created by a single 90° (^{15}N) pulse. Since the components of ^{15}N magnetization are in an antiphase relationship, a delay t_r is introduced to allow the magnetization to come into phase.[4b] At this point the experiment proceeds as described by Bax and Freeman.[3]

Some novel examples of long-range NH couplings observed by this technique are shown in Figure 2. The spectra are projections of a portion of the two-dimensional ^{15}N FT-NMR spectra onto the F_1, i.e., J frequency, axis. Each 2D spectrum was acquired in ca. 30 min. and processed in the usual way.[3] Where comparison is possible (vide infra), the observed J values are in good agreement with similar coupling constants observed in related compounds.[2]

The advantages of combining polarization enhancement with the selective 2D-J method are seen by comparing the 3- and 4-bond J spectra of 6-methoxyquinoline with its one-dimensional, proton-coupled INEPT spectrum obtained in the same total time (ca. 2h).[5] Clearly the coupled spectrum is too poorly resolved to give any indication of the 4-bond couplings or how the observed 3-bond splittings should be assigned. By contrast, all but the 4-bond coupling between H(5) and N, which we estimate to be less than 0.1 Hz,[6] are resolved and unambiguously assigned via the 2D-J spectra. To our knowledge the J values reported here for the 3-bond (H(8),N) and 4-bond (H(5),N) and (H(7),N) pairs are the only examples of J_{NH} couplings for these particular geometries.

The values of the 3-bond coupling constants in the aliphatic systems are also of interest for they depend on the dihedral angle θ and provide calibration of the relationships between θ and $^3J_{NH}$.[7,8] In 2-pyrrolidinone the observed values for $J_{NH(3)} = 1.6$ and $J_{NH(4)} = 1.4$ Hz (Figure 2B) are in good agreement with calculated values (1.6 (ref 6) and 1.5 Hz (ref 7), respectively) for θ's of 120°.[9] The rotationally averaged $\langle {}^3J_{NH} \rangle$ in N-methylacetamide (1.63 Hz) also agrees well with the calculated value of 1.8 Hz.[7]

To summarize, we have demonstrated that a polarization-transfer sequence preceeding the selective 2D-J experiment markedly increases sensitivity while retaining the spectral simplicity and high resolution inherent in the 2D-J experiment.[10] Clearly the technique facilitates the observation of ^{15}N–^{1}H coupling constants at natural abundance (0.37%) without requiring an excessive investment in spectrometer time or in amounts of sample. This experiment will be particularly useful for measuring $^3J(NC'C_\alpha H)$ in polypeptides, which to date provides the only experimental way to estimate the backbone torsional angle, ψ, in solution.[11] For example, applying this technique to valinomycin we find a value for ^3J(N(D-Val)H(D-Hyv)) consistent with that previously reported[12] from ^{15}N-enriched valinomycin.[13]

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Registry No. Nitrogen-15, 14390-96-6; 6-methoxyquinoline, 5263-87-6; 2-pyrrolidinone, 616-45-5; N-methylacetamide, 79-16-3.

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(5) Conventional ^{15}N spectra are of little value here for there is virtually no Overhauser enhancement of ^{15}N in this compound.

(6) A null value was also found for a similar $^4J_{NH}$ involving the (H(5),N(1)) and (H(6),N(10)) pairs in 1,10-phenanthroline.

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(10) For the experiment described here the principal limitation on the resolution in the F_1 or J dimension appears to be dephasing of the ^{15}N coherence in t_1 by the "random-field" relaxation of the protons which are scalar coupled to ^{15}N (Shoup, R. R.; VanderHart, D. L. *J. Am. Chem. Soc.*, **1971**, *93*, 2053–2054; and Vold, R. R.; Vold, R. L. *J. Chem. Phys.* **1976**, *64*, 320–332), and this will be the subject of a separate publication. As noted in ref 3, a secondary limitation arises when the selectively flipped proton is tightly coupled to other protons. Some selectivity may be lost and the splitting patterns in the J dimension may contain extra lines. See, for example: Bodenhausen, G.; Freeman, R.; Morris, G. A.; Turner, D. L. *J. Magn. Reson.* **1977**, *28*, 17–28.

