Vibrational Circular Dichroism of Six-Membered-Ring Monoterpenes. Consistent Force Field, Fixed Partial Charge Calculations

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Abstract: The vibrational circular dichroism (VCD) of several monoterpenes has been calculated by using the consistent force field, fixed partial charge method. In the case of menthene, limonene, and menthenol good agreement was found between the calculated and experimental VCD for the lowest energy conformer. As previously predicted by Polavarapu, Diem, and Nafie, the VCD was shown to be dominated by CH_2 stretching modes. The relative phase of these modes was dependent on the substituent being axial or equatorial, and consequently the overall phase of the VCD was seen to be conformationally sensitive. This calculational model was also applied to carvone, pulegone, and menthol but had less success due in part to the approximate force field. These results serve to support the applicability of the FPC model to VCD in the CH stretching region when conservative spectra are observed.

Vibrational circular dichroism (VCD) has great potential as a stereochemical tool due to its ability to sample several probes of the molecular chirality.[1] The simplest, general theoretical model for VCD is the fixed partial charge (FPC) model.[2] In previous papers we have found good agreement between FPC calculated VCD and experimental results in the saturated CH stretching region of spirononadiene[3] and 3-methylcyclohexanone[4] by using normal modes derived from the consistent force field (CFF) energy minimization routine.[5] In the latter study it appeared that the FPC model would work best for those systems whose VCD originated in the interaction and relative motion of the CH stretches themselves. Such a situation should give rise to a conservative VCD spectrum in the CH stretching region which in turn would be indicative of a favorable FPC situation.

In their original VCD paper, Nafie et al.[6] noted the similarity and conservative nature of the menthol and the 3-methylcyclohexanone VCD. In a recent work, Polavarapu, et al.[7] found that the VCD of limonene, menthene, and menthenol were nearly conservative and very similar and hence appeared to be dominated by the CH_2 stretches in the cyclohexene ring that were common to all three molecules. These monoterpene systems thus appear to be useful for testing our hypothesis regarding the applicability of the FPC model. In addition, pulegone and carvone were readily available and offer small structural changes in the six-membered ring, thus allowing the consequent effects on the VCD to be sought in the FPC calculations.

In order to calculate the VCD, however, a structure, force field, and set of effective charges are needed. For menthene and limonene, both hydrocarbons, the CFF should give an accurate evaluation of the structure and the relative energies of the various conformations and, as we have previously shown,[3,4] a qualitatively useful vibrational force field. However, the CFF parameters are less extensively optimized for ketones, and adequate alcohol parameters are not available. Our approach then is to concentrate on the hydrocarbons which should be the best test of our hypothesis. Calculations for the other molecules use a force field of reduced quality and, hence, are somewhat less reliable. They will be discussed primarily by comparison to the limonene and menthene results. The charges in all cases are derived from CNDO calculations, but the values are scaled to reproduce the integrated absorbance spectra.[4]

Experimental Section

Limonene, *p*-menth-1-ene, *p*-menth-1-en-9-ol, carvone, pulegone, and menthol were all obtained as resolved isomers (Aldrich) and studied without further purification in dilute CCl_4 solution. VCD and absorption spectra were obtained on a previously detailed infrared CD instrument[8] as single scans with a resolution of 10.6 cm^{-1}, time constant of 10 s, sample concentration of 0.2 M, and path length of 0.25 mm (except for carvone, 8-cm^{-1} resolution and 0.75-mm path). For all except carvone and menthol, racemic samples were not available for obtaining base lines. Since the base line of VCD racemic samples in this region was featureless, though not flat, the spectra of the other compounds could be obtained by subtracting either CCl_4 or (±)-carvone base lines with no significant differences. The data in this paper have been replotted with these base lines subtracted.

Calculations

The geometries of the minimum energy conformations were determined by optimizing them from 16 different systematically chosen starting distortions of the six-membered ring for each molecule. In menthene, menthenol, limonene, and carvone only two basic ring conformers were determined. Energies of the rotamers of the isopropyl group for the lowest energy structures were also determined starting from these minimum energy ring conformations. The CFF calculations for pulegone and menthol led to a greater number of conformational minima, and only the lowest energy structures will be discussed. The relative energies are tabulated in Table I, and the structures are discussed in the following section. Since in our previous work with 3-methylcyclohexanone[4] and 3-methylcyclopentanone[9] we have obtained similar stability patterns with the CFF and Allinger's molecular mechanics force field,[10] we have not carried out a comparative study here. For menthol and menthenol the standard parameter set was extended by adding O–H force constants that reproduced observed vibrational frequencies. Relative energies of the rotamers of the OH group were also evaluated to ascertain the importance of that group in the minimization and subsquent FPC calculations.

By use of Schellman's FPC equations[2a] and net atomic charges

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(1) Reviews of VCD: L. A. Nafie and M. Diem, *Acc. Chem. Res.*, **12**, 296 (1979); P. J. Stephens and R. Clark in "Optical Activity and Chiral Discrimination", S. F. Mason, Ed., Reidel, Boston, 1979, p 263.

(2) J. A. Schellman, *J. Chem. Phys.*, **59**, 4678 (1973); **60**, 343 (1974).

(3) T. A. Keiderling and P. J. Stephens, *J. Am. Chem. Soc.*, **101**, 1396 (1979).

(4) R. D. Singh and T. A. Keiderling, *J. Chem. Phys.*, in press.

(5) A. Warshel and M. Levitt, *QCPE*, **10**, 247 (1974); A. Warshel, *Mod. Theor. Chem.* **8**, 133 (1976).

(6) L. A. Nafie, T. A. Keiderling, P. J. Stephens, *J. Am. Chem. Soc.*, **98**, 2715 (1976).

(7) P. L. Polavarapu, M. Diem, L. A. Nafie, *J. Am. Chem. Soc.*, **102**, 5449 (1980).

(8) C. N. Su, V. J. Heintz, and T. A. Keiderling, *Chem. Phys. Lett.*, **73**, 157 (1980); T. A. Keiderling, *Appl. Spectrosc. Rev.*, in press.

(9) R. D. Singh and T. A. Keiderling, to be published.

(10) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Am. Chem. Soc.*, **95**, 3893 (1973), and references therein.

