ers[1i] and Dewey[1j] and should be considered when asparagine and glutamine-derived active esters are used in peptide synthesis.

References and Notes

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(3) Z-Ala(CN)-OH: mp 128–129°; $[\alpha]^{25}\text{D}$ −43.2 (±0.4) (*c* 1, DMF) $R_f = 0.2$ in ethyl acetate (90):pyridine (5.4):acetic acid (1.6):water (3).

(4) Z-ASu: mp 69–74°; $[\alpha]^{25}\text{D}$ −35.7 (±0.4) (*c* 1, 95% EtOH), $R_f = 0.7$ in the solvent system of ref 3.

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Raman Circular Intensity Differential Spectroscopy. The Spectra of (−)-α-Pinene and (+)-α-Phenylethylamine

Sir:

The feasibility of using Raman spectroscopy to investigate the chirality of dissymmetric compounds was first discussed in a series of theoretical papers[1,2] by Barron and Buckingham. The method, which must be seen in the more general framework of optically active scattering,[3] is highly attractive as it allows the use of vibrational optical activity for configurational assignments.

The appropriate measure of the effect is the circular intensity differential (CID) Δ, defined as[1]

$$\Delta_{\parallel,\perp} = \frac{(I_r^{\parallel,\perp} - I_l^{\parallel,\perp})}{(I_r^{\parallel,\perp} + I_l^{\parallel,\perp})}$$

$I_r^{\parallel,\perp}$ and $I_l^{\parallel,\perp}$ are the intensities of the scattered light 90° to the incident right (r) and left (l) circularly polarized light, with an analyzer oriented parallel (‖) and perpendicular (⊥) to the scattering plane, respectively.

Experimental verification of the effect has proved difficult, and first reports[5,6] were based on artifacts. The CID's subsequently reported by Barron, Bogaard, and Buckingham[4,7,8] for a few Raman bands are confirmed as genuine by our observations. In addition, we also present the first measurement of complete difference spectra in parallel polarization, namely for the two compounds (−)-α-pinene and *d*-(+)-α-phenylethylamine. Based on these spectra a sector rule is presented for a methyl group in a chiral environment. This is the first example of future sector rules in vibrational optical activity[2] which will emerge for various largely localized group frequencies.

Our instrumentation is shown schematically in Figure 1. The polarization of the laser beam was varied between right and left circular with square wave modulation. Synchronous single photon counting was used to avoid drift problems.[9] $(I_r^{\parallel} - I_l^{\parallel})$ and $(I_r^{\parallel} + I_l^{\parallel})$ were measured at each wavenumber increment and processed on line[10] by an IBM 1800 computer. The digital data were filtered with a 15 point (14 cm^{-1} interval) cubic smoothing function. The slit width was 8 cm^{-1}. We were successful in using the microcapillary sample handling technique[11] for R-CID. The microcapillary technique has been shown to have a high accuracy for the measurement of depolarization ratios.[12] In addition, we have also constructed a capillary cell with a flat, strain-free bottom end which has allowed us to precisely monitor the circular polarization of the laser beam after passing through the cell. Pilot measurements using internal nonoptically active standards in an optically active sample have also been performed to assure the validity of our results. The optical purity of the compounds measured was checked prior to the measurements on a Cary 60, and the compounds were stable under our measuring conditions. Typical sample sizes ranged from 50 to 200 μg.

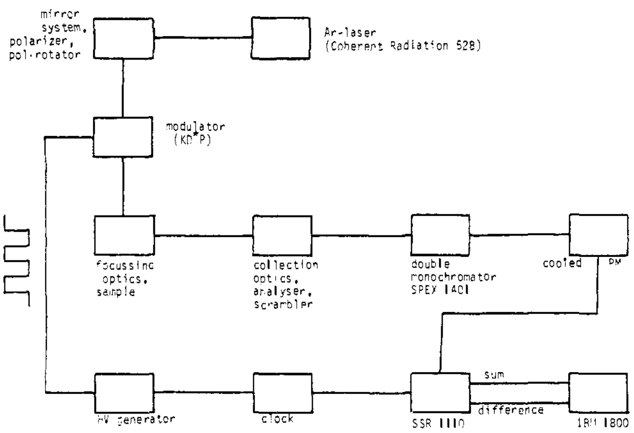


Figure 1. Experimental block diagram.

