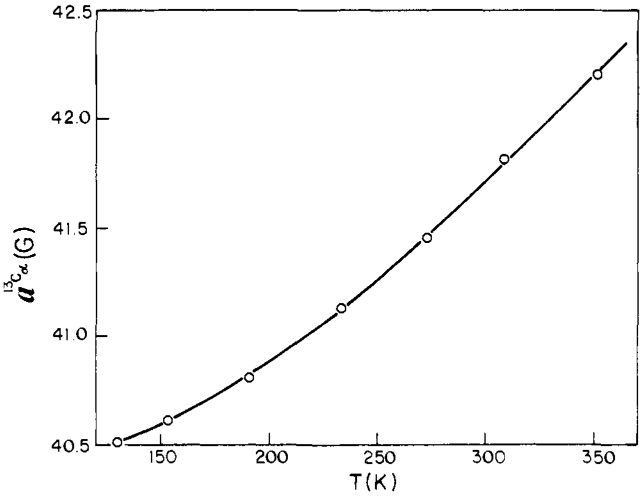


Figure 1. Hyperfine interaction (gauss) of the α carbon nucleus of isopropyl as a function of temperature. Experimental data are represented by circles; the curve is the best fit hypercotangent function.

hexafluoride radicals[12] have been studied in greater detail. In all of these cases, the experiments are somewhat equivocal since the data do not lead directly to results which can be compared with those obtained by another technique. We therefore take the view that the EPR approach to vibrational analysis has not been critically tested.

The purpose of this paper is to examine the feasibility of using EPR routinely to determine vibrational parameters. We have therefore chosen to study the umbrella inversion mode of the isopropyl radical for which the frequency has been very recently determined by an infrared technique[13] Using isotopically labeled material we have measured the ^{13}C hyperfine splitting due to the α carbon ($a^{^{13}C_\alpha}$) as a function of temperature. A simple analysis of the data yielded a vibrational frequency which was in excellent agreement with infrared data.[13] The force constant obtained for the vibration was further applied to predict the "out of plane" vibrational frequencies for a number of simple alkyl radicals and good agreement was obtained with the literature values.

As a second and quite separate stage, we have applied a theoretical approach to predict vibrational parameters. The relationships between such parameters and hyperfine splittings have been investigated theoretically, particularly in the case of methyl.[7,10,14-20] However, in several instances experimental data such as vibrational frequencies or force constants have been introduced into the treatments. A far more satisfactory test of theory, which we have adopted in this work, is to predict vibrational properties from *calculated* hyperfine parameters. Using the INDO molecular orbital approach we have obtained results in fair agreement with experiment.

Experimental Section

Materials. 2-Bromo-*2*-^{13}*C*-propane (90 atom % enriched), isooctane (spectroscopic grade), and propane were commercially available and were used without further purification. Hexa-*n*-butylditin and di-*tert*-butyl peroxide were purified by distillation before use.

Radical Generation. The isopropyl radical was generated by photolysis of mixtures of 2-bromo-*2*-^{13}*C*-propane (10% v/v) and hexa-*n*-butylditin (10% v/v), in isooctane or propane as solvent.

$$n\text{-}Bu_6Sn_2 \xrightarrow{h\nu} 2n\text{-}Bu_3Sn\cdot$$

$$n\text{-}Bu_3Sn\cdot + Br^{13}CH(CH_3)_2 \rightarrow n\text{-}Bu_3SnBr + \cdot^{13}CH(CH_3)_2$$

$$2\cdot^{13}CH(CH_3)_2 \rightarrow \text{nonradical products}$$

Addition of a small amount of di-*tert*-butyl peroxide ($\lesssim$10% v/v) led to an increase in the concentration of isopropyl.