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Table I. CFF Relative Total Energies of Menthene, Limonene, Menthenol, Carvone, and Pulegone Conformers[a]

menthene		limonene		menthenol[b]		carvone		pulegone[c]	
conformer	energy	conformer	energy	conformer	energy	conformer	energy	conformer	energy
EQ (G')	−1.748	EQ (C)	−3.282	EQ (G')	−2.970	EQ (C)	−2.805	C-EQ	−3.012
EQ (G)	−1.536	EQ (T)	−1.988	EQ (G)	−1.870	EQ (T)	−1.298	C-AX	−2.180
EQ (T)	−0.748	AX (T)	0.000	EQ (T)	−0.998	AX (C)	−1.085	F-EQ	−1.632
AX (G')	−0.125			AX (T)	0.000	AX (T)	0.000	F-AX	−0.643
AX (T)	−0.055							B-AX	0.000
AX (G)	0.000								

[a] Energies in kcal/mol referenced arbitrarily to the highest energy conformer in the set. T, G, G', and C stand for trans, gauche 1, gauche 2, and cis rotamers, respectively, while EQ and AX stand for equatorial and axial orientation of the substituent with respect to the ring. [b] Potential parameters for the O and H atoms in the hydroxyl group, not included in the QCFF/PI program, were obtained by fitting the infrared frequencies associated with this group. [c] In pulegone, C, F, and B stand for chair, folded, and boat conformations of the ring, respectively.

Table II. Charge Scaling Factors and the Net Atomic Charges on the Atoms of Various Chiral Molecules As Calculated by the CNDO/S–CI Method[a]

	menthene	limonene	menthenol	carvone	pulegone	menthol
atom[c]	7.74[b]	6.04[b]	7.78[b]	3.51[b]	4.24[b]	8.27[b]
C_1	0	0	0	0	−15	−15
H_1					+15	+15
C_2	−75	−75	−75	0	−45	−45
H_3	+15	+15	+15	+35	+25	+25
C_3	−25	−25	−25	−25	−45	−45
H_3	+25	+25	+25	+35	+25	+25
C_4	−15	+5	−15	+5	−100	−15
H_4	+15	+30	+15	+30		+15
C_5	−25	−25	−25	−15	+285	+45
H_5	+25	+25	+25	+45		+45
O_5					−460	−315
H_0						+175
C_6	−25	−25	−25	+285	−25	−45
H_6	+25	+25	+25		+45	+25
O_6				−455		
C_7	−65	−65	−65	−65	−75	−75
H_7	+20	+20	+20	+30	+25	+25
C_8	−15	+20	−15	+20	+80	0
H_8	+15		+15			+25
C_9	−65	−150	+65	−150	−60	−70
H_9	+20	+30	+30	+30	+40	+25
O_9			−315			
H_0			+175			
C_{10}	−65	−65	−70	−65	−60	−70
H_{10}	+20	+30	+20	+30	+40	+25

[a] Charges are listed for only one H atom in a CH_2 or CH_3 group in units of 10^{-3} e. [b] The scale factor is calculated by taking the square root of the ratio of the experimental dipolar strength and that calculated for the best structure in each system. [c] Atom numbering scheme follows convention of starting at the methyl substituent and numbering around the ring through the double bond toward the isopropyl group.

from CNDO/S–CI[11] the vibrational dipole (absorption) and rotational (VCD) strengths were determined. For purposes of comparison to experiment, these calculated spectra were plotted as the sum of Gaussian line shapes 10 cm^{-1} in half-width centered at each calculated frequency. This width was chosen to best reflect the observed overall absorption line shape and the observed ϵ value of the peaks while not obscuring any features due to excessive overlap caused by inaccurate frequency determination. These CNDO charges result in dipole strengths that are considerably lower than those found experimentally and were thus scaled to match the integrated absorption intensity over the CH stretching region.[4] The actual scaling factors used are listed in Table II along with the CNDO charges. For menthene only, the effects of modifying the force field to better reproduce the experimental frequencies and intensities were explored. Since no significant improvement was noted, further study of force-field effects was not pursued.

Results and Discussion

The six molecules studied here were chosen for tractability as well as their similar structures. In this section each will be discussed separately and comparisons between them will be noted. Some general results bear preliminary mention, however. Of the six, menthene, limonene, menthenol, and carvone all have a cyclohexene ring in common. These four show two basic structural types which can be classified as having the isopropyl group either axial (AX) or equatorial (EQ), with the EQ structure always being lower in energy. The double bond in the ring substantially restricts the allowed conformations permitting only the groups at the 4 and 5 positions to pucker out of the plane of the ring. In pulegone and menthol, without this restriction, many more conformations result.

This AX vs. EQ nature of the isopropyl group also affects the relative phase of the quasi-degenerate CH_2 stretching vibrations. This results in a sign change for the resultant CH_2 VCD and makes the overall pattern conformationally sensitive. The splitting of the E-like methyl group asymmetric stretch is also sensitive to the AX–EQ change, but the effect is so small, due to the overlap of the modes, that it is prevented from making a major contribution to the VCD. Overall, the calculated CH stretching VCD is dominated by the CH_2 groups and is, in turn, conformationally dependent. This calculated result is consistent with the conclusions of Polavarapu et al.[7] based on the experimental spectra and emphasizes the value of comparative empirical study of the VCD of molecules with similar structure.

Menthene. In Figure 1 are illustrated the conformers of

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(11) J. DelBene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807 (1968); J. DelBene, H. H. Jaffe, R. L. Ellis, and J. G. Kuehnlenz, *QCPE*, **10**, 174 (1970).

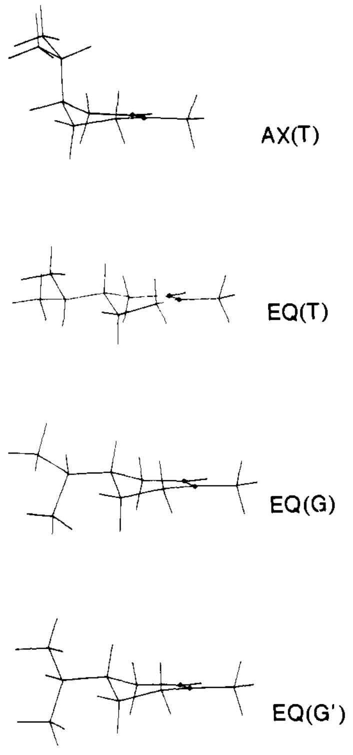

Figure 1. Minimum energy conformers AX and EQ and the rotamers T, G, and G′ (see text) of menthene as calculated using the CFF parameters. Filled circles indicate location of the double bond.

menthene which we have studied. The perspective is chosen to emphasize the planarity of the carbons at the 6, 1, 2, and 3 positions (numbering from the methyl through the double bond toward the isoproyl) and the displacement of C_4 above and C_5 below the plane. It should be noted that the AX conformer is shown with the opposite configuration to emphasize structural similarity. Rotamers of only the lower energy EQ conformation are presented as the three AX rotamers are very close in energy and presumably contribute little to the spectra (Table I). The rotamers can be characterized as having the methyl C–H bonds trans, EQ (T), or gauche, EQ (G) and EQ (G′). While EQ (G) and EQ (G′) are very close in energy, they are significantly lower than EQ (T) and the three AX conformers and hence should dominate the spectra of room temperature samples.

