Vibrational Circular Dichroism of Spirononadiene. Fixed Partial Charge Calculations

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Abstract: A simple and general method for calculation of vibrational circular dichroism (VCD) is evaluated by comparison to the previously unreported experimental VCD of (+)-1,6-spiro[4.4]nonadiene in the CH stretching region. The fixed partial charge model of VCD was used together with the consistent force field. This combination allows determination of minimum-energy conformations and VCD for many related molecules with one parametrization. Comparison to the data showed qualitative agreement with calculated VCD for the CH_2 stretches but not for the olefinic CH stretches. Effects of various parameter changes on the calculations are discussed.

Introduction

Vibrational circular dichroism (VCD) is a new technique of promise for structural determination of chiral molecules in solution.[2] Recent work has shown VCD to be measurable in a wide variety of compounds and in a number of different vibrational modes.[2-4] To date, published interpretation of actual data has been proposed for only a few quite limited cases.[4,5]

Several theoretical models for VCD have been proposed.[6-10] Owing to its simplicity and ease of application, the "fixed partial charge" (FPC) model for VCD as formulated by Schellman[8] is of primary interest to this work. This method determines the electric and magnetic transition moments for a given normal mode from the motion of partial charges placed on each atom. Consequently, a normal mode analysis is necessary, but the electron-vibration interaction is modeled very simply. This FPC formulation has been shown to be a component of two recently proposed, more complex theories for VCD based on anharmonicity corrections[9] and on localized molecular orbitals[10] but offers more promise of practical application to a wide variety of molecules.

With the above in mind, we have modified available, Cartesian-based[8] normal coordinate analysis programs to also calculate VCD for several small molecules using the FPC model. Since force fields for alkanes and alkenes are readily available, we decided to test the method first on 1,6-spiro[4.4]nonadiene (Figure 1), a relatively simple hydrocarbon for which we have measured VCD for the CH stretching modes. Since the detailed molecular geometry of this molecule in solution is unknown, we have utilized the Warshel-Levitt consistent force field (CFF) program QCFF/PI[11] to establish reasonable equilibrium geometries of the different possible conformations and generate normal modes for each. The combination of "molecular mechanics" and FPC-VCD calculation, introduced by Schellman,[8] offers promise of wide applicability, if successful, because force fields are optimized for classes of molecules rather than individual ones. Hence, one set of parameters can be used to generate geometries, vibrational spectra, and VCD for many generically related molecules.

This paper then is a test of the FPC-CFF combination's utility for analysis of the VCD for the CH stretching modes of an optically active alkene, spirononadiene. Since both the CFF normal modes and the FPC-VCD are approximate, qualitative comparison of calculated and experimental spectra is emphasized.

Experiment

1,6-Spiro[4.4]nonadiene was obtained in both the resolved (+) and racemic (±) forms from Dr. H. Gerlach.[12] It was studied without further purification as dilute solution in spectrograde CCl_4. An insufficient amount was available for study of VCD concentration dependence; but, from our previous experience, such effects are expected to be small in a nonpolar molecule at this dilution.

Spectra were measured with the USC instrument using procedures described previously.[2] The resulting VCD and absorption spectra are shown in Figure 2, where they have been digitized, smoothed, and replotted to be linear in wavenumber and molar extinction coefficient, ϵ. It is important to note that this spectrum is smaller in magnitude of both $\Delta\epsilon$ and $\Delta\epsilon/\epsilon$ than many previously reported spectra.[2-5] Hence the quantitative reliability of smaller features such as those at 2960, 2983, and 2875 cm^{-1} is in doubt. Base lines are scans of the (±) compound at similar concentration with path length adjusted to give absorption strengths identical with those of the (+) compound. The observed data are summarized in Table I for comparison with calculations.