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Vibrational Circular Dichroism in (*S*)-(−)-Epoxypropane. Measurement in Vapor Phase and Verification of the Perturbed Degenerate Mode Theory

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Vibrational circular dichroism (VCD)[1] and Raman optical activity (ROA)[2] are recently developed spectroscopic techniques and are gaining increased attention for deducing molecular stereochemistry. In order to relate the experimental VCD and ROA to configurational details, simple conceptual models are also developed.[3] Of these models the perturbed degenerate mode theory[2,4] emphasizes the optical activity in vibrational modes of a methyl group. In a chiral environment the degenerate modes of a methyl group can be split into individual components, and such degeneracy-lifted modes are predicted to exhibit bisignate optical activity with the sign order reflecting the configuration of the chiral center to which the methyl group is attached.

The antisymmetric stretching, deformation, and rocking modes are the three degeneracy-lifted pairs of vibrations for the methyl group in a chiral environment. Liquid-phase VCD associated with the former two types of modes has been examined in the literature[5] but that associated with rocking modes has not been reported so far. To avoid condensed-phase effects and for comparisons to theoretical predictions, either matrix isolation[6] or vapor phase VCD measurements would be most appropriate. Here we report the first vapor-phase VCD measurement to verify the aforementioned theoretical concept; also the VCD features observed in vapor phase are compared with those observed in liquid phase to examine the phase effects. This is also the first report of VCD in degeneracy-lifted methyl rocking modes.

The measurements are carried out on a Fourier-transform infrared spectrometer described elsewhere.[7] A higher sensitivity MCT detector with $D^* = 2 \times 10^{10}$ and operating range of 5000–720 cm^{-1} is employed in the present studies. Vapor-phase measurements are made with the sample held in a 5-cm gas cell with KBr windows. For measurements in liquid phase, a variable path length cell with a 25-μm path length is employed. The base line and instrumental artifacts in VCD spectra are eliminated by subtracting the spectra of a racemic sample from those of the enantiomer.

The methyl group modes of epoxypropane are identified through the comparison of its infrared absorption spectra (Figures 1 and 2) with those of ethylene oxide[8] and monodeuterated ethylene oxide.[9] The bands in liquid phase at 1456 and 1446 cm^{-1} are considered to be associated with the degeneracy-lifted antisymmetric methyl deformation modes; the intense band at 1407 cm^{-1} is associated with the symmetric methyl deformation mode; the

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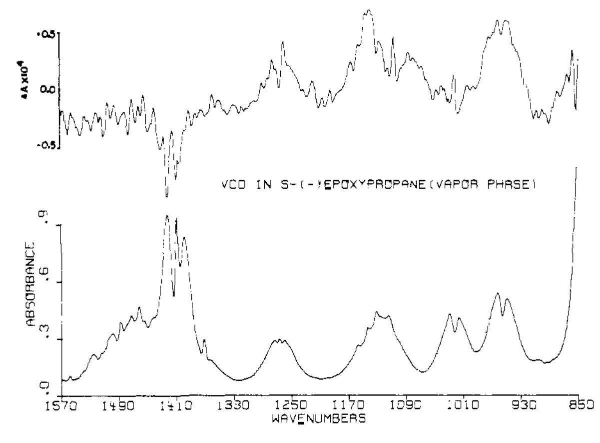

Figure 1. Vapor-phase vibrational circular dichroism in (*S*)-(−)-epoxypropane. The bottom trace is infrared absorption and the upper trace is VCD spectrum. VCD is obtained from 12 500 ac scans and 160 dc scans at 4-cm^{-1} resolution.