Table I. EPR Parameters for the Isopropyl Radical in Solution as a Function of Temperature

T, K[a]	g[b]	$a^{^{13}C_\alpha}$, G[b]	a^{H_α}, G[b]	a^{H_β}, G[b]
131	2.002 675 (4)	40.516 (14)	22.226 (16)	24.711 (14)
153	2.002 675 (2)	40.616 (7)	22.173 (8)	24.709 (7)
191	2.002 695 (2)	40.812 (6)	22.052 (7)	24.716 (6)
191	2.002 705 (2)	40.824 (7)	22.059 (8)	24.723 (6)
233	2.002 690 (3)	41.136 (9)	21.983 (11)	24.684 (9)
233	2.002 690 (3)	41.124 (10)	22.003 (11)	24.691 (10)
273	2.002 688 (2)	41.452 (7)	21.904 (8)	24.676 (7)
273	2.002 695 (2)	41.457 (8)	21.887 (10)	24.662 (8)
309	2.002 700 (2)	41.817 (7)	21.842 (8)	24.672 (7)
309	2.002 702 (3)	41.811 (11)	21.846 (13)	24.669 (11)
352	2.002 680 (6)	42.209 (19)	21.707 (23)	24.587 (19)
352	2.002 676 (3)	42.211 (10)	21.704 (12)	24.576 (10)

[a] Error limits ±0.5 K. [b] The numbers shown in brackets are one standard deviation in the last significant figure as obtained by least-squares fitting (see Experimental Section).

The samples were photolyzed directly in the cavity of a standard Varian E104 spectrometer using a 500-W high-pressure mercury-arc lamp. Most of the infrared and much of the visible radiation was removed by passing the light through a quartz filter (8-cm path length) containing an aqueous solution of cobalt and nickel sulfates. After filtration the heating effect at the sample was reduced to 0.8°.

Measurement of EPR Parameters. At each temperature the precise field and microwave operating frequencies were measured for ~15 of the "second-order" lines[21] of the spectrum, using an NMR gaussmeter and frequency counter. Corrections for the difference in magnetic field between the position of the NMR probe and that of the sample were made using tetracene$^{+}\cdot$ as a standard.[22]

Once the field and frequency had been determined for each line, the spectral parameters were computed using an exact solution of the isotropic Hamiltonian. An iterative least-squares procedure[23] was then applied which adjusted the parameters so as to obtain the best fit to all of the measured lines. Standard deviations were approximately ±0.01 G for each of the hyperfine splittings and $\pm 0.3 \times 10^{-5}$ for g. It should be noted that a complete error estimate for g gave $\sigma = \pm 1.0 \times 10^{-5}$, which results from additional systematic errors introduced in the field correction procedure. As has been previously observed,[24] changing the signs of quantum numbers associated with the EPR transitions frequently indicated that the smallest deviations were obtained when a^{H_α} was opposite in sign to $a^{^{13}C_\alpha}$ and a^{H_β}. However, application of the F test[25] indicated that such observations had very poor statistical confidence levels.

Results and Discussion

Vibrational Analysis. The EPR parameters for isopropyl as a function of temperature are shown in Table I, and are in good agreement with literature values.[26] The hyperfine splitting due to the central carbon atom, $a^{^{13}C_\alpha}$, increases monotonically with increasing temperature (Figure 1) indicating that the radicals, on average, take on more s character at the higher temperatures. When considered along with the magnitude of $a^{^{13}C_\alpha}$, these observations are most simply explained if the out of plane vibration of C_α behaves as a harmonic oscillator, with the hypothetical "planar" [27] structure at the minimum of the potential energy curve. The criteria for testing this model are the quality of fit obtained with the experimental data and the accuracy of the vibrational frequency as compared with data available from infrared spectroscopy.[13] It is assumed that the effect of solvent on the hyperfine parameters is negligible.[28]

