Raman Optical Activity in 1-Halogeno-2-methylbutanes: Observation of Conformer Dependent Circular Intensity Differentials in Carbon–Halogen Stretching Modes

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Summary Observations of Raman optical activity in the carbon–halogen stretching modes of both 1-chloro- and 1-bromo-2-methylbutanes demonstrate the unique sensitivity of this new chiroptical technique to the optical activity of individual conformers of the molecular skeleton.

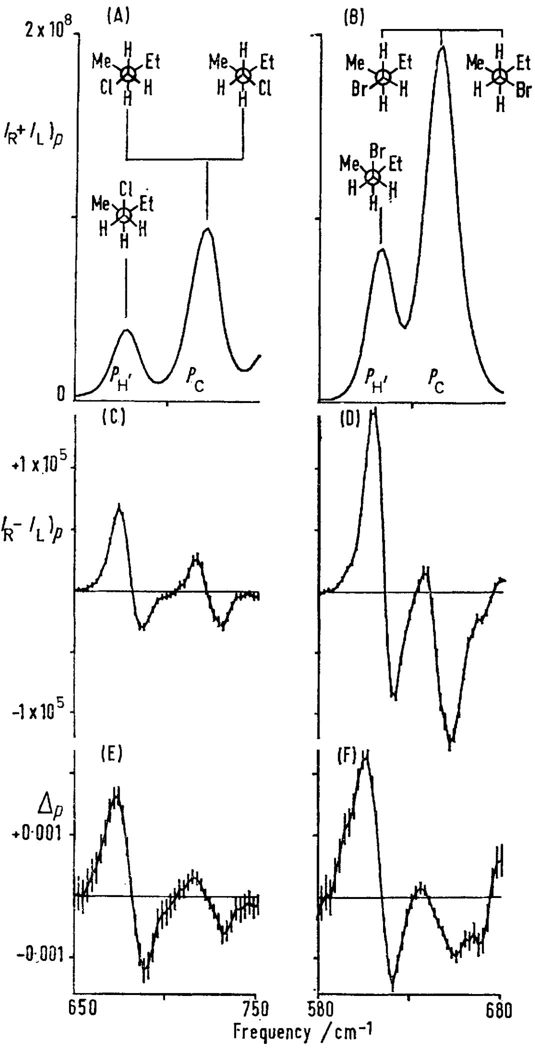

Figure. (A) Depolarized Raman spectrum $(I_R + I_L)_p$ of (*S*)-(+)-1-chloro-2-methylbutane ($[\alpha]_D^{25}$ + 1·49) (R–Cl) in the C–Cl stretching region (10 cm^{-1} resolution, 300 s counting time/data point, 1 data point/2·5 cm^{-1}, display results from a 3-point average). Depolarization ratios: $\rho_n(P_{H'}) = 0{\cdot}13$, $\rho_n(P_C) = 0{\cdot}28$. (B) Depolarized Raman spectrum $(I_R + I_L)_p$ of (*S*)-(+)-1-bromo-2-methylbutane ($[\alpha]_D^{25}$ + 3·80) (R–Br) in the C–Br stretching region (same conditions as for A). Depolarization ratios: $\rho_n(P_{H'}) = 0{\cdot}13$, $\rho_n(P_C) = 0{\cdot}26$. (C) Difference spectrum $(I_R - I_L)_p$ for R–Cl observed simultaneously with A; vertical bars indicate the statistical error. (D) Difference spectrum $(I_R - I_L)_p$ for R–Br observed simultaneously with B. (E) Normalized circular intensity differentials, $\Delta_p = (I_R - I_L)_p/(I_R + I_L)_p$ for R–Cl; vertical bars indicate the statistical errors in Δ_p. (F) Normalized circular intensity differentials for R–Br. Spectra C and E are computer averages of four separate experiments, spectra D and F are averages of two experiments; statistical errors depicted are those for a single experiment.