Calculations

Initial calculations were done with the Warshel-Karplus (WK) CFF parameters that were determined for a series of alkenes.[13] Four possible conformations which differ by the relative puckering of the two rings were energy minimized and found to be within 0.1 kcal of each other. Arbitrarily labeling the pucker of each ring as U (the CH_2 group opposite the double bond moved up toward the double bond of the other ring) or D (CH_2 down toward the CH_2's of the other ring) the four are UU, UD, DU, and DD. The four conformations are indicated schematically in Figure 1. If both rings have the same degree of ring pucker, UD and DU will be the same; however, two minima were found: D puckered more than U and U more than D. Hence, VCD calculations were made for all four conformations, since observed spectra should be an average of them. For the sake of comparison, a calculation was also made with each ring flat which was found to be a local minimum of the potential surface.

The WK parameters result in a pucker for cyclopentene of only 9° and a range from 7 to 13° for spirononadiene (depending on conformation). Since cyclopentene is known to be bent by about 25°,[14] in another series of calculations the parameter set was modified to reproduce cyclopentene's geometry. It was possible to accomplish this by increasing the $C(sp^3)-C(sp^3)$ and $C(sp^2)-C(sp^3)$ torsional parameters. Four conformations were again found for the spirononadiene with energies within 2 kcal of each other. Effects of this parameter change are discussed below.

VCD was calculated using eq 12 of ref 8. All calculations were done in extended precision; effects of roundoff errors were checked and found not to be significant.

In addition to a force field from which the normal modes can be derived, a set of partial charges is required for VCD calculation in the FPC model. Since no unique way of determining

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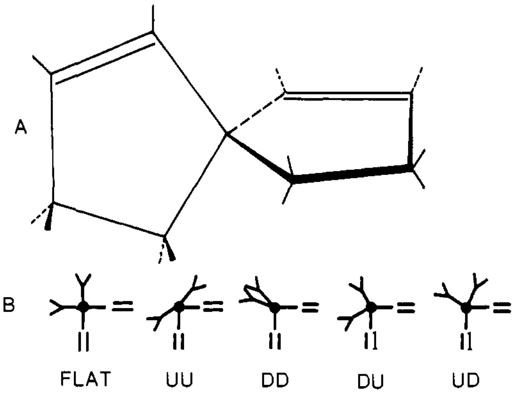

Figure 1. (A) Configuration of the (+)-(5*S*)-1,6-spiro[4,4]nonadiene molecule. (B) Figures indicate schematically the puckering of the various conformations of spirononadiene.

these exists, several relative charge distributions were explored. If all charges are multiplied by a scaling parameter, Schellman's equations[8] are such that both D, the dipole strength, and R, the rotational strength, vary with the square of such a parameter. The calculated magnitudes of the D and R values thus were scaled so that the observed intensity of the =C—H stretching band at 3050 cm^{-1} was matched by the calculation. This band was chosen due to its resolution from the others and its ease of assignment. Effects of this choice on calculated relative intensities and VCD are discussed below.

Results

A summary of the calculational results for the CH modes using the WK parameters for the four puckered conformers and the flat geometry is given in Table II. The frequencies calculated in the CH stretching region for all five cases occurred in pairs having less than 2 cm^{-1} separation. In other words, the calculated frequency spectrum appears to be a doubling of that expected for a disubstituted cyclopentene reflecting little interaction between halves of the molecules. These VCD results are indicated pictorially in Figure 3 as a stick diagram. The *relative* charges used for the results in Table II are H = 1, C(sp^2) = −1, and C(sp^3) = −2 with the spirocarbon charge set equal to zero. Changing this latter charge from +2 to −2 had no significant effect. Similarly, varying the ratio of the C(sp^2) to C(sp^3) charges from 0.5 to 1.5 also had little effect aside from altering the relative magnitudes of the =CH and CH_2 D and R values.

There is considerable qualitative similarity between the calculated VCD of different conformers. This is particularly evident in the sign patterns of the highest energy asymmetric CH_2 (as) stretches and the lowest energy symmetric CH_2(s) stretches.

