Raman Optical Activity of Pinenes, Carenes, and Related Molecules

By **Laurence D. Barron,*** and **Brian P. Clark,** Chemistry Department, The University, Glasgow G12 8QQ

Raman circular intensity difference spectra between 80 and 2 000 cm^{-1} of (+)- and (−)-α-pinene, (−)-β-pinene, (−)-cedrene, (+)-car-3-ene, (+)-car-2-ene, (−)-caryophyllene, and (−)-β-bourbonene are presented. A stereochemical correlation in bands originating in skeletal modes of the two pinenes is pointed out. Other features noted include effects in bands characteristic of the *gem*-dimethyl group and out-of-plane olefinic hydrogen deformations.

VIBRATIONAL optical activity spectra, obtained using the Raman circular intensity difference (c.i.d.) technique, of some pinenes, carenes, and related molecules are presented and compared to see what common features emerge. The basic references, together with the experimental details, are given in the preceding paper.[1]

DISCUSSION

Figures 1—7 show the depolarized Raman circular intensity sum and difference spectra of, respectively, (+)- and (—)-α-pinene, (—)-β-pinene, (—)-cedrene, (+)-car-3-ene, (+)-car-2-ene, (—)-caryophyllene, and (—)-β-bourbonene. The complete Raman c.i.d. spectrum of (—)-α-pinene has been published previously by Hug *et al.*,[2] and is virtually identical with that shown here.

By examining the Raman spectra of 13 molecules which all have pinane-type skeletons, Freeman and Mayo have discovered seven common bands between 1 100 and 375 cm^{-1} which they attribute to skeletal vibrations.[3] The frequencies of these bands are given in the Table. The spectra of two molecules in this series, α- and β-pinene, are presented here (Figures 1 and 2) and it is interesting to compare the Raman optical activity of corresponding skeletal modes. Of the seven Raman bands in the correlation only two, at 1 082 and 656 cm^{-1}, do not show significant c.i.d.s in both α- and β-pinene. The statistically significant parts of the c.i.d.s in the remaining five bands have been shaded black. Comparing the spectrum of the (—)-enantiomer of α-pinene with that of (—)-β-pinene, both molecules

Seven pinane-type skeletal frequencies (cm^{-1}) identified by Freeman and Mayo [3]