In Figure 2 are illustrated the calculated CFF–FPC VCD for the four conformers of Figure 1 as well as the experimental spectrum for comparison. Our experimental data for this and the other previously measured compounds agree with published spectra.[6,7] It is clear from Figure 2 that rotation of the isopropyl group has only a minor effect on the calculated VCD. The three EQ conformers give very similar VCD for all but the high energy (2970 cm^{-1}) modes. For that band, the spectrum of EQ (G) agrees better with experiment than does that of EQ (G′), the lowest energy structure; but, considering their relative energies, an equilibrium between the two structures would neither be unexpected nor in conflict with the experiment.

In evaluating the overall effectiveness of the FPC for this spectrum, it should be remembered that the force field is general and that the calculated and experimental frequencies are somewhat in disagreement. Our criterion for success is thus a *qualitative* reproduction of the sign pattern of the VCD. The magnitudes will be affected by the frequency calculation in that overlaps are altered. We have chosen to represent the data as a sum of lines with 10-cm^{-1} half-widths at $1/e$ in order to emphasize all the features and deemphasize the overlap. From comparison with experiment, this width may be too narrow and may be the cause of the calculated spectra being about three times larger in magnitude than the experimental spectrum. For example, increasing the half-width to 15 cm^{-1} causes nearly a factor of 2 reduction in VCD magnitude and hence a closer agreement with experiment.

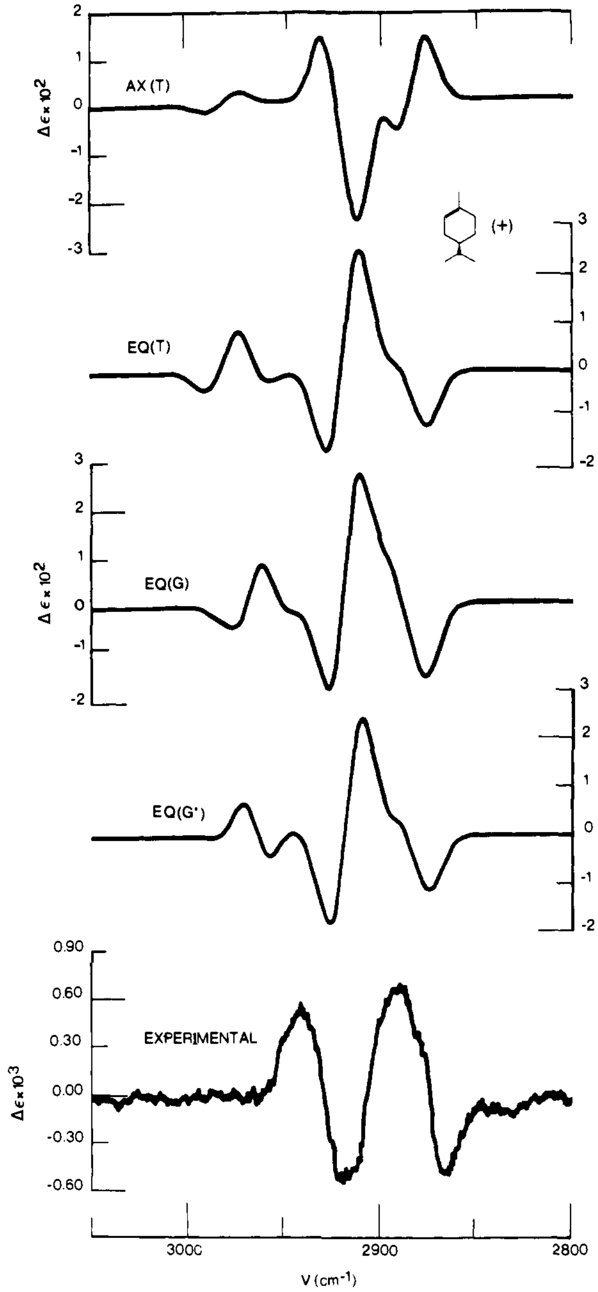

Figure 2. Experimentally observed (0.2 M in CCl_4, resolution 10.6 cm^{-1}, bottom) and theoretically calculated VCD using the CFF parameters and SCNDO charges for (+)-menthene for the conformers of Figure 1. The overall line shapes in the calculated spectra are a result of summing Gaussian functions of 10-cm^{-1} half-width at $1/e$ centered on each normal mode of vibration in the whole CH stretching region.

The most striking result of the calculations is that the AX (T) structure leads to a VCD with a nearly total sign reversal from the three EQ results. The EQ structures all lead to a pattern of features which resembles the experimental spectrum better than does the AX. This conclusion is reinforced by detailed analysis of the normal modes which show that the asymmetric CH_2 stretches of the EQ contribute to the high-energy large positive and negative features. These correlate to the 2920- and 2950-cm^{-1} experimental bands, respectively, which lie in the region normally attributed to such modes. In other words, a shift of the calculated Eq (G′) or Eq (G) spectrum by 20 cm^{-1} to lower energy would bring it into very close agreement in shape as well as expected assignments with the experimental results.

It should be noted that a nearly pure =CH stretching mode was calculated to lie at 3100 cm^{-1} and to have vanishingly small

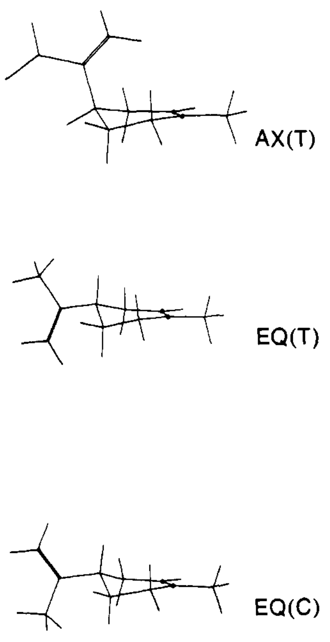

Figure 3. Minimum energy conformers, AX and EQ, and the rotamers T and C (see text) of limonene as calculated using CFF parameters. Filled circles indicate location of the ring double bond.