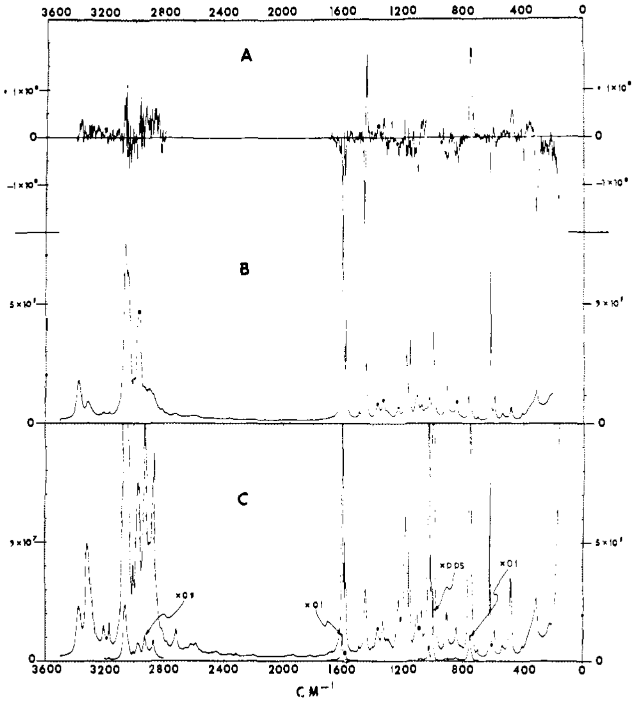


Figure 2. Difference and sum spectra for *d*-(+)-α-phenylethylamine in photon counts: (A) $(I_r^{\parallel} - I_l^{\parallel})$, (B) $(I_r^{\parallel} + I_l^{\parallel})$, (C) $(I_r^{\perp} + I_l^{\perp})$. $(I_r^{\parallel} - I_l^{\parallel})$ for the polarized line at 1002 cm^{-1} is omitted and, the peak at 755 cm^{-1} is doubtful. See error discussion.

Sum $(I_r^{\parallel} + I_l^{\parallel})$ and difference $(I_r^{\parallel} - I_l^{\parallel})$ spectra for the two compounds are given in Figures 2 and 3, and CID's in Table I. The accuracy of the data, and the possibility of observing an artifact, depend on the count rate and on the degree of polarization of a band. Bands with $\zeta > 0.15$ appear