1 082 ± 3
852 ± 13
822 ± 4
758 ± 17
656 ± 26
472 ± 12
387 ± 12

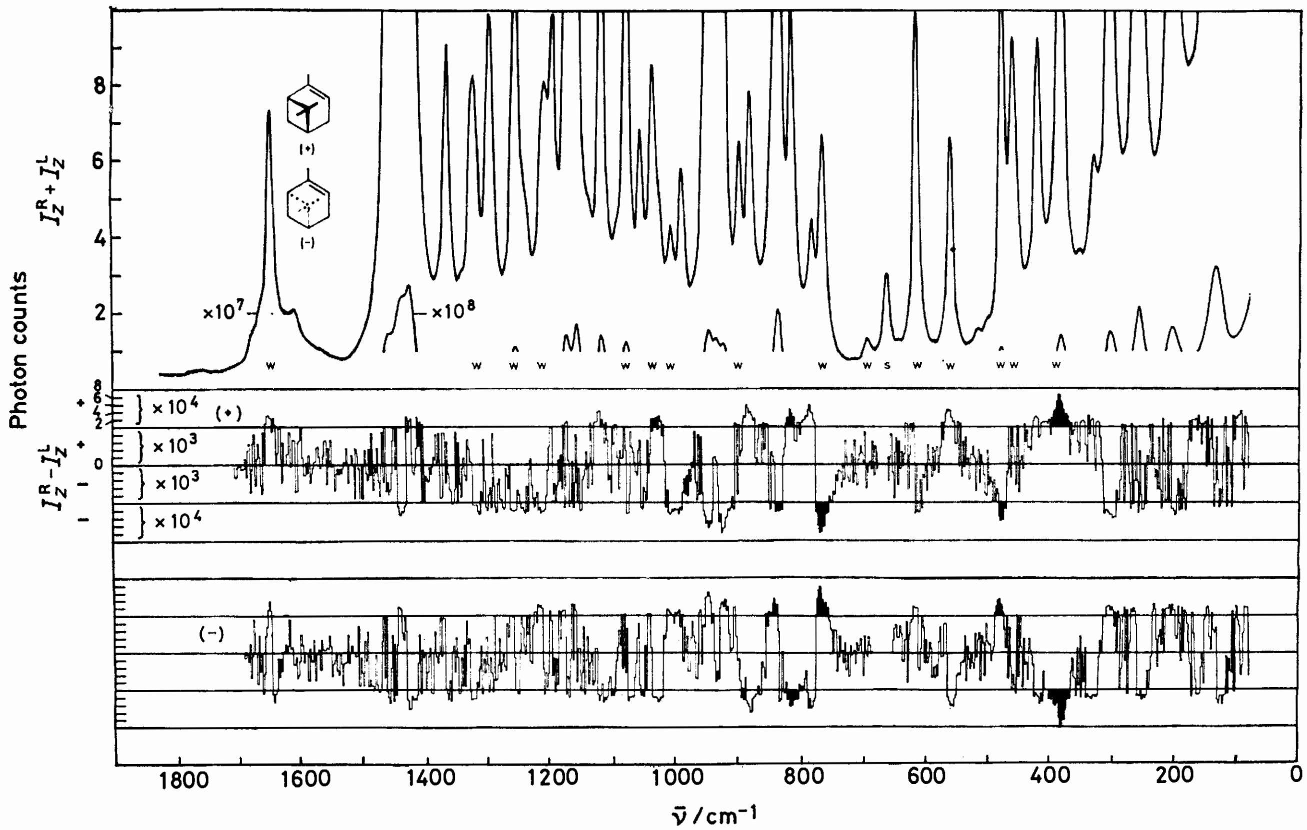

FIGURE 1 The depolarized Raman circular intensity sum and difference spectra of neat (+)- and (—)-α-pinene