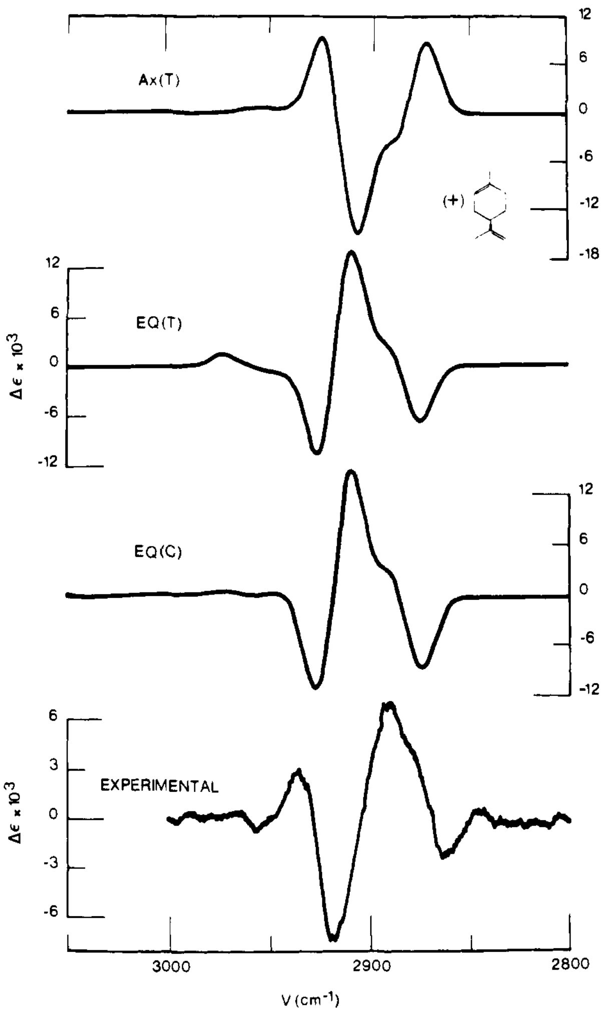

Figure 4. Experimentally observed (0.2 M in CCl_4, resolution 10.6 cm^{-1}, bottom) and theoretically calculated VCD using the CFF parameters and SCNDO charges of (+)-limonene for the conformers of Figure 3. The overall line shapes in all the theoretical spectra are a result of summing the Gausian functions of 10-cm^{-1} full half-width centered on each calculated normal mode of vibration in the whole CH stretching region.

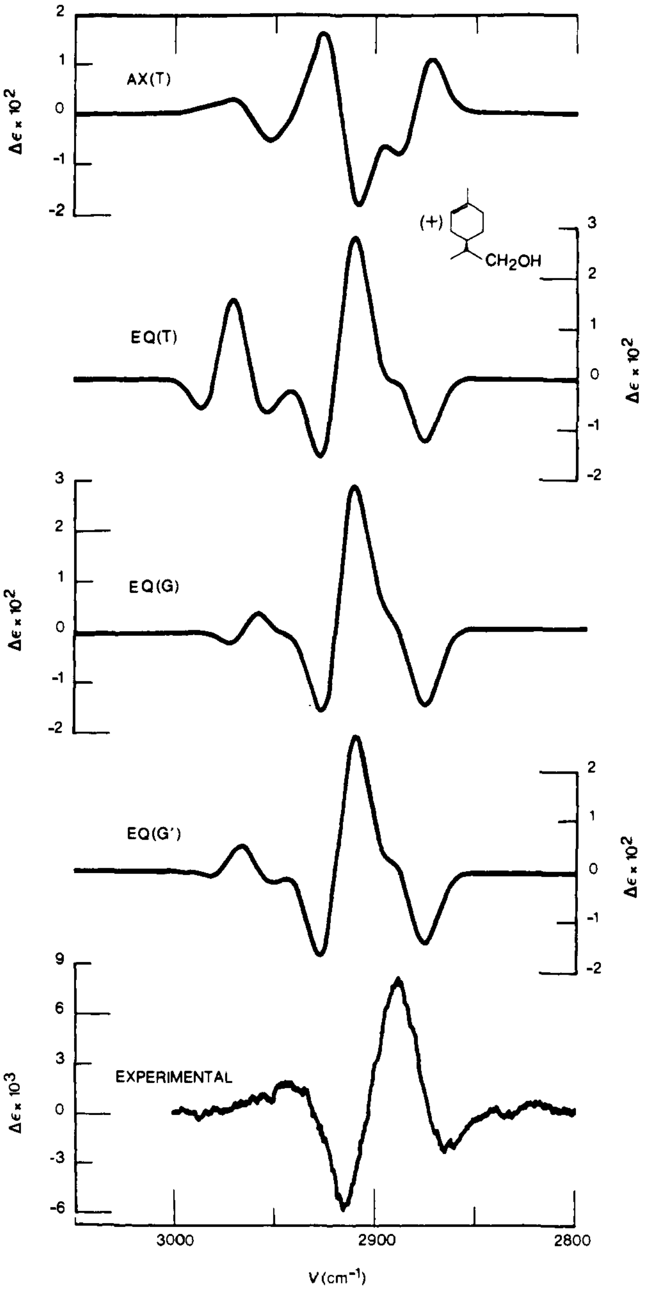

Figure 5. Experimentally observed (0.2 M in CCl_4, resolution 10.6 cm^{-1}, bottom) and theoretically calculated VCD using the CFF parameters and SCNDO charges of (+)-menthenol for the EQ (T) and AX (T) conformers. The overall line shapes in all the theoretical spectra are a result of summing the Gaussian functions of 10-cm^{-1} half-width centered on each calculated normal mode of vibration in the whole CH stretching region.

VCD. No experimental bands were found at that frequency, but this mode could be assigned to the weak ═CH absorption band at 3015 cm^{-1} which also seems to have very little VCD. Use of a modified force field[4] for EQ (G′) had the effect of changing the sign of the highest energy VCD band and thus improved the fit. A splitting into two bands of the positive contribution near 2890 cm^{-1} was also found. The CFF always predicts more contribution of tertiary CH stretches to high energy CH_3 (as) modes than would be expected from group frequency considerations.[12] This appears to be the source of the sign change near 3000 cm^{-1} and may be the reason the EQ (G) calculation appears to fit the data slightly better than the EQ (G′).

Limonene. Limonene differs from menthene only in having an

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(12) L. J. Bellamy, "Advances in Infrared Group Frequencies", Methuen, London, 1968.