For small displacements, $a^{^{13}C_\alpha}$ can be expressed in terms of a power series in the *normal* coordinate ϕ for the out of plane vibrational mode:

$$a^{^{13}C_\alpha}(\phi) = a_0 + a_2\phi^2 + a_4\phi^4 + \ldots \qquad (1)$$

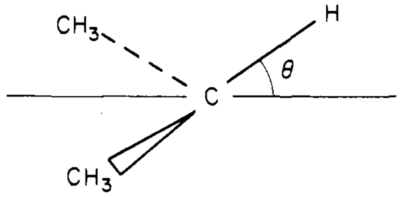
The terms in odd powers of ϕ are zero[7] because the vibration is symmetric about the "planar" configuration. There are, furthermore, good reasons[7] to believe that the quartic and higher terms are negligible. Using the average value $\overline{\phi^2}$ for each level of a simple harmonic oscillator and applying Boltzmann statistics for the ensemble of radicals we obtain

$$a^{^{13}C_\alpha}(T) = a_0 + a_2\left[\frac{h}{8\pi^2\nu}\coth\left(\frac{h\nu}{2kT}\right)\right] \qquad (2)$$

where ν is the vibrational frequency. As a further simplification we can separate the *normal* coordinate into a term involving the reduced mass and a spatial *symmetry* coordinate,[30] θ. If the vibration is unique then θ is simply related to ϕ and the force constant F_θ as follows:

$$\theta = 2\pi\nu\phi/F_\theta^{1/2} \qquad (3)$$

In the case of the isopropyl radical, the coordinate θ is chosen to be the angle between the C-H bond and the C-C-C plane.



In terms of this symmetry coordinate the hyperfine interaction and the potential energy of vibration are given by

$$a^{^{13}C_\alpha}(\theta) = a_0 + a_2'\theta^2$$

$$2U = F_\theta\theta^2$$

After this transformation we obtain

$$a^{^{13}C_\alpha}(T) = a_0 + a_2'\frac{h\nu}{2F_\theta}\coth\left(\frac{h\nu}{2kT}\right) \qquad (4)$$

The experimental data, i.e., values of $a^{^{13}C_\alpha}$ at different temperatures, were fitted to eq 4 using a nonlinear regression procedure to obtain the best fit for the various parameters. The results were $a_0 = 37.12 \pm 0.18$ G, $a_2'h\nu/2F_\theta = 3.29 \pm 0.19$ G, and $h\nu/2k = 270.0 \pm 8.9$ K, where the errors represent one standard deviation. The fitted curve is shown in Figure 1. It follows directly that $\nu = 375 \pm 12$ cm^{-1} for the inversion of $^{13}\dot{C}H(CH_3)_2$.

To obtain the vibrational frequency for $^{12}\dot{C}H(CH_3)_2$ we need to correct for the $^{13}C/^{12}C$ isotope effect. Assuming a standard geometry[31] (see below) (i.e., bond lengths of 1.54 (C-C) and 1.08 Å (C-H) and ∠CCC = 120°), we obtain $F_\theta = (6.56 \pm 0.42) \times 10^{-2}$ mdyn Å rad^{-2}. This leads to a vibrational frequency for $^{12}\dot{C}H(CH_3)_2$ of 380 ± 12 cm^{-1}, in excellent agreement with the value of 375 cm^{-1} observed by infrared.[13]

Vibrational Frequencies for Other Alkyls. We can further extend the calculation by assuming that this force constant for the out of plane vibration is transferable throughout the series $\cdot CH_3$, $\cdot CD_3$, $\cdot CH_2CH_3$, $\cdot CH(CH_3)_2$, $\cdot C(CH_3)_3$. This kind of assumption[32] is not uncommon in vibrational analyses and is equivalent to assuming that the potential well is the same throughout the series and that only changes in the reduced masses affect the frequencies. On this basis the vibrational frequencies for the out of plane motion can be easily calculated.[30] The results of these extremely simple calculations are shown in Table II. They are clearly in excellent agreement with the available experimental data.

Table II. Out of Plane Vibrational Frequencies for Simple Alkyl Radicals

radical	ν, cm^{-1} calcd[a]	ν, cm^{-1} exptl
$\cdot CH_3$	596	617[b]
$\cdot CD_3$	462	463[b]
$\cdot CH_3CH_2$	499	541[c]
$(CH_3)_2\dot{C}H$	380[d]	375,[c] 380[e]
$(CH_3)_3C\cdot$	202	

[a] A force constant of 0.0656 mdyn Å rad^{-2} was used in these calculations. [b] A. Snelson, *J. Phys. Chem.*, **74,** 537 (1970). [c] J. Pacansky, D. E. Horne, G. P. Gardini, and J. Bargon, *ibid.*, **81,** 2149 (1977). [d] Reference frequency for calculation of force constant. [e] This work.