In real spectra, the line shape will cause cancellation of oppositely signed contributions to the VCD from modes close in energy. These considerations suggest that the UD and DU conformations will yield weaker VCD than the UU and DD conformations since in UD and DU the R from one mode of a near-degenerate pair is often canceled by that from the other mode; but in UU and DD reinforcement or, at least, less cancellation is found. On the other hand, in averaging the R values from different conformations, the DD and UU contributions to pairs of modes tend to cancel, making their sums quite small. The result of averaging is in qualitative agreement with the flat calculation (Figure 3), but, for some modes, does differ significantly quantitatively.

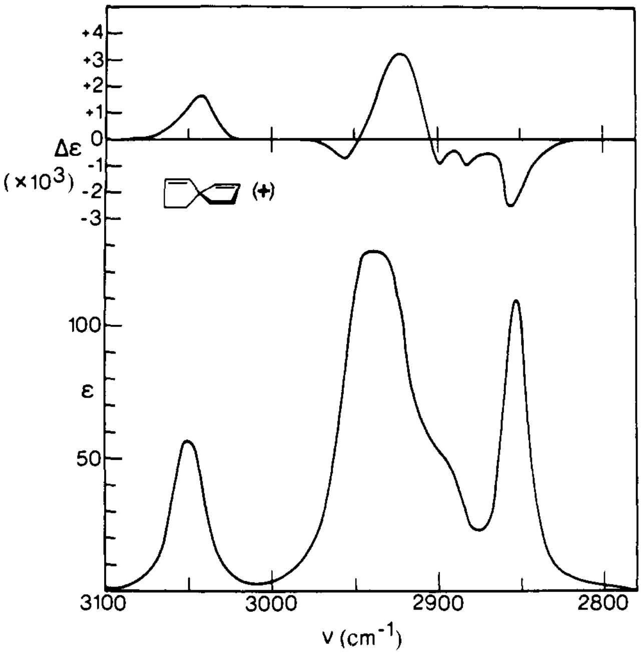

Figure 2. VCD and absorption spectra of (+)-(5*S*)-1,6-spiro[4.4]nonadiene in the CH stretching region. Spectra were run on a 0.1 M CCl_4 solution in a 0.4-mm path length cell with a spectral resolution of 6 cm^{-1}. Random noise was less than $\Delta\epsilon = 0.8 \times 10^{-3}$ peak to peak at the absorption maxima. Variations in the base line obtained by scanning the (±) compound were less than $\Delta\epsilon = 1.5 \times 10^{-3}$. Original spectra were digitized, smoothed, and replotted in terms of ϵ, $\Delta\epsilon$, and wavenumbers.

Table I. Experimental Data Summary for (+)-Spirononadiene

	absorption		VCD	
mode[a]	frequency, cm^{-1}	dipole strength[b] $\times 10^{-39}$, (esu cm)^2	frequency, cm^{-1}	rotational[b] strength $\times 10^{-44}$, (esu cm)^2
=CH	3053	5.4	3045	+2.2
CH_2(as)	2935	18	(2960)	(−0.4)
			2924	+8
?	2893	(4)[c]	(2893)	(−0.9)
			(2875)	(−1.1)
CH_2(s)	2851	9	2856	−4

[a] Conventional group frequency assignments (ref 15). [b] Calculated assuming Gaussian band shape: $D = 1.63 \times 10^{-38}\ \epsilon_0\Delta/\nu_0$; $R = 0.41 \times 10^{-38}\ (\Delta\epsilon_0)\Delta/\nu_0$. ϵ_0, $\Delta\epsilon_0$, peak heights; ν_0, center frequency; Δ, half width. [c] Assume $\Delta = 15$, ϵ_0 at ν_0.