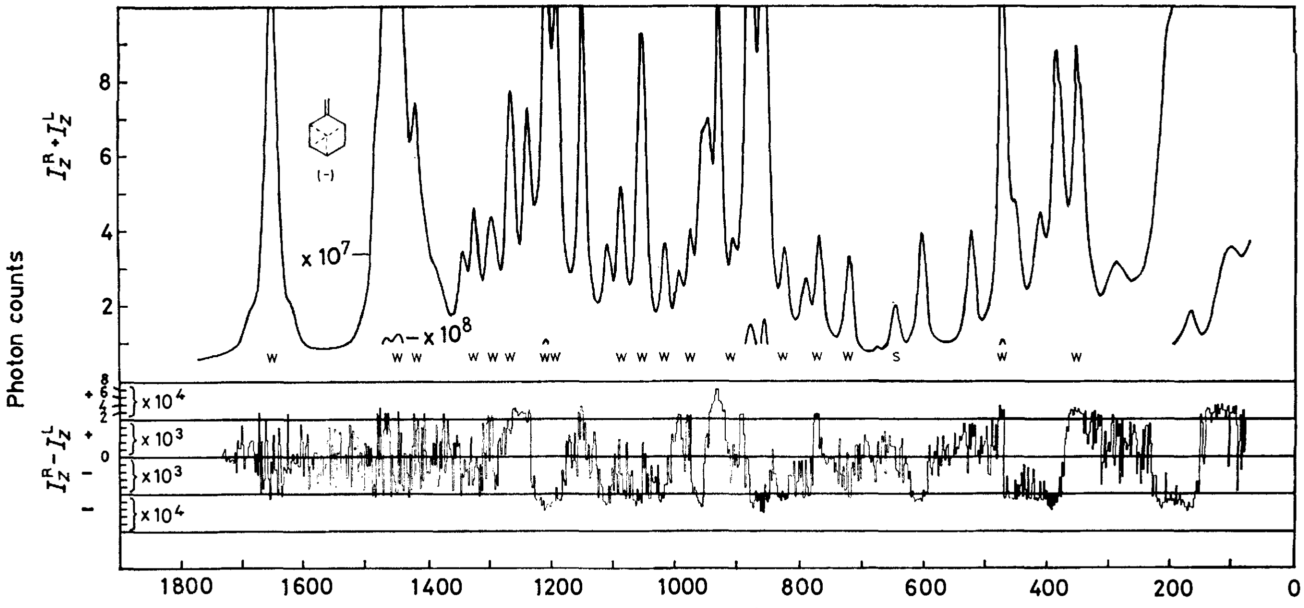

FIGURE 2 The depolarized Raman circular intensity sum and difference spectra of neat (—)-β-pinene

having ' analogous ' absolute configurations, we see that four of the five Raman c.i.d.s, at 387, 472, 758, and 822 cm^{-1}, have the same sign in the corresponding bands while the remaining one, at 852 cm^{-1}, changes sign. It would be interesting to examine the Raman optical activity of spectra of other pinane-type molecules to discover if the correlations persist.

Mayo and Freeman have also published a five-band correlation for the Raman spectra of cedrane-type molecules.[4] Unfortunately, in the spectrum of (—)-cedrene (Figure 3), only one skeletal mode, at 780 cm^{-1}, which is strongly polarized and hence particularly sensitive to artifacts,[5] shows any significant Raman optical activity. It is worth noting that, due to the considerable size of molecules with the cedrane skeleton and the resulting complexity of their Raman spectra, in order to compile the list of skeletal vibrations an intensity constraint had to be imposed in which the empirical selection was limited to the seven most intense bands in the spectrum.[4] It may be that the Raman optical activity spectra of a series of related molecules could be used to identify bands of similar origin, should this type of study be undertaken in the future.