Table III. INDO I Unpaired Spin Densities for Isopropyl

atom	unpaired s spin density geometry A[b]	unpaired s spin density geometry B	isotropic hyperfine[a] interaction, G geometry A[b]	isotropic hyperfine[a] interaction, G geometry B
C_α	0.0367	0.0445	30.1	36.5
H_α	−0.0345	−0.0356	−18.6	−19.2
C_β	−0.0193	−0.0138	−15.9	−11.3
$H_\beta{}^1$	0.0052	0.0033		
$H_\beta{}^2$	0.1105	0.0670	40.7[c]	24.7[c]
$H_\beta{}^3$	0.1105	0.0670		

geometry	bond length, Å C_α–H_α	bond length, Å C_α–C_β	bond length, Å C_β–H_β	bond angle, deg $\angle C_\beta C_\alpha C_\beta$	bond angle, deg $\angle C_\alpha C_\beta H_\beta$
A	1.121	1.431	1.126	128.0	113.0
B	1.080	1.540	1.080	120.0	109.5

[a] Calculated using the empirical conversion factors of ref 34, p 131. [b] Energy-optimized geometry for a C_{2v} configuration in which C_α, H_α, $2C_\beta$'s, and $2H_\beta$'s are all coplanar. [c] Average of H_β's appropriate to free rotation about C_α–C_β.

Molecular Orbital Calculations. INDO semiempirical MO calculations have been reasonably successful in predicting the hyperfine interactions in many free radicals. In spite of the uncertainty regarding the appropriate factors for converting spin density to gauss, it is fair to say that the method almost invariably generates results in semiquantitative agreement with experiment.[34] There has, however, been some criticism[19] of the method when used to predict the effects of vibrations on nuclear hyperfine interactions. The results of our INDO calculations for the isopropyl radical presented in Tables III and IV are in fair accord with the experimentally determined isotropic hyperfine interactions and their temperature dependences.

The computations were carried out using a minimal basis set of valence s and p atomic orbitals and the INDO I ($K = 1$) parametrization.[35] Since internal rotation of the methyl groups about the C_α-C_β bonds was shown to have only a very small effect on both the total energy and the isotropic hyperfine interactions, attention was confined to one particularly symmetric structure. In that conformation one proton from each methyl group falls in the carbon-atom plane and approaches its equivalent in the other methyl group most closely. Local trigonal symmetry was assumed for the methyl groups. Within these constraints all bond angles and distances were varied until an energy minimum was obtained for which the geometry and unpaired s spin densities are given in Table III under geometry A. The results of a calculation for a "standard" geometry (B in Tables III and IV) are also reported. In the lowest energy configuration the α proton lay in the (nodal) plane of the carbon atoms.

The effects of vibration were simulated for both geometries by carrying out the INDO calculation at 5° intervals of the out of plane angle up to $\theta = 25°$. When the increments in energy or hyperfine interaction were fitted to polynomials in θ it was found that only the terms in θ^2 were significant, i.e., the vibration was harmonic. Least-squares fits to parabolic functions of the type $(a - a_0) = a_2'\theta^2$ were excellent, with standard deviations in the constants of proportionality being ~1%. These

Table IV. Parameters for the Dependence of Isotropic Hyperfine Interactions on the Out of Plane Angle[a] in Isopropyl

	C_α		H_α		H_β		
	a_0, G	a_2', G rad^{-2}	a_0, G	a_2', G rad^{-2}	a_0, G	a_2', G rad^{-2}	ν cm^{-1}
exptl[c]	37.12 ± 0.18	57.8 ± 3.3	−23.11[d] ± 0.06	16.0 ± 0.8	24.98 ± 0.05	−4.2 ± 0.6	375 ± 12
INDO[e] A	30.1	86.2	−18.6	12.8	40.7	−9.5	699
INDO[e] B	36.5	115.9	−19.2	26.2	24.7	−8.0	501