Because the CFF does not quantitatively reproduce the experimentally determined cyclopentene geometry, we used altered torsional potentials that gave the proper minimum energy cyclopentene geometry but had difficulty in finding the minima for spirononadiene. UU converged to an energy minimum with both rings bent by ~25°; DU had one ~25° bend and one ~10° bend with one negative frequency and the other conformers converged to a saddle point having two negative vibrational frequencies and remaining less bent (9–11°). The DD and UD conformers with flatter rings gave VCD values not changed significantly from those in Table II, while the UU and DU gave VCD for some modes substantially different in magnitude from Table II but with the same sign pattern.

Although not included in the table, all calculations gave similar calculated VCD for the C=C stretches at around 1600 cm^{-1}. Two bands of roughly equal magnitude but opposite signs were predicted to be split by a few wavenumbers. The sum of these would be a sigmoidal VCD band that goes first negative then positive as wavelength is increased. This was a general result, not affected significantly by large geometry changes or small charge changes. Only by making the presumably unlikely choice of C(sp^2) charge opposite in sign of C(sp^3) charge was this order reversed.

Table II. Calculated Rotational Strengths for (+)-Spirononadiene in the CH Stretching Region with All H at +0.1 e Charge

	=CH				CH_2(as)				CH_2(s)			
mode[a]	O-O	O-I	I-O	I-I	I-I	I-O	O-I	O-O	O-I	O-O	I-I	I-O
frequency, cm^{-1} [b]	3100.7	3100.4	3098.5	3098.5	2936.7	2935.8	2913.6	2912.2	2893.3	2892.5	2881.2	2880.2
dipole[b] strength	1.2	0.9	1.8	1.3	3.9	3.7	0.2	0.2	1.2	1.0	1.8	1.8
UU[c]	1.83	−1.33	0.16	−0.90	−49.14	44.84	7.72	1.24	0.89	1.06	−7.16	0.87
DU[c]	−1.16	1.20	−1.46	1.33	−60.09	59.93	4.01	−2.94	0.82	−0.76	7.11	−8.03
UD[c]	−3.99	3.78	−12.32	12.51	−58.65	59.62	−1.55	0.65	−1.54	−0.18	18.08	−16.45
DD[c]	−5.22	4.78	−12.47	12.99	−55.53	59.68	−0.06	−7.32	−1.70	−1.07	13.59	−7.80
flat[c]	−9.43	9.32	−11.05	11.09	−63.27	63.93	2.33	−2.48	−0.48	−0.70	20.61	−19.93
av[c]	−2.14	2.11	−6.53	6.48	−55.85	56.02	2.53	−2.10	−0.38	−0.24	7.91	−7.86

[a] Approximate description of the mode. O, out of phase; I, in phase. The first letter indicates relative motion on each half of the molecule; the second letter represents the relationship between halves. Some modes are highly localized on one half of the molecule and in some cases the modes in a pair have the opposite order. This latter is only true for the =CH and CH_2(s) bands. Designations are for the DD and UD where they disagree. [b] Averaged over UU, DU, UD, and DD. Units of dipole strength are $\times 10^{-39}$ (esu cm)^2. [c] Units of rotational strength are $\times 10^{-44}$ (esu cm)^2.