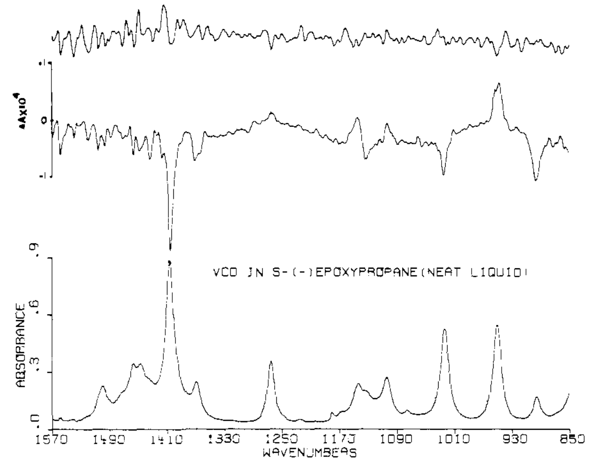

Figure 2. Liquid-phase vibrational circular dichroism in (*S*)-(−)-epoxypropane. The bottom trace is absorption spectrum and the middle trace is the VCD spectrum, which is obtained from 6250 ac scans and 80 dc scans at 4-cm^{-1} resolution. The top most spectrum is the difference between two such VCD measurements and represents the level of spectral reproducibility.

bands at 1023 and 950 cm^{-1} are associated with the degeneracy-lifted methyl rocking modes. The bands in vapor phase show splittings due to the resolution of rovibrational P, Q, and R band contours.

From the VCD spectra (Figures 1 and 2) it is noted that the symmetric methyl deformation mode exhibits negative VCD, but the degeneracy-lifted antisymmetric methyl deformation modes do not show any noticeable VCD features either in vapor or liquid phase. The degeneracy-lifted methyl rocking modes, however exhibit bisignate VCD both in vapor and liquid phases and support the theoretical concepts.[2,4] In vapor phase, the low-frequency component (at 950 cm^{-1}) exhibits sizeable positive VCD while the high-frequency component exhibits a small negative VCD. In liquid phase, VCD associated with both components is of nearly equal intensity. This difference in relative intensities is attributed to the Coriolis interactions[10] in vapor phase, because the absorption intensity perturbations at 1023 and 830 cm^{-1} in vapor phase point to the presence of such interactions.

Other differences apparent in vapor- and liquid-phase VCD spectra can be explained by broad rovibrational band contours in vapor phase. A striking difference in Figures 1 and 2 is noticed around 1130 cm^{-1} where a positive–negative–positive VCD triplet is present in liquid phase and a single positive VCD band is present in vapor phase. VCD bands are significantly broader in vapor phase due to the resolution of P, Q, and R band contours. As a consequence, VCD observed in vapor phase around 1130 cm^{-1} is actually the resulting sum of overlaping VCD contributed by P, Q, and R branches of three individual bands at 1143, 1130, and 1104 cm^{-1}. Similarly, the negative VCD at 1371 cm^{-1}, which is associated with the C*–H deformation mode, observed in liquid phase is submerged under VCD associated with the P branch of methyl symmetric deformation mode.

These observations suggest that, to explain vapor-phase VCD features quantitatively, the existing theoretical models need to be modified to incorporate Coriolis interactions and rovibrational transitions.

In the vapor-phase VCD spectrum, some fine structure corresponding to the P, Q, and R splittings of the absorption spectrum is evident. This fine structure gives the appearance of noise in both absorption and VCD spectrum. However, the noise level in vapor-phase spectrum is approximately the same as that in liquid phase, since in both spectra (see Figures 1 and 2) the overall absorption is nearly equal and the instrumental conditions are identical. The identification of fine structure is not essential for VCD intensities, because such fine structure should be broadened out by using pressure broadening techniques,[11] to obtain accurate intensity information.

Another significant observation in the present measurement is that the dissymmetry factor ($\Delta A/A$) is greater than 10^{-4} for most of the bands; for the molecules studied in the literature, the dissymmetry factors above 10^{-4} were less common. The maximum value noted here is 5×10^{-4}, for the band at 895 cm^{-1}, which is associated with the ring deformation and symmetric C–O stretch. This is one of the very few large values observed[12] thus far.

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^{19}F MAS-NMR of Fluoridated Hydroxyapatite Surfaces

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High-resolution NMR of solids by magic-angle spinning (MAS) promises to be a useful spectroscopic technique for the characterization of solid surfaces.[1] We demonstrate here that high-field ^{19}F MAS-NMR can be used to provide new information about the fluoridation of hydroxyapatite surfaces. Calcium hydroxyapatite, $Ca_5(OH)(PO_4)_3$, is the prototypical mineral of bone and

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