# Raman Circular Intensity Differential Observations on Some Monoterpenes

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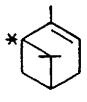
*Summary* Circular intensity differentials have been recorded in the low-frequency Raman spectra of the optically active monoterpenes α-pinene, β-pinene, borneol, and carvone, but were not measurable in camphor and fenchone.

The suggestion that Rayleigh and Raman scattered light from optically active molecules should show polarization effects which could provide new information about their structure and configuration[1–3] has recently been experimentally confirmed in several simple optically active liquids.[4,5] The polarization effect observed is a circular intensity differential (CID) defined by

$$\Delta_\alpha = (I_\alpha^R - I_\alpha^L)/(I_\alpha^R + I_\alpha^L)$$

where $I_\alpha^R$ and $I_\alpha^L$ are the scattered intensities with α-polarization in right and left circularly polarized incident light. Observations now reported of Raman CIDs in several monoterpenes could originate in "skeletal ring" vibrations involving asymmetric carbon atoms.



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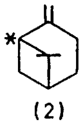

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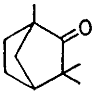

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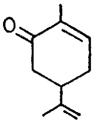

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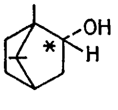

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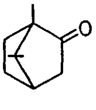

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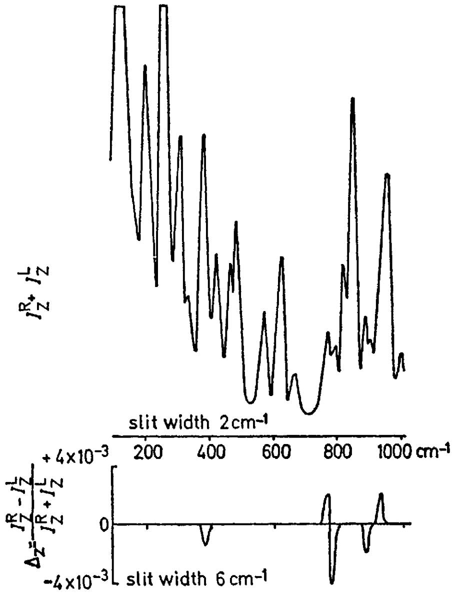

Figure 1. *The Raman and Raman CID spectra of* (−)-*α-pinene for scattered light linearly polarized parallel to the scattering plane. The background was subtracted from the Raman intensities in estimating* $\Delta_z$.

We studied the liquids α-pinene (**1**), β-pinene (**2**), fenchone (**3**) and carvone (**4**), and the solids borneol (**5**) and camphor (**6**) in both $CCl_4$ and MeOH solution. The component $I_z$ of the light scattered at 90° and linearly polarized parallel to the scattering plane was sampled since, for reasons discussed previously,[4] only this component was free of spurious contributions in our instrument. A number of Raman CIDs were found between *ca.* 300 and 1100 cm$^{-1}$ in α- and β-pinene, the most significant being shown in Figures 1 and 2. The (+)- and (−)-enantiomers of α-pinene gave mirror-image CIDs; only (−)-β-pinene was available. (−)-Borneol in $CCl_4$ and MeOH solution (almost saturated) showed a significant CID couplet with $\Delta_z$ *ca.* $+2{\cdot}5 \times 10^{-3}$ at *ca.* 922 cm$^{-1}$ and *ca.* $-1 \times 10^{-3}$ at *ca.* 950 cm$^{-1}$. Carvone showed a number of CIDs between *ca.* 200 and 1200 cm$^{-1}$ some of which (at *ca.* 635 and 703 cm$^{-1}$, for example)

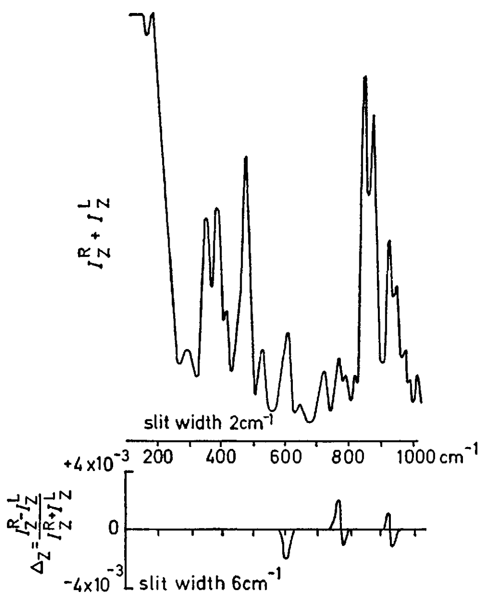

FIGURE 2. *The Raman and Raman CID spectra of* (—)-*β-pinene.*

were almost as large as those in the pinenes. Very small effects ($|\Delta_Z| < 0{\cdot}5 \times 10^{-3}$) were apparent in the camphor solutions, but none were found in fenchone.

In some situations relative chiralities can be assigned qualitatively by merely considering the groups bonded to an asymmetric atom. Thus the starred asymmetric atoms in the pinenes are highly chiral since the four bonds terminate in very different structural units. The starred asymmetric atom in borneol is probably more chiral than the other two, which are similar to the two in camphor. The two asymmetric centres in fenchone are much less chiral. The asymmetric centre in carvone would appear to be only weakly chiral, and the large CIDs could be connected with the rigidity conferred on the ring by three adjacent $sp^2$-hybridized carbon atoms.

The CIDs in the pinenes and carvone occur in the region normally assigned to "skeletal ring" vibrations.[6,7] Although the CIDs in α- and β-pinene are of similar magnitude and occur in the same general region, the actual frequencies are rather different since skeletal frequencies are sensitive to structural changes.

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