All the molecules presented here are unsaturated, and

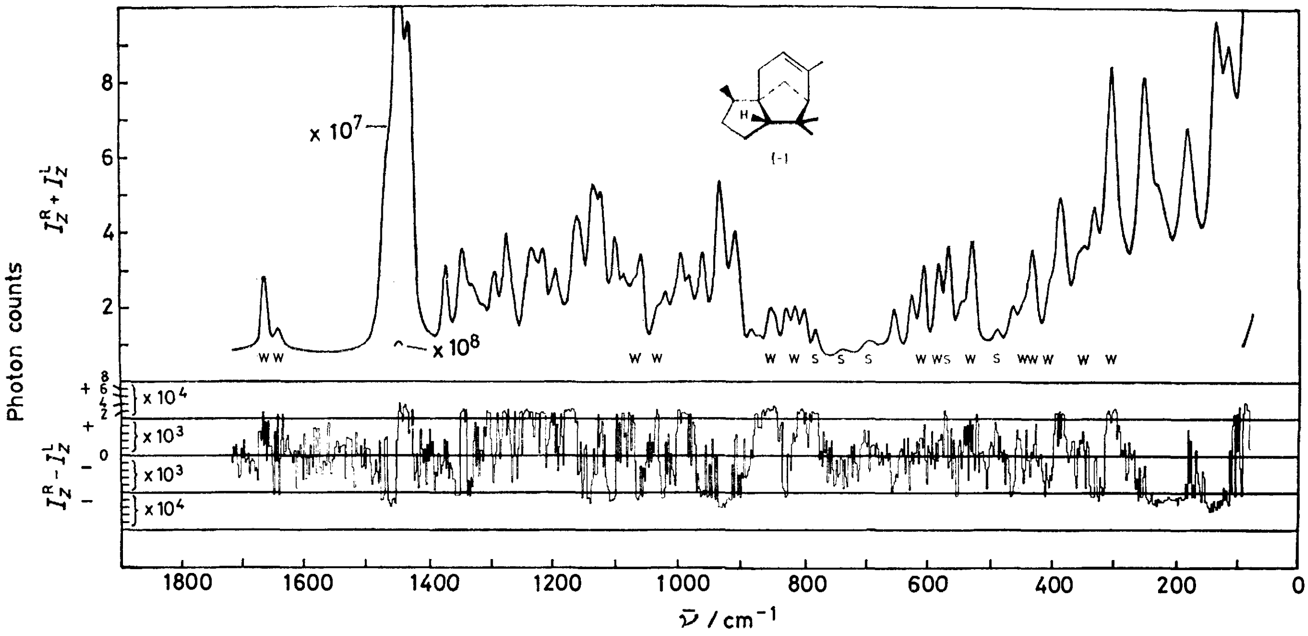

FIGURE 3 The depolarized Raman circular intensity sum and difference spectra of neat (—)-cedrene

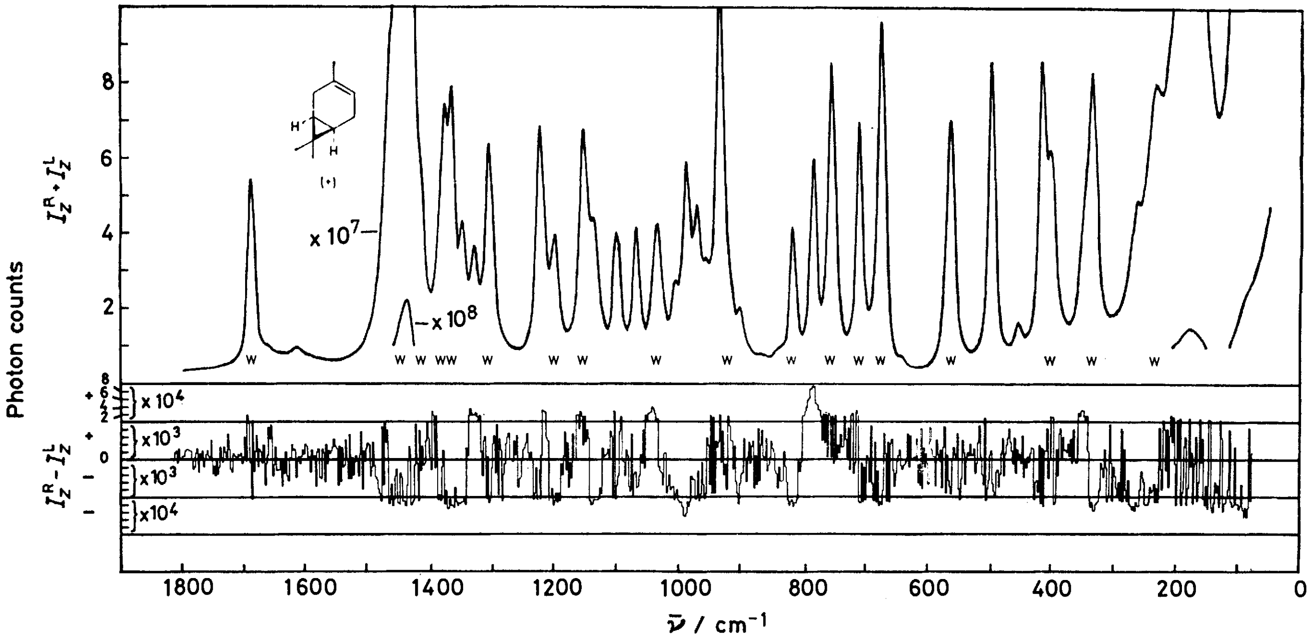

FIGURE 4 The depolarized Raman circular intensity sum and difference spectra of neat (+)-car-3-ene