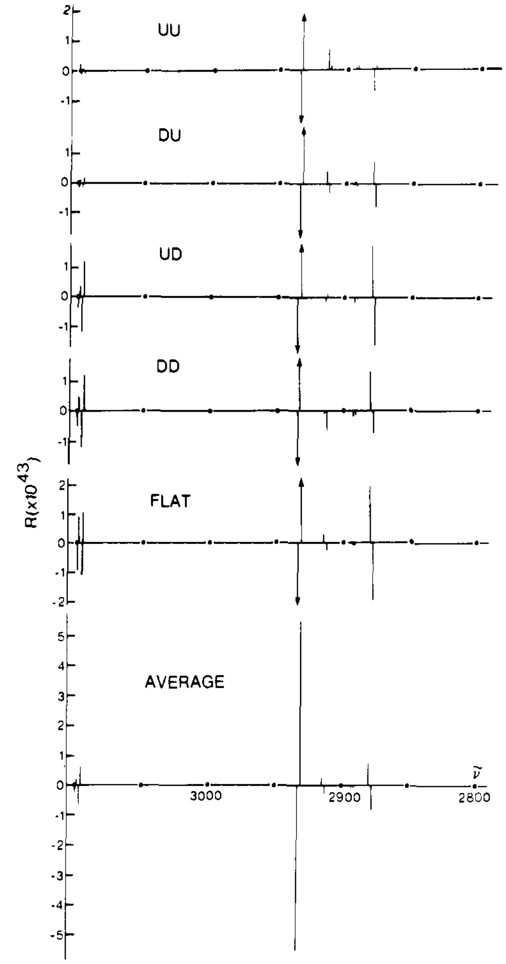

Figure 3. Stick diagram of the calculated rotational strengths of (+)-spirononadiene in the CH stretching region. Values correspond to Table II but the 2935-cm^{-1} R's have been truncated to conserve space. The splitting of near-degenerate modes has been exaggerated for clarity.

Discussion

The main purpose of this research is to explore the applicability of coupling the FPC model to the CFF for purposes of interpreting VCD data of medium-sized molecules. A major problem preventing the direct comparison of Tables I and II is that spectral overlap of transitions can have dramatic effects on the resultant line shape and magnitudes of the observed VCD. Factors such as line widths and frequency splittings are quite important in the final comparison yet are not well determined. For some of our VCD calculations, we have also done line-shape simulations by using Gaussian lines of varying widths and by splitting the pairs of lines by more and less than calculated.

First we shall analyze gross qualitative features present in the calculations that should appear through the effects of line-shape averaging. As alluded to above, there are several striking consistencies. In the CH_2 stretching region the two largest features of every calculation are the two highest energy CH_2(as) stretches. These form a pair split by 1-2 cm^{-1} with oppositely signed VCD, the higher energy one being negative. The magnitude of R for these modes is three to five times larger than that for other modes. With the alternate parameter set that gives increased pucker of the rings, the magnitude of R decreases, but also evidences less cancellation. This is shown in Table III, data set C, for the UU conformer. The net effect when line shape is taken into account is that the more puckered the rings, the larger the predicted CH_2(as) VCD.

Except for the UU case, the lowest energy pair of CH_2(s) stretches also have relatively large R magnitudes and have a consistent sign relationship with the lower one being negative. Increasing the pucker in this case, however, increases the R values as well as increases the difference between them, again giving a net increase to the predicted VCD.

The magnitudes of R for lower energy CH_2(as) and higher energy CH_2(s) stretches are appreciably smaller than those discussed above and show no striking consistencies between conformers other than that the CH_2(s) VCD is much smaller than the CH_2(as) VCD.

The R values of the olefinic CH stretches also have a consistent sign pattern, except for UU, and are moderately large; but, because the modes are predicted to have such small splitting, large cancellation is expected when line shape is taken into account. For all the calculations, the net effect is a very small negative VCD (10-100 times less than that of the CH_2 region).

From the above considerations, an overall pattern emerges for the calculated VCD averaged over the four conformations. In the olefinic CH region, a very small skewed band is expected to be dominated by a negative lobe to higher energy. In the CH_2(as) region a large sigmoidal feature with a negative lobe to higher energy is expected. The lowest energy CH_2(s) feature should be negative with a small positive lobe to higher energy which is somewhat canceled by contributions from the higher energy CH_2(s) modes.

The experimental results for the CH_2 region qualitatively reflect the calculations. The CH_2(as) region is sigmoidal with the lower energy positive lobe being larger, as expected. The CH_2(s) region has a large, skewed negative feature lowest in energy that appears to be distorted by an unobserved positive component to higher energy. The middle CH_2(as) and CH_2(s) modes seem to be of dominantly negative rotational strength.