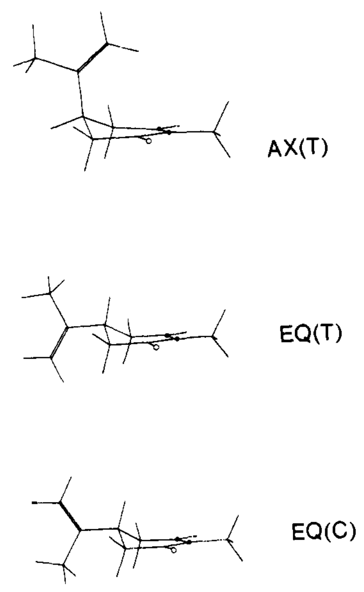

Figure 6. Minimum energy conformers, AX and EQ, and the rotamers T and C (see text) of carvone as calculated using the CFF parameters. Filled circles indicate the ring double bond; open circle indicates the carbonyl.

isopropylene instead of an isopropyl group. The added double bond eliminates one methyl group and a tertiary CH. This structural difference, in contrast to their very similar CH stretching VCD and CH deformation Raman CID, led Polavarapu, et al.[7] to propose that the ring CH_2's were responsible for the major VCD features. Our analysis demonstrates that the same conclusion holds for the FPC calculations.

The ring conformations found for limonene were virtually identical with those of menthene with EQ again being lower in energy. In this case, two rotamers are possible, having the isopropylene double bond trans to the C*-H, EQ (T), or cis, EQ (C), as shown in Figure 3. The CFF favors the EQ (C) by ~1.5 kcal/mol, implying that other conformers should not be important at room temperature (Table I).

The calculated VCD using the CFF-FPC with the charges and scaling factor in Table II are shown in Figure 4 along with the experimental spectrum. The AX calculated VCD is nearly completely opposite in sign to that of the EQ conformers and is a worse fit to the experimental spectrum. The two rotamers give very similar calculated VCD as might be expected, since the isopropylene is just flipped 180° with respect to the ring and the CH_3 and $=CH_2$ groups lead to only small rotational strengths.

Again a slight shift to lower energy would bring the limonene calculated and experimental VCD into register. The high-energy bands (3100 cm^{-1}) due to the CH stretches on the double bonds have not been plotted in the calculated spectrum since significant VCD was neither predicted nor seen. The good fit to limonene and menthene point out the utility of CFF for hydrocarbons and emphasize that the coupling of hexene CH_2 vibrations dominates the VCD. Their relative phase and hence the sign of their VCD is found to be primarily dependent on AX or EQ substitution. However, the spectra of the two molecules are different. This is most notable at the positive 2940-cm^{-1} band which is much smaller in limonene than menthene and, gratifyingly, is also calculated to be smaller. This band has significant CH_3 contribution which explains the change.

Menthenol. In essence, the same results are found for menthenol which has a CH_2OH substituted for one of the CH_3 groups of the isopropyl of menthene. The experimental spectrum is again best fit by the EQ conformers which are also lower in energy than the AX (Figure 5). The calculated VCD is quite insensitive to rotation of the OH group as might be expected from the minor effects of the isoproprpyl rotation. The added chiral center has no obviously large effect on the overall VCD. Since the force constants for the OH group are not optimized, the relative energies of Table I may be less significant than for the previously discussed molecules.

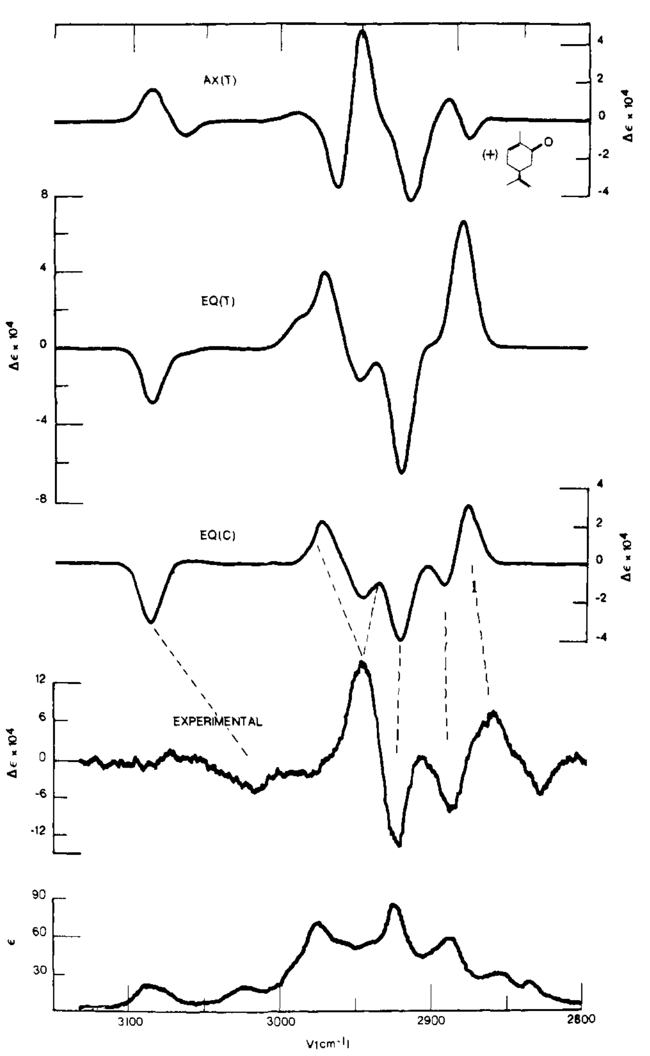

Figure 7. Experimentally observed (0.2 M in CCl_4 and 8-cm^{-1} resolution, bottom) and theoretically calculated VCD using the CFF parameter and SCNDO charges of (+)-carvone for the conformers of Figure 7. The overall line shapes in all the theoretical spectra are a result of summing the Gaussian functions of 10-cm^{-1} full half-width centered on each calculated normal mode vibration in the whole CH stretching region. The experimental absorption is also plotted below the VCD for sake of comparison.

Carvone. As a test of the sensitivity of the VCD to small changes in the ring conformation, carvone was studied. Differing by substitution of a C=O group for the limonene CH_2 at the sixth position, carvone has only the isopropylene substituted C_4 free to pucker out of the plane formed by the other five ring carbons. The resulting ring conformations are still classifiable as AX and EQ with their rotamers being similarly EQ (T), AX (T) and EQ (C), AX (C) as illustrated in Figure 6. However, the absorption and VCD spectra of carvone are more complex than for the previously described systems and appear to be more resolved (Figure 7, bottom). In addition, both the VCD and absorption spectra are significantly reduced in magnitude (by factors of 5 and 2, respectively) than was found with limonene. These results may be due to carvone having one less ring CH_2 group than limonene but probably are also affected by the increased planarity of the ring in carvone. Similar effects of planarity on intensity were found for the spirononadiene VCD.[3]

Under low-resolution display conditions (15-cm^{-1} half-width), the calculated VCD spectra of carvone are deceptively similar to the above discussed menthene, limonene, and menthenol results. However, close inspection of the 10-cm^{-1} half-width plots in Figure 7 reveals striking differences. First of all, the AX spectrum is

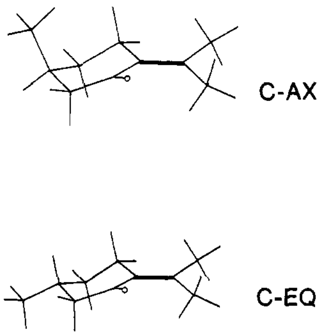

Figure 8. Minimum energy conformers of pulegone having the ring in the lowest energy C form with the 1-methyl group in either the AX or EQ position as calculated using the CFF parameters. Open circle indicates the carbonyl.