we have found that vibrations involving out-of-plane deformations of olefinic hydrogen atoms are consistently producing Raman optical activity effects. A trisubstituted double bond gives rise to an out-of-plane CH deformation in the region 790—840 cm^{-1}.[6] This band is seen clearly at 820 cm^{-1} in the Raman spectrum of (+)-car-3-ene (Figure 4) and generates a negative c.i.d. The corresponding Raman band in (+)-car-2-ene (Figure 5) occurs at 830 cm^{-1} and, although quite strongly polarized, its attendant positive c.i.d. is probably genuine. The opposite signs of the corresponding c.i.d.s in (+)-car-3-ene and (+)-car-2-ene indicate that the intramolecular environments of the olefinic hydrogen atoms in the two molecules are such as to induce enantiomeric chirality in the two deformations. In larger molecules it is difficult to pick out these out-of-plane olefinic CH deformation bands. In the case of α-pinene (Figure 1), Freeman and Mayo eliminate two bands at 820 and 845 cm^{-1} as being skeletal modes,[3] leaving only the Raman band at just under 790 cm^{-1} as the candidate for the deformation. This shows a large Raman c.i.d., negative in the (—)-enantiomer. However, there is also a Raman band at 790 cm^{-1} in the spectrum of (—)-β-pinene which shows a hint of a negative c.i.d. If

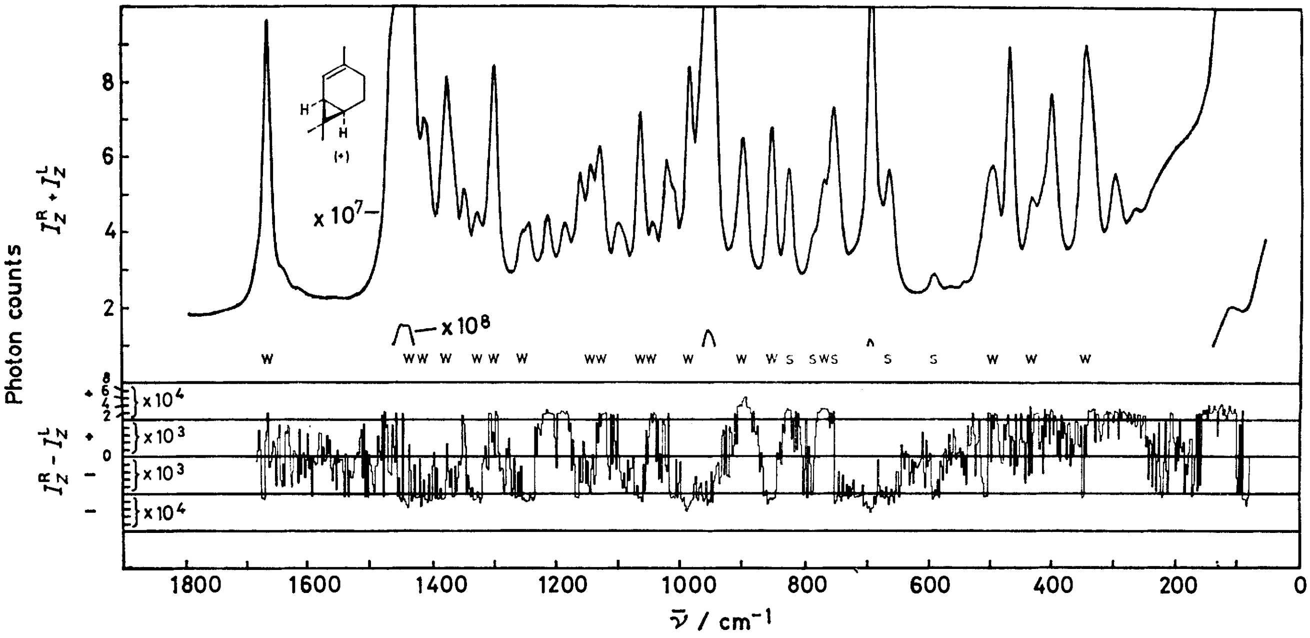

FIGURE 5 The depolarized Raman circular intensity sum and difference spectra of neat (+)-car-2-ene