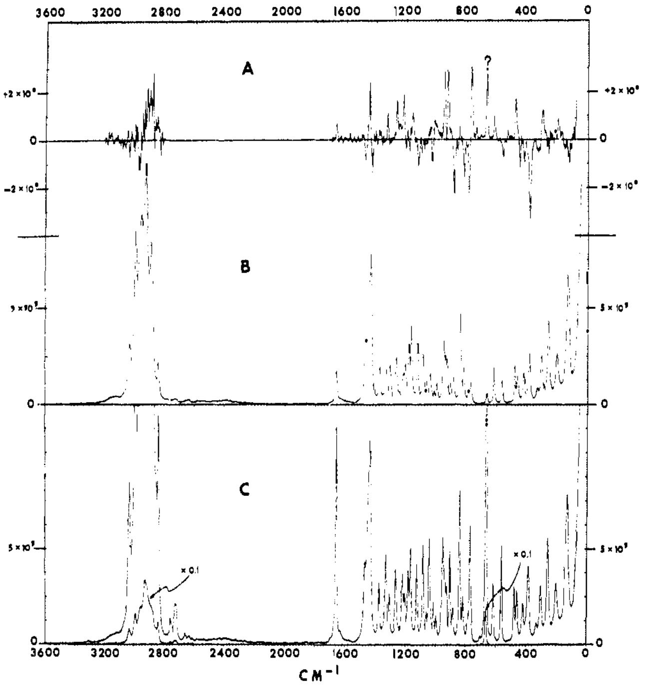


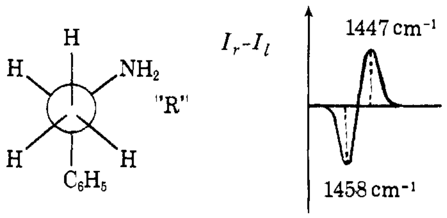
Figure 3. Difference and sum spectra for (−)-α-pinene in photon counts: (A) ($I_r^{\parallel} - I_l^{\parallel}$), (B) ($I_r^{\parallel} + I_l^{\parallel}$), (C) ($I_r^{\perp} + I_l^{\perp}$). The peak in (A) at 665 cm^{-1} is doubtful. See error discussion.

Table I. Raman CID's of *d*-(+)-α-Phenylethylamine and (−)-α-Pinene

d-(+)-α-Phenylethylamine		(−)-α-Pinene			
$\tilde{\nu}$(cm^{-1})	$\Delta_{\parallel} \times 10^3$	$\tilde{\nu}$(cm^{-1})	$\Delta_{\parallel} \times 10^3$	$\tilde{\nu}$(cm^{-1})	$\Delta_{\parallel} \times 10^3$
315	−0.85	300	+0.50	951	+0.85
364	+0.35	330	−0.45	1015	+1.10
402	−0.90	386	−1.15	1034	−1.25
479	+0.70	423	−0.45	1045	+0.30
622	−0.20	480	+0.80	1127	−0.35
850	−0.40	562	−0.65	1164	+0.65
915	−0.30	620	+0.50	1222	+1.25
1080	+0.30	771	+2.50	1246	+0.90
1105	−0.50	789	−2.60	1268	+0.70
1447	+0.60	821	−0.70	1328	+0.65
1458	−0.80	888	−1.50	1430	−0.25
		910	+0.65	1446	+0.35
		928	+1.15	1476	−0.30
		942	(−0.05)		

"safe". We estimate that absolute errors for the CID's are below 2×10^{-4}, and relative errors between 10 and 40%.

We reserve a detailed discussion of our data for a subsequent paper.[13] Clearly, the wealth of chiral information in Figures 2 and 3 is striking. Negligible CID's were found in the CH stretch region and below 250 cm^{-1}. As stated previously,[14] the degenerate antisymmetric CH_3 deformation mode centered at 1450 cm^{-1} has important potential for probing the local chiral environment of methyl groups. In α-phenylethylamine the local degeneracy of the methyl group is removed by the asymmetric environment, and a sizable CID couplet is found.



As more experimental data become available, the splitting and sign can doubtlessly be correlated with the nature of various substituents, and a more general sector rule established. In our present case, we would expect no sign change by, e.g., replacing the phenyl group with a substituted phenyl group. In α-pinene the spectral region is complicated by overlapping bands from three methyl groups. For complex molecules this might limit the usefulness of this sector rule.

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MINDO/3 Study of ^{14}N Nuclear Quadrupole Coupling Constants

Sir:

Attempts to calculate NQ (nuclear quadrupole) coupling constants for polyatomic molecules have not as yet been too successful.[2] While satisfactory results have been obtained from detailed ab initio SCF calculations, these are limited to fairly small molecules, and attempts to use semiempirical methods such as CNDO have not proved too satisfactory. We wish to report some calculations of ^{14}N coupling constants by MINDO/3[3] which seem to suggest that it may provide a solution to this problem.

In the LCAO MO approximation, the electronic contribution to the field gradient tensor for nucleus α is given[2] by:

$$\langle q^{\alpha}_{e}\rangle = -e \sum_{i\alpha}\sum_{j\alpha} P_{i\alpha,j\alpha} q^{\alpha}_{i\alpha,j\alpha} - 2e \sum_{i\alpha}\sum_{j\beta} P_{i\alpha,j\beta} q^{\alpha}_{i\alpha,j\beta} - e \sum_{i\beta}\sum_{j\gamma} P_{i\beta,j\gamma} q^{\alpha}_{i\beta,j\gamma} \qquad (1)$$