[a] Parameters are the best fits to the expression $a = a_0 + a_2'\theta^2$, θ being the out of plane angle as defined in the text. [b] Frequency of the out of plane vibration of $(CH_3)_2{}^{13}\dot{C}H$. [c] Experimental data were fitted to $a = a_0 + a_2'(h\nu/2F_\theta)\coth(h\nu/2kT)$. Parameters for H_α and H_β were obtained using the value of $h\nu/2k$ derived from the C_α fit. [d] Sign choice for the a_0 value based on INDO results. [e] Geometries for INDO A and B are given in Table III.

constants are assembled in Table IV where they are compared with the values derived from fitting the experimental data (Table I) to expression 4. The INDO vibrational frequencies given in Table IV were derived from the fits of incremental energy vs. θ^2 and the appropriate reduced masses.

The overall agreement between the INDO calculations and the experimental results is fair with the standard geometry model B giving somewhat better predictions than the energy-optimized geometry A. Both structures considerably overemphasized the steepness of the potential well governing the out of plane vibration and the modulation of the ^{13}C hyperfine interaction. It has been suggested[19] that the reason for this bias possibly lies in the inability of the INDO method to account quantitatively for the lack of orbital following. Evidently, the INDO method cannot be trusted to give more than qualitative indications of the temperature dependence of hyperfine interactions. However, it is clear that the accuracy of the predictions based on geometry B for a *vibration-free molecule* is remarkably good and tends to support the use of standard geometries in INDO calculations for hydrocarbon radicals.

The INDO coupling constants are, of course, the values for a vibration-free molecule and must be compared with the a_0 values, *not* the values measured at (or extrapolated to) low temperatures. It should be noted that, although our a_0 values given in Table IV do not contain a zero-point vibrational contribution from ν_6, the out of plane vibration, such contributions from the remaining internal modes are not necessarily insignificant. A substantial zero-point vibrational modulation of the hyperfine interactions is possible, in principle, for certain high-frequency modes even though they make no contribution to the temperature dependences within the experimental temperature range.[20]

Criticisms of the Technique. The EPR approach to vibrational analysis is subject to the criticism that it takes an oversimplified view of the potential function for the vibration. There are indications that potential functions of this kind may not be truly harmonic. For example, in the case of the methyl radical[33] a careful analysis of the vibrational frequencies due to isotopically substituted species indicates that a quartic term in the normal coordinate contributes to the potential function steepening the walls of the well. Ab initio calculations[36,37] on the ethyl radical[38] indicate a nonplanar geometry with the optimum planar geometry being disfavored by 0.46 kcal/mol. It is equally clear that the orientation of the substituent groups with respect to the radical center can lead to variations in energy. The implications of these calculations have been discussed in detail by Houle and Harding.[40] In principle it would therefore seem that the choice of a simple harmonic potential function is an oversimplification. However, in practice the experimental data suggest that this is not the case. As long as these energy differences between different configurations and conformations are small as compared to the vibrational energy levels then it would seem that to a good approximation the simple harmonic function is satisfactory. A more difficult problem is the possibility that the out of plane vibration is coupled to the torsion of the methyl groups in the simple alkyls. While this is unlikely to be the case for isopropyl and smaller radicals for which the out of plane vibration has at least twice the frequency of the methyl torsional mode, it may well contribute to the difficulties associated with the *tert*-butyl problem.[9]

A further simplifying assumption which we have used is that the ^{13}C hyperfine interaction is a quadratic function of the out of plane angle. It should be noted that for a vibrational frequency of 380 cm^{-1} the classical amplitudes for θ are large (19.4° for $\nu = 0$). However, it seems unlikely that terms in the fourth and higher powers of angle contribute significantly[7] to $a^{^{13}C_\alpha}$ for the temperature range of our experiments. The excellent agreement between calculated and observed vibrational frequencies shown in Table II is either remarkably fortuitous or an indication that the underlying assumptions are essentially correct. Initial results of a similar study of the ethyl radical tend to eliminate serendipity as the cause and support the simplified approach adopted here.