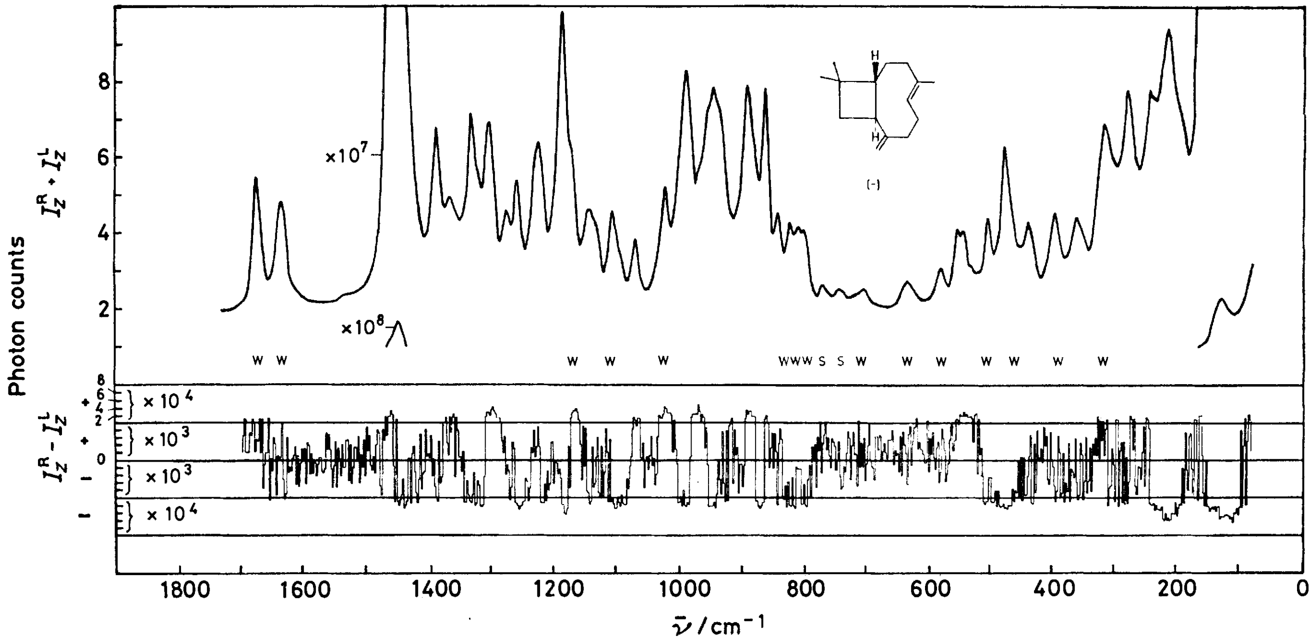

FIGURE 6 The depolarized Raman circular intensity sum and difference spectra of neat (—)-caryophyllene

these two bands are of similar origin, it could be that the Raman band at 845 cm^{-1} is not, in fact, a skeletal mode but the CH deformation and that the skeletal mode actually occurs at 875 cm^{-1}, although this is outwith the range quoted by Freeman and Mayo. This band at 875 cm^{-1} shows a negative c.i.d. in (—)-α-pinene and if it is the skeletal mode then all five of the Raman c.i.d.s associated with corresponding skeletal modes in (—)-α- and (—)-β-pinene have the same sign. Cedrene and caryophyllene, which both contain a trisubstituted olefinic group, have complicated Raman spectra (Figures 3 and 6). (—)-Cedrene shows three Raman bands in the appropriate region: one of them, at 820 cm^{-1}, is a skeletal mode [4] and shows no c.i.d.; the remaining two at 805 and 835 cm^{-1} both show c.i.d.s, positive and negative respectively. There are also three candidates in (—)-caryophyllene: at 825, 815, and 800 cm^{-1}, the first and third of which generate negative Raman c.i.d.s. The out-of-plane, in-phase, vinylidene CH_2 deformation occurs within the fairly small spectral range 885—895 cm^{-1}.[6] This narrower range helps to identify the band. The three molecules in this series with a vinylidene group give corresponding Raman c.i.d.s. This band occurs at 885 cm^{-1} in (—)-β-pinene (Figure 2) as the