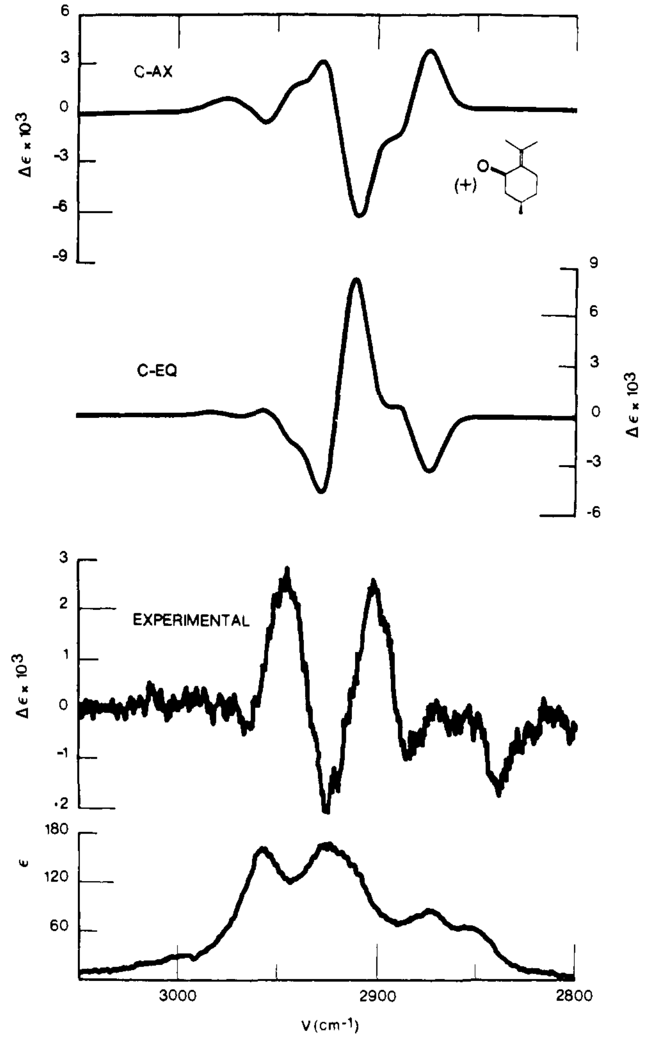

Figure 9. Experimentally observed (0.2 M in CCl_4 and resolution 10.6 cm^{-1}, bottom) and theoretically calculated VCD using the CFF parameters and SCNDO charges of (+)-pulegone for the conformers in Figure 9. The overall line shapes of the calculated spectra are a result of summing the Gaussian functions of 10-cm^{-1} half-width centered on each normal mode of vibration in the whole CH stretching region.

not a complete sign reversal from the EQ results. In fact the most prominent band (2920 cm^{-1}) appears to have the same sign in both. In general the asymmetric stretching VCD flips sign while the symmetric does not. Secondly, the =CH modes are calculated to have substantial VCD unlike any of the previous molecules. Finally, in analyzing the normal modes, it is clear that some carvone modes correlate well with those of limonene while others, especially those dominated by asymmetric CH_2 stretches, do not. The overall pattern appears to be a sign reversal of the limonene pattern that is shifted to higher energy and split. The reason for this difference is that the high-energy CH_3 (as) stretches contribute in the opposite sense for carvone and evidence less cancellation, while the low-energy CH_2 (s) stretches also have the opposite sense from limonene and the middle CH_2 (as) stretches are significantly different in character since there are two rather than three CH_2 groups.

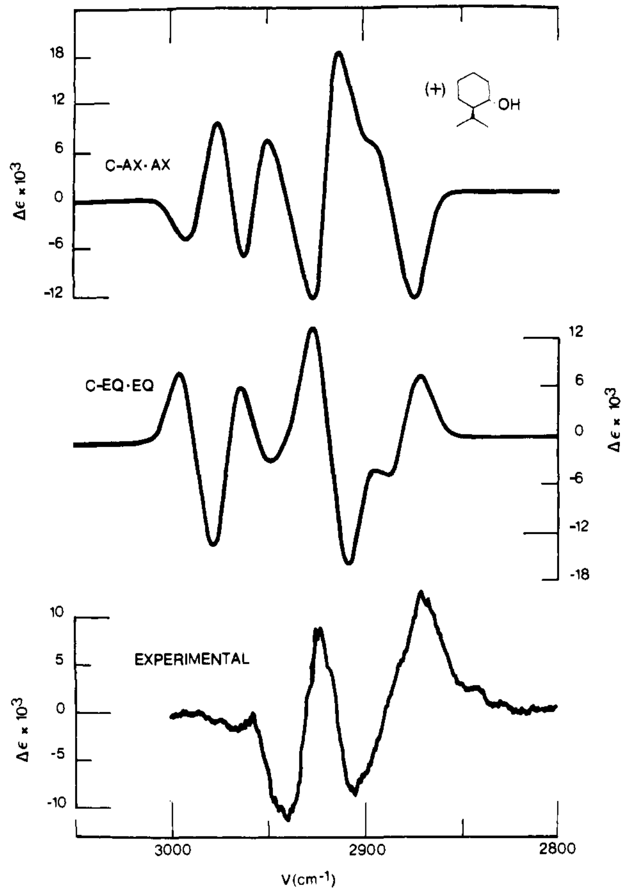

Figure 10. Experimentally observed (0.2 M in CCl_4 and resolution 10.6 cm^{-1}, bottom) and theoretically calculated VCD using the CFF parameters and the SCNDO charges of (+)-menthol for the two lowest energy ring conformers C-EQ-EQ and C-AX-AX. The overall line shapes in the theoretical spectra are a result of summing Gaussian functions of 10-cm^{-1} half-width centered on each calculated normal mode of vibration in the whole CH stretching region.