Table III. Comparison of Calculated Rotational Strengths for the UU Conformation with Variations in the CFF-FPC Parametrization

parame-ters[a,b]		=CH				CH_2(as)				CH_2(s)			
		O-O	O-I	I-O	I-I	I-I	I-O	O-I	O-O	O-I	O-O	I-I	I-O
A	$\bar{\nu}$	3100.8	3100.4	3098.7	3098.6	2936.9	2935.8	2914.4	2912.5	2893.7	2892.6	2881.3	2879.7
	D	1.1	1.1	1.5	1.6	4.0	3.7	0.3	0.0	1.3	1.0	1.8	1.6
	R	1.83	−1.33	0.16	−0.90	−49.14	44.84	7.72	1.24	0.89	1.06	−7.16	0.87
B	$\bar{\nu}$	3100.7	3100.4	3098.7	3098.6	2936.9	2935.8	2914.4	2912.5	2893.7	2892.6	2881.3	2879.7
	D	1.1	1.1	1.5	1.6	8.1	7.5	0.6	0.1	2.6	2.0	3.8	3.4
	R	1.83	−1.34	−0.06	−0.79	−100.82	91.83	15.79	2.57	1.78	2.13	−14.65	1.77
C	$\bar{\nu}$	3101.3	3100.8	3099.3	3099.2	2938.4	2937.0	2918.5	2917.2	2896.8	2894.2	2882.6	2879.9
	D	1.1	1.0	1.4	1.6	3.5	3.9	0.6	0.2	1.3	1.1	0.6	1.4
	R	4.10	−2.75	3.06	−4.84	−34.51	25.32	14.60	1.14	2.83	1.56	−10.38	0.10
D	$\bar{\nu}$	3068.0	3067.7	3061.6	3061.4	2944.3	2943.2	2921.6	2919.9	2864.4	2862.8	2851.6	2849.7
	D	0.9	1.0	1.7	1.7	4.0	3.7	0.2	0.0	1.4	1.1	2.0	1.9
	R	0.24	−0.21	4.43	−4.83	−50.23	45.65	6.65	0.59	1.53	1.13	−5.45	0.51

[a] Parameter sets are A, regular WK CFF (Table II); B, alter FPC changes to fit CH_2 integrated intensity; C, alter CFF to fit cyclopentene pucker; D, alter CFF to fit cyclopentene frequencies. [b] $\bar{\nu}$, frequency in cm^{-1}; D, dipole strength in 10^{-39} (esu cm)^2; R, rotational strength in 10^{-44} (esu cm)^2.

This overall picture fits the average calculated VCD of the four conformations quite well as illustrated in Figure 4, the line-shape simulations corresponding to the Table II VCD calculations with the WK parameters.

However, in the olefinic CH region the observed relative magnitude of the VCD is much larger than calculated and is the wrong sign. It is slightly lower in energy than the absorption maxima but does not appear obviously skewed by an undetected higher energy negative feature. There is no simple way to reconcile the calculations with the =CH results.

It is interesting to note that another recurring pattern can be found if the R values of pairs of modes are summed. The resulting 6 sums from the 12 modes correspond to the three types of internal coordinates. These six sums for each conformation have a stable sign pattern (+ − − + + −) that varies only by phase between UU, DU and UD, DD, flat.

Having shown that the calculations when averaged over the four conformers qualitatively predict the observed CH_2 VCD but fail for the =CH, we must evaluate the quantitative agreement. The results from Table II are illustrated in Figure 4 with Gaussian line shapes (fwhh = 20 cm^{-1}). The calculated $\Delta\epsilon$ values for the average VCD of the four conformers are the same order of magnitude as the experimental values for the CH_2(as) modes. Calculated $\Delta\epsilon$ values for the CH_2(s) region are five to ten times smaller than observed and for the =CH region 20-50 times smaller. It must be remembered that these line-shape calculations are very dependent on both line widths and splittings of pairs of modes. For example, increasing the splitting by only 1 cm^{-1} from the Table II values more than doubles predicted $\Delta\epsilon$ values.