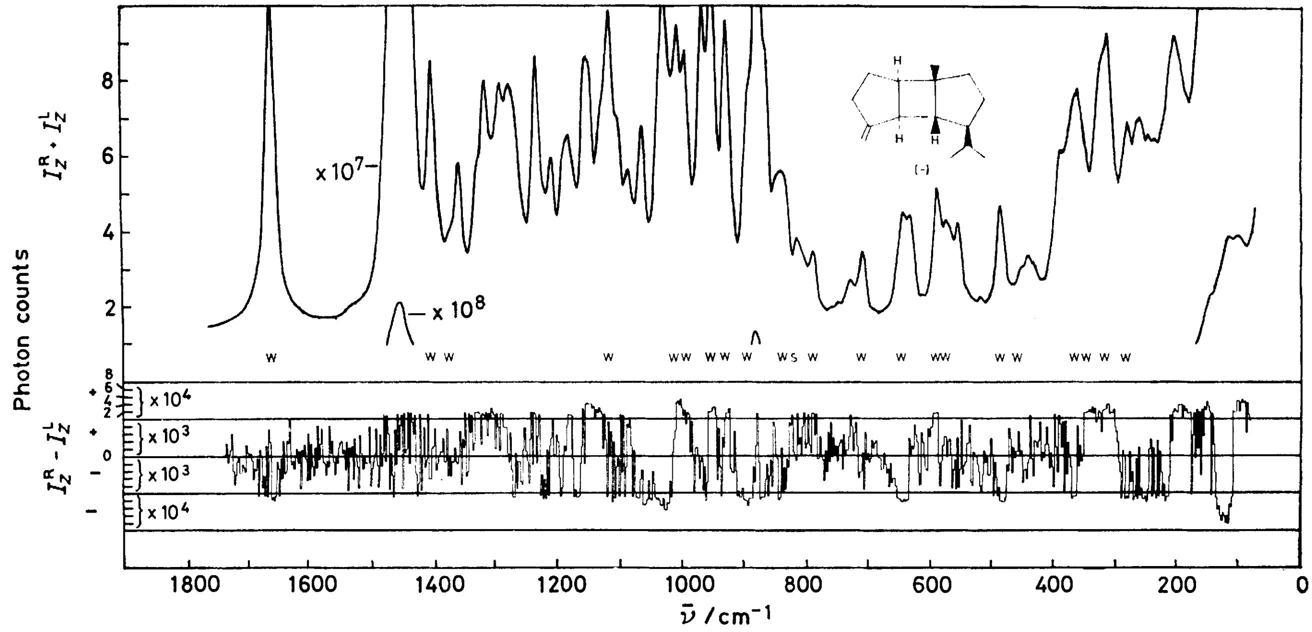

FIGURE 7 The depolarized Raman circular intensity sum and difference spectra of neat (—)-β-bourbonene

shoulder of a lower frequency skeletal band and exhibits a small positive c.i.d. The Raman band at 890 cm^{-1} in (−)-caryophyllene (Figure 6) shows a positive c.i.d. and that at 890 cm^{-1} in (−)-β-bourbonene (Figure 7) shows a negative one. All that may be done here is to point out these effects; the molecules are too complex for any stereochemical correlations to be made at present. Other examples of Raman c.i.d.s in these olefinic CH and CH_2 deformations are given in the preceding paper.[1]

The isopropyl group produces two Raman bands at *ca.* 1 140 and 1 170 cm^{-1} arising from an interaction of the two methyl rocking modes together with C–C stretching.[6] Raman c.i.d.s have been observed previously in these modes.[1] The couplet present in the optical activity spectrum of (−)-β-bourbonene (Figure 7) associated with Raman bands at 1 145 and 1 170 cm^{-1} could be due to the isopropyl group.