However, the oscillating pattern of experimental VCD features is still best reflected by the EQ (C) calculated spectrum. Since this is also the lowest energy conformer, the CFF–FPC model can be viewed as qualitatively useful with the major differences between calculated and experimental results being attributable to the calculated frequencies allowing either too much or too little overlap. The qualitative correlation has been indicated in Figure 7 by the dotted connecting lines. The =CH VCD calculated near 3080 cm^{-1} could be assigned to the negative VCD near 3025 cm^{-1}, but there is certainly absorption due to =CH near 3080 cm^{-1} that has no apparent VCD. This lack of FPC correlation for olefinic modes was noted earlier in our spirononadiene study.[3]

The magnitude of the calculated carvone VCD spectra is substantially (a factor of 25) below that of limonene. This is in part due to the lower absorption intensity (used to scale the charges) and is part due to the increased planarity and increased cancellation of overlapping bands. Hence the experimental carvone values are larger than the calculated values in contrast to the situation found for limonene, menthene, and menthenol.

Pulegone. Whereas carvone had a flatter ring than limonene, pulegone has a more flexible one. The adjacent C=C and C=O bonds somewhat restrict the ring geometry but do evidence substantial dihedral angles in our calculations. We have found five stable conformations which, in order of increasing energy, can

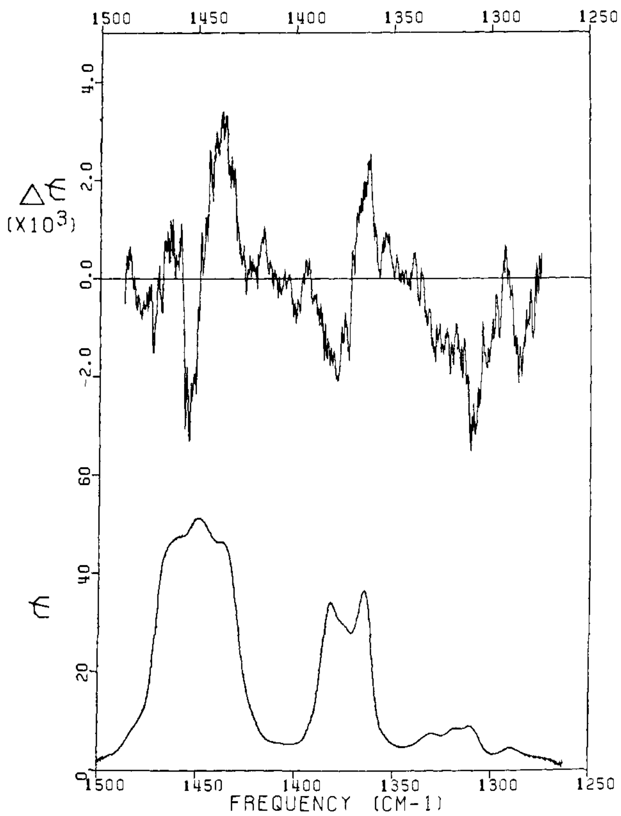

Figure 11. VCD and absorption spectra of (+)-menthene in the CH deformation region. Spectra were obtained on a 0.1 M CCl_4 solution, path 0.1 cm, time constant 10 s. The VCD base line was obtained using ±-α-pinene which has a similar absorption spectrum in this region, and care was taken to minimize artifacts.

be labeled C-EQ, C-AX, F-EQ, F-AX, and B-EQ where C, F, and B stand for chair, folded, and boat ring conformations in analogy to our methylcyclohexanone study.[4] It can be seen in Figure 8 that the C=C—C=O dihedral angle changes sign on going from C to F or B. For pulegone, AX and EQ refer to the methyl group orientation with respect to the ring. Since the restricted motion of the ring is about the bond between the C=C and C=O groups, C-EQ and C-AX of (+)-pulegone are analogous in conformation to EQ and AX of (+)-menthene. There are no rotamers of pulegone.

The calculated VCD reflects this similarity of ring structure. As seen in Figure 9, the C-EQ and C-AX geometries give VCD nearly opposite in sign and of the same sense as was found for the menthene EQ and AX structures. The unchanged band at 3000 cm^{-1} is due to the CH_3 (as) stretches whose environment can change very little in pulegone. This agreement with the earlier discussed hexenes is in contrast to the carvone results and emphasizes the dominance of the VCD by the interacting CH_2 groups and the importance of their relative phase as determined by EQ or AX. Pulegone as well as limonene, menthene, and menthenol has three CH_2 groups while carvone has only two.

The agreement with experiment is not as good as found in the other cases. However, the lowest energy C-EQ clearly gives a better pattern than does the C-AX. This deviation may be in some part due to the effects of the twisted unsaturated parts of the molecules. Recent reports of calculation of the polarization contribution to the VCD of twisted biphenyl compounds indicate this to be a possible source of significant rotational strength.[13]

Menthol. The most flexible of the six molecules we have studied is menthol. It has a variety of cyclohexane chair and boat forms due to the combinations of different rotamers possible. In terms of VCD, it has interactions of three ring CH_2 groups, three CH_3 groups, and three chiral centers. The two lowest energy ring conformers are chairlike, with one having both the methyl and isopropyl axial, C-AX-AX, and the other both equatorial, C-EQ-EQ. Each of these has six rotamers which we denote as T, G, and G′ of the isopropyl group as in menthene and A and B for the OH group directed into or out of the ring. In our calculations, using only crude OH parameters, these rotamers have a significant effect on the energy causing a variation of as much as 2 kcal. Since the OH parameters are not optimized, the relative energies of these configurations may be in error, and we thus have not enumerated them.

Two points about the calculated menthol VCD are worth mentioning, however. The general shape of the VCD of the lower energy, primarily CH_2 modes is not significantly affected by rotations of the isoproyl group or of the hydroxyl group, and the VCD of the C-AX-AX can be seen to be a nearly complete sign reversal of that of the C-EQ-EQ. Both of these results are consistent with the above interpretation of the VCD for six membered rings containing three CH_2 groups and fit our general scheme of CH_2's dominating the observed VCD. The higher energy modes which are strongly contributed to by CH_3 (as) stretches do change somewhat with change in rotamer.

Comparing the C-EQ-EQ and C-AX-AX (both T, A) spectra in Figure 10 with experiment, it is clear that the lower energy bands are better fit by the C-EQ-EQ. The bands at 2870, 2900, and 2920 cm^{-1} correlate quite well while the higher energy region shows some differences which may be rotamer dependent or may be due to the C*–H modes which the CFF calculates to be too high in energy.[4] Unfortunately our energy calculations place C-AX-AX lower than C-EQ-EQ by ~1.1 kcal. We can only attribute this disagreement at present to either a failure of the CFF force field as extended to include OH or a failure of the FPC model with OH-containing molecules. The latter has been noted previously and attributed to lone pair effects.[14] Considering the consistency of the spectra and calculations we have presented in this paper, we favor the former explanation.