Reports of Raman optical activity (ROA) to date have demonstrated that the effect exists and that it is measurable when the proper precautions are exercised.[1] With the exception of methyl antisymmetric deformations[2,3] and, possibly, methyl torsions,[2] circular intensity differentials (CID's) have generally been reported for vibrational bands which cannot be unambiguously assigned to specific vibrational modes with presently available information. We report here the first observation of ROA in readily assigned[4] C–Cl and C–Br stretching modes, namely those of (*S*)-(+)-1-chloro- and (*S*)-(+)-1-bromo-2-methylbutanes. This is also the first reported evidence of CID's from distinguishable conformers. These observations illustrate ROA to have a dramatic and direct sensitivity to molecular conformation and support the contention[3] that ROA will be a uniquely powerful tool in conformational analysis.

Measurements were made with an instrument rebuilt from the original unit[5] in order to minimize the sources of artifacts which appeared in our first attempt at ROA studies. Square wave polarization modulation of 488 nm Ar^{+} laser radiation, ellipticity monitoring, synchronous photon counting, and off-line data processing were utilized. We easily reproduced literature values of Δ_p.[†,1,2]

The ROA results (Figure) illustrate the distinct similarity of the CID's observed in the carbon–halogen stretching modes of the chloride and bromide with the same absolute configuration; a strong couplet appears in the lower frequency band with a somewhat weaker couplet appearing in the higher frequency band. In the chloride, the 681 cm^{-1} band is assigned[4] to $P_{H'}$ conformers (see Figure) and the 723 cm^{-1} band to P_C (P_{Me} and P_{Et}) conformers. A conformational analysis[6] of this system indicates that two $P_{H'}$ conformers contribute to the 681 cm^{-1} band whereas two P_{Me} and three P_{Et} conformers contribute to the 723 cm^{-1} band. I.r. spectra[6] of the Ar and Ne matrix-isolated chloride exhibit components in both the 681 and the 723 cm^{-1} bands which are consistent with these analyses. Therefore, the couplet in the 681 cm^{-1} band undoubtedly arises from the two $P_{H'}$ conformers and the one in the 723 cm^{-1} band is the residual of contributions from the five P_C conformers. Since higher resolution Raman spectra of the liquid bromide exhibit a band structure in the C–Br stretching region which is similar to that of the matrix-isolated chloride in the C–Cl stretching region, CID's in the C–Br stretching modes can be assigned in a similar fashion.

A chirality function[7] analysis of these substituted butanes produces some interesting results: the two $P_{H'}$ conformers are predicted to have opposite optical activity whereas the optical activity of the three P_{Et} conformers should be opposite to that of the two P_{Me} conformers. Thus, the presence of a couplet in the $P_{H'}$ band could reflect the difference in the molecular chirality of two populated conformers which differ by ethyl group orientation and the couplet in the P_C band could reflect the difference in the molecular chirality of P_{Et} and P_{Me} conformers. The carbon–halogen stretching mode would, thereby, be a direct and

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[†] $\Delta = (I_R - I_L)/(I_R + I_L)$; the subscripts *p* (parallel) and *s* (perpendicular), which refer to the scattering plane (F. A. Jenkins and H. E. White, 'Fundamentals of Optics,' McGraw-Hill, New York, 1957, 3rd Edn., Ch. 25), are used to avoid specification of a specific co-ordinate system as found in ref. 1 and to avoid confusion with the standard notation used in ordinary Raman spectroscopy as found in ref. 2. (+)-α-Pinene, $[\alpha]_D^{23}$ + 46·64: Δ_p (770 cm^{-1}) = $-2{\cdot}5 \pm 0{\cdot}4 \times 10^{-3}$, and Δ_p (788 cm^{-1}) = $+1{\cdot}8 \pm 0{\cdot}4 \times 10^{-3}$; (−)-α-Pinene, $[\alpha]_D^{25}$ −41·9: Δ_p (770 cm^{-1}) = $+\ 1{\cdot}1 \pm 0{\cdot}3 \times 10^{-3}$, and Δ_p (788 cm^{-1}) = $-1{\cdot}6 \pm 0{\cdot}4 \times 10^{-3}$.

sensitive probe of the chirality of the flexible 2-methylbutane skeleton.

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