The *gem*-dimethyl group gives rise to two bands of similar origin at slightly higher frequencies.[6] The Raman c.i.d.s in these bands indicate that the situation is more complicated than in the isopropyl group, presumably due to increased participation of C–C stretching. Take the cases of (+)-car-3-ene and (+)-car-2-ene (Figures 4 and 5). In the former there are two relatively isolated bands at 1 195 and 1 220 cm^{-1} which we assign to the *gem*-dimethyl group. These generate a Raman c.i.d. couplet. In (+)-car-3-ene, however, two new bands occur in the region of 1 250 cm^{-1} and one new one appears just above 1 200 cm^{-1}. The result is that the couplet observed in car-2-ene is replaced by two positive effects. Coupling to the higher frequency bands at 1 250 cm^{-1} could be indicated by them showing negative c.i.d.s. With two molecules as similar as α- and β-pinene one might expect the Raman optical effects due to their *gem*-dimethyl groups to be similar also. However, the complexity of the Raman spectra in the region of 1 200 cm^{-1} in these molecules precludes any meaningful comparison. A c.i.d. couplet in (−)-β-pinene (Figure 2) centred at 1 240 cm^{-1} encompasses six Raman bands altogether. Perplexingly, the Raman optical activity in the same region in (−)-α-pinene (Figure 1) is limited to a small positive feature at *ca.* 1 220 cm^{-1}. The couplet centred at 1 170 cm^{-1} in the Raman optical activity spectrum of (−)-caryophyllene (Figure 6) could originate in the *gem*-dimethyl group. Cedrene (Figure 3) also contains a *gem*-dimethyl group but the complexity of the Raman spectrum and the presence of three other methyl groups in the molecule make band assignments almost impossible in this region.

The two (+)-carenes (Figures 4 and 5) reveal several Raman c.i.d. effects of uncertain origin which correlate in sign. Best examples are the positive effects common to both molecules at *ca.* 1 050 cm^{-1}, the negative effects at *ca.* 990 cm^{-1}, and the large positive effects at *ca.* 780 cm^{-1}.

Finally, we should mention that chiral organic molecules containing methyl groups often show large optical activity in broad, weak, depolarized Raman bands below *ca.* 300 cm^{-1} that originate in methyl torsion vibrations,[7,8] and this could be the origin of some of the large c.i.d.s at low frequency in several of the spectra shown here.

We are grateful to Dr. D. H. Grayson for the samples of (+)-car-2-ene and (+)-car-3-ene, to Dr. A. L. Porte for the sample of (−)-caryophyllene, and to the S.R.C. for an equipment grant and a Research Studentship to B. P. C.

[8/973 *Received, 24th May,* 1978]

REFERENCES

[1] L. D. Barron and B. P. Clark, preceding paper.

[2] W. Hug, S. Kint, G. F. Bailey, and J. R. Scherer, *J. Amer. Chem. Soc.*, 1975, **97**, 5589.

[3] S. K. Freeman and D. W. Mayo, *Appl. Spectroscopy*, 1970, **24**, 595.

[4] D. W. Mayo and S. K. Freeman, *Appl. Spectroscopy*, 1970, **24**, 591.

[5] L. D. Barron and A. D. Buckingham, *Ann. Rev. Phys. Chem.*, 1975, **26**, 381.

[6] N. B. Colthup, L. H. Daly, and S. F. Wiberley, ' Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1975.

[7] L. D. Barron, *Nature*, 1975, **255**, 458.

[8] L. D. Barron and A. D. Buckingham, *J. Amer. Chem. Soc.*, 1979, **101**, 1979.