Conclusion

This study, by comparing six, six-membered-ring structures, has demonstrated that the CFF–FPC model has utility for extracting conformational information from the CH stretching VCD. In particular we have shown that the dominant VCD is a result of the coupling of CH_2 groups and is markedly dependent on whether substituents are placed axially or equatorially on the ring. This substitution controls the phase of the CH_2 coupling which in turn controls the sign of the dominant VCD peaks. This general trend was seen as expected in menthene, limonene, and menthenol which have nearly identical ring structures but was also evident in pulegone and menthol which have three CH_2 groups on the ring and have substantially puckered rings. However, carvone with two CH_2's gave a different sign pattern even though the ring was quite similar to that of the first three molecules.

The agreement found between calculated and experimental VCD for all the compounds tends to confirm the importance of the CH_2 coupling. This coupling is not unlike the coupled-oscillator-like VCD we have found for dimethyl tartrate OH and C=O bands[15] and poly(benzyl glutamate) amide I bands.[16] In each of these cases strong electric dipole transitions get much more rotational strength from interaction with another near degenerate transition than by other mechanisms. This is similar to the situation in electronic CD for electric dipole allowed transitions. In the CH stretching region the motions are inherently very symmetric and are only weakly coupled to other types of motion. However, the degenerate motions always occur in coupled sets and provide a sensitivity to the molecular asymmetry and con-

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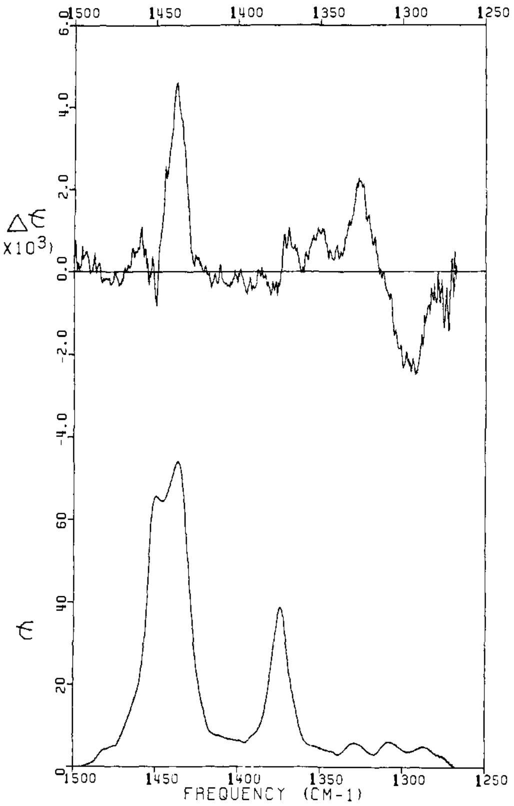

Figure 12. VCD and absorption spectra of (+)-limonene in the CH deformation region. Spectra were obtained on a 0.2 M CCl_4 solution, path 0.05 cm, time constant 10 s. The VCD base line was obtained as an average of the (+) and (−) spectra.

formation. It is this type of VCD mechanism that the FPC model is best able to mimic, and thus these molecules become most appropriate for FPC analysis.

In the bending region, the CH deformations mix with many other types of motions such that an appropriate description of the normal modes is less likely with the CFF. Similarly the FPC model may be less useful for such modes. Hence, we have not extended our analysis to the mid-IR region. However, for sake of comparison with the Raman CID, mid-IR VCD of these compounds is presented in the Appendix.

Appendix

To illustrate the increased complications attendant with interpretation of mid-IR (CH deformation) VCD and to provide some data which can be directly compared to the Raman CID, we present in this appendix VCD and absorption spectra of some of the compounds described in this paper. In Figure 11 is the VCD of menthene from 1500 to 1250 cm^{-1}. The VCD peaks approximate the alternating sign pattern found by Polavarapu et al.[7] in the Raman CID in this region. However, as can be seen in Figure 12, the limonene VCD does not have the same pattern nor does it resemble the Raman CID measured by Barron.[17] This difference is in striking contrast to the CH stretching VCD which have both similar appearance and equivalent interpretations in these molecules.

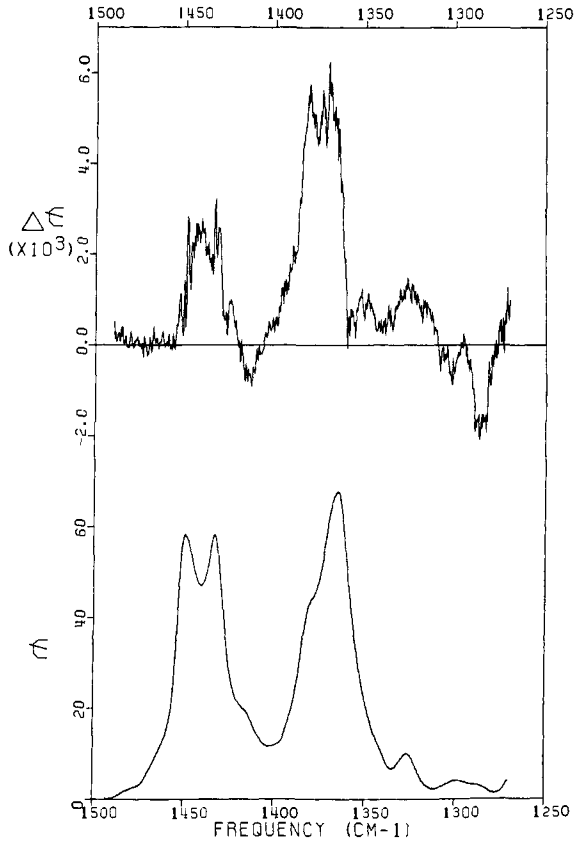

Figure 13. VCD and absorption spectra of (+)-carvone in the CH deformation region. Spectra were obtained on a 0.14 M CCl_4 solution, path 0.05 cm, time constant 10 s. The VCD base line was obtained as an average of the (+) and (−) spectra.

The Raman CID has an oscillation in sign that is suggestive of an origin in the coupling of like modes. This and the similarity of spectra between like molecules prompted Polavarapu et al.[7] to assign the CID to the CH_2 deformations and to continue on to draw a parallel interpretation of the CH stretches. In contrast to those results, the carvone VCD in this region (Figure 13) is nearly monosignate, having a sign reversal in this range at only 1282 cm^{-1}. Such a result implies that the modes in this region, CH_2 and CH_3 deformations,[18] must be substantially interacting with lower energy modes and thus may prove quite difficult to model with the FPC theory, especially if an approximate force field such as the CFF is used. Hence we have retricted our earlier analysis to the CH stretching region of molecules with nearly conservative VCD.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and Professor L. A. Nafie for preliminary communication of his paper on these molecules.

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