Summary

The EPR data indicate that the umbrella inversion mode for isopropyl behaves as a simple harmonic oscillator. The EPR experiment led directly to a measure of the vibrational frequency which was in good agreement with infrared data. Moreover, the force constant obtained from the analysis could be used with considerable success to predict the analogous vibrational frequencies for a series of alkyl radicals. INDO molecular orbital calculations were in fair agreement with the experimental observations.

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References and Notes

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(32) We emphasize that these calculations are based on the assumption of a harmonic oscillator. It should be noted that in the case of *tert*-butyl the experimental data[9] suggest that the out of plane vibration is governed by a double minimum potential function. It may be that such a function applies to all simple, acyclic alkyl radicals but that the effects are only detected when the vibrational frequency is less than the barrier to inversion (e.g., *tert*-butyl[9]) or when the data are of such precision as to allow the detection of slight anharmonic effects (e.g., methyl[33]).
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The Inertial Contribution to Vibrational Optical Activity in Methyl Torsion Modes

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Abstract: Simple expressions are obtained for the Raman and infrared optical activity generated by the oscillations in space of a chiral molecular frame that accompany a methyl torsion vibration in the molecule. Substitution of methyl groups at different points permits the structure of chiral molecules to be probed about different torsion axes. The theory is most straightforward when the torsion axis is a principal axis of inertia of the molecule, and is applied to oscillations of a bridged biphenyl about its twofold proper rotation axis.

Vibrational optical activity spectra can now be obtained using two complementary techniques: infrared circular dichroism (CD), a measure of the small difference in the absorption of left and right circularly polarized infrared radiation;[2,3] and the Raman circular intensity difference (CID), which results from a small difference in the intensity of vibrational Raman scattering in right and left circularly polarized incident visible light.[4-13] Vibrational optical activity is expected to be a useful new means of determining stereochemistry (conformation and absolute configuration) in chiral molecules since, unlike electronic optical rotation and circular dichroism, which only provide stereochemical information about chromophoric groups and their immediate intramolecular environments, every part of a molecule can contribute to a vibrational optical activity spectrum. On account of technical difficulties, related to the fact that the dynamical nature of optical activity reduces its magnitude at low frequencies, the spectral region below about 1600 cm^{-1} is inaccessible to infrared CD at present; most studies have involved carbon-hydrogen stretching modes. On the other hand, the complete vibrational spectrum is accessible to the Raman CID technique, with the region from about 80 to 2000 cm^{-1} (containing, in particular, deformations and torsions) usually showing the largest effects.

It is important to understand how vibrational optical activity is generated in typical structural units in chiral molecules, and to develop simple procedures for extracting stereochemical information from the signs and magnitudes. The methyl group could be valuable in this respect since chiral molecules often contain methyl groups showing distinctive Raman CIDs in some of their characteristic modes of vibration.[5,7,10] The torsion is perhaps the simplest of the characteristic vibrational modes of the methyl group; it provides a novel way of probing the stereochemistry of the rest of the molecule.[7] There seems to be little possibility of observing in the near future vibrational optical activity in methyl torsion modes using infrared CD because the corresponding frequencies occur in the far infrared (from about 100 to 300 cm^{-1}).

The origin of infrared and Raman intensity and optical activity in a methyl torsion vibration can be understood by considering the simplest situation in which the threefold proper rotation axis of the methyl group is also a principal inertial axis of the molecule. Since first- and second-rank tensorial properties of an object with a threefold or higher proper rotation axis are unaffected by rotations about that axis, the electric dipole moment, polarizability, and optical activity of the methyl group, referred to the principal internal axis system, do not change in the course of the torsion vibration. The origin of any infrared or Raman intensity or optical activity must therefore be sought in the rest of the molecule. Two mecha-

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