In summary, the calculations are in rough quantitative agreement with the observed CH_2 data, but the effects of poorly determined parameters needed in the line-shape analysis prohibit conclusive statements regarding the absolute magnitude of the calculated rotational strengths.

We have also investigated the effects of varying geometry, charges, and frequencies on the calculated VCD. The results of these parameter variations are listed in Table III for just the UU conformer. The resultant line shapes of the average VCD of the four conformers due to each parameter variation are illustrated in Figure 5. As mentioned before, increased pucker of the rings, most prominent in the UU case, increases the calculated VCD in the CH_2 region by reducing cancellation between pairs (Table IIIC) but leads to the same qualitative line shape (Figure 5C).

Agreement in magnitude between calculated and observed VCD was facilitated for the CH_2 modes by altering the charge distribution to give a better match to experimental integrated intensity. (The D values in Table II are fit to the =CH intensity but are low for the CH_2 intensity.) To fit the CH_2's, the olefinic CH charges were reduced to 0.7 relative to the CH_2 charges. After scaling, the resultant CH_2 R's (Table IIIC) and calculated VCD line shape (Figure 5B) increased by a factor of ~2 in magnitude. A better fit of the original charge set to the data would thus result from scaling to the integrated CH_2 intensity rather than the =CH peak, but an overestimate of the =CH D would result. However, in this model it is not unreasonable to have different charges for the two different kinds of H's.

As can be seen by a comparison of Tables I and II the observed and calculated frequencies do not agree. This is due to the approximate nature of the general CFF force field. To probe the consequences of improved frequency fit on the cal-

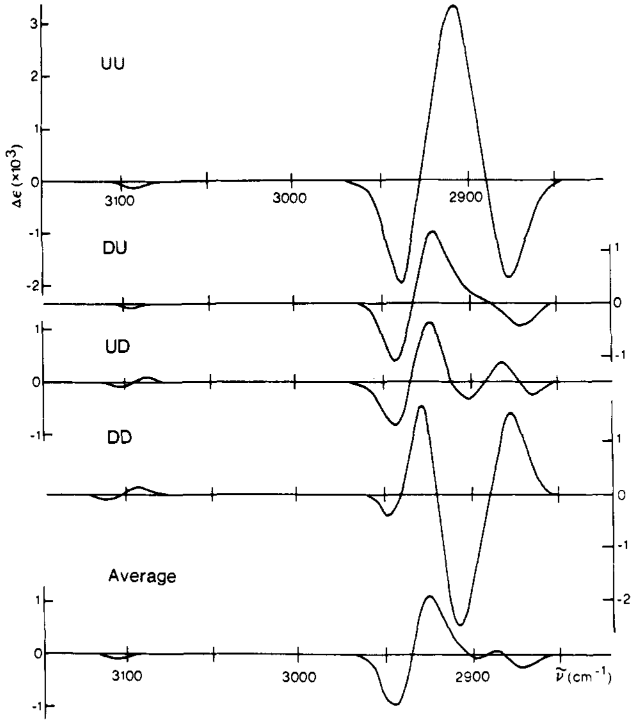

Figure 4. Calculated line shapes determined by summing Gaussians of 20-cm^{-1} full width at half height for each calculated R of (+)-spirononadiene. Plots correspond to the calculations in Table II with the WK parameter set.

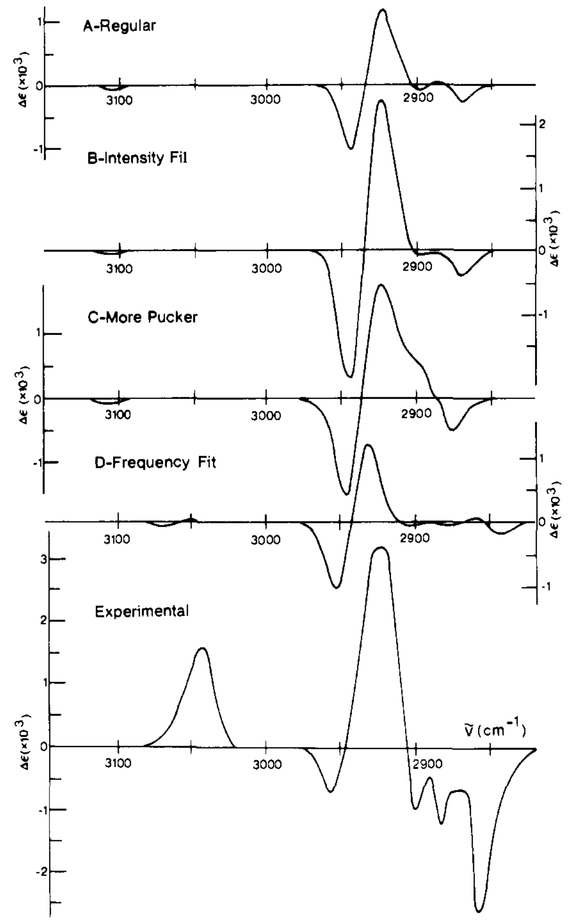

Figure 5. Calculated line shapes, using 20-cm^{-1} full width at half height Gaussians, for the VCD of (+)-spirononadiene. The four different parameter sets are A, the regular WK CFF parameters (Table II); B, FPC charges altered to match observed integrated =CH and CH_2 intensities independently; C, CFF parameters altered to match cyclopentene pucker; D, CFF parameters altered to fit cyclopentene CH stretching frequencies. The bottom spectrum is the experimental result.

culated VCD, new interaction force constants were added to the standard QCFF/PI parameter list.[11,13] These were first adjusted along with the stretching constants to give, for cyclopentene, rough agreement with assigned spectra.[16] When the spirononadiene VCD was recalculated with these parameters, no significant qualitative changes were noted (Table IIID), implying an insensitivity to small changes in force constants. The major effect found was an increased separation of the CH_2(s) and CH_2(as) modes which after line-shape analysis led to an even better agreement with observed spectra (Figure 5D).

Examination of the calculated and experimental line shapes in Figure 5 reemphasizes the stability of the qualitative features of the FPC-CFF VCD and its agreement with the CH_2 stretching VCD. Previous reports have maintained that the FPC model typically underestimates the VCD by an order of magnitude.[5,17] In this case, for the CH_2(as) modes reasonable agreement is found. But, for the olefinic CH stretches, the FPC results are both the wrong sign and magnitude. There are several possible reasons for this disagreement with experiment. The CFF may give inadequate geometry by forcing the double bond system to be too planar or it may give inadequate normal modes by underestimating the interaction of these internal coordinates with the remainder of the molecule. Alternatively, the FPC model may be inadequate to describe the VCD of modes involving unsaturated systems. This latter cause could parallel recent reports that conventional FPC severely underestimates VCD associated with the motion of atoms containing lone pairs.[17] We have no basis at present to discriminate between these suggested causes for the poor fit to the olefinic CH VCD.

Conclusions

We believe that this work has shown that the CFF-FCP method of VCD calculation may have practical utility in that it predicts correct orders of magnitude and, for the CH_2 modes, realistic sign relationships for this molecule. The failure of the CFF-FPC to give quantitative VCD predictions for all the modes may be best understood by recalling that both methods are approximate; in particular, the force field does not include many off-diagonal interaction terms or anharmonic effects. A problem in the case at hand is the existence of several conformations. To circumvent this, we are currently exploring the CFF-FPC method's applicability to rigid hydrocarbon systems. In addition we are exploring detailed differences in the VCD calculated for this molecule using other available hydrocarbon force fields.

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