

Raman Optical Activity due to Isotopic Substitution: (1S)-4,4-Dideuterioadamantan-2-one

By LAURENCE D. BARRON*

(Chemistry Department, The University, Glasgow G12 8QQ)

and HENK NUMAN and HANS WYNBERG

(Department of Organic Chemistry, The University, Groningen, The Netherlands)

Summary Observations of Raman optical activity in CH_2 and CD_2 deformation modes of (1S)-4,4-dideuterioadamantan-2-one reinforce the expectation that vibrational optical activity measurements will become a powerful new means of studying the stereochemistry of molecules that owe their chirality to isotopic substitution.

MEASUREMENTS of vibrational optical activity should become a powerful new means of studying the stereochemistry (conformation and absolute configuration) of molecules that owe their chirality to isotopic substitution. This is because the conventional electronic optical activity, in the form of optical rotation and c.d. of visible and near u.v. radiation, of such molecules can be very small, whereas, in the case of deuterium substitution, the vibrational chirality of the skeleton in the region of the deuterium atoms is expected to be large. The Raman circular intensity differential technique¹ is particularly favourable since it provides complete vibrational optical activity spectra from *ca.* 50 to 4000 cm^{-1} and can therefore study c.d. deformation modes, which are expected to show the largest effects. In contrast, these modes are not accessible at present to the complementary i.r. c.d. technique since the latter cannot penetrate below *ca.* 2000 cm^{-1} (although it can still be used to study C-D stretching modes²).

Recently, Raman optical activity was reported in C-D deformation modes in (S)-(+)-[α -²H]benzylalcohol.³ Since only a few milligrams are usually available of molecules owing their chirality to isotopic substitution, and the minimum quantity that can be studied with our present instrument is *ca.* 20 mg, it has not been possible to follow up these measurements with studies of a series of related compounds. However, a sufficient quantity of another rather different example, (1S)-(-)-4,4-dideuterioadamantan-2-one, has recently been prepared:⁴ although we are unable to deduce stereochemical information from the Raman optical activity spectrum reported here, the effects are sufficiently large and specific to emphasise the potential value of Raman optical activity measurements in such molecules.

Measurements were made with an instrument described previously;^{1,5} as before, the depolarized Raman circular intensity sum ($I_z^R + I_z^L$) spectrum is presented on a linear scale and the difference ($I_z^R - I_z^L$) spectrum is presented on a scale that is linear within each decade range but logarithmic between ranges. The sample of (1S)-(-)-4,4-dideuterioadamantan-2-one ($[\alpha]_{578}^{21} - 2.8^\circ$; *c* 1.0, 96% ethanol), estimated to have 98% deuterium content,⁴ was studied as a near-saturated solution in both MeOH and CS_2 in order to obtain the complete Raman optical activity spectrum clear of solvent bands.

Significant Raman optical activity features were observed only between *ca.* 800 and 1300 cm^{-1} , the spectrum in CS_2

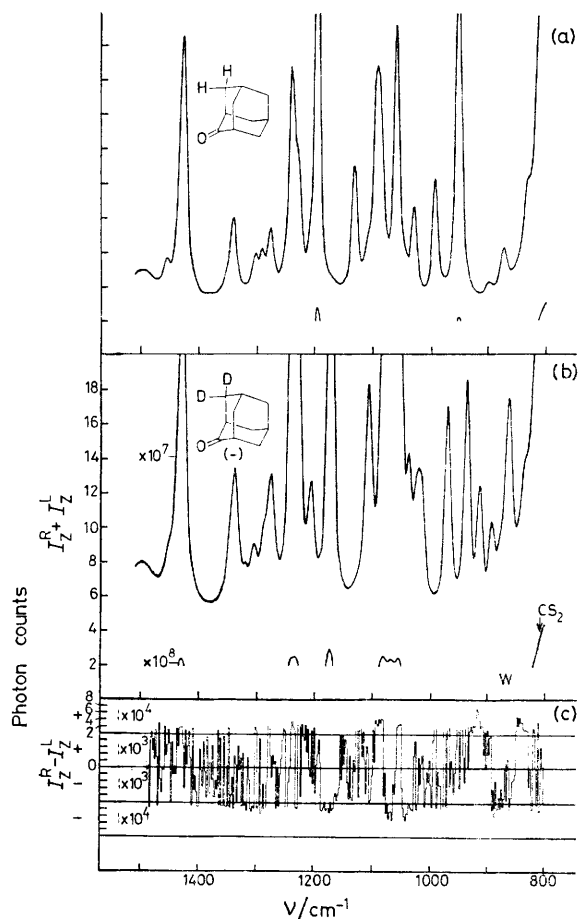


FIGURE. (a) The depolarized Raman circular intensity sum spectrum (arbitrary intensity units) of adamantanone in CS_2 . (b) and (c) The depolarized Raman circular intensity sum and difference spectra of (1S)-(-)-4,4-dideuterioadamantan-2-one in CS_2 . Instrumental conditions: laser power 3 W, laser wavelength 488 nm, slit width 11 cm^{-1} , scan speed 0.5 $\text{cm}^{-1} \text{min}^{-1}$.

solution being shown in the Figure. The spectrum of the non-deuteriated parent compound is shown for comparison. It can be seen that deuteration changes the conventional Raman spectrum considerably, indicating significant mixing between CD_2 modes and the other modes in this region (CH and CH_2 deformations, and C-C stretches). Significant optical activity band structures are seen in the regions from *ca.* 1150 to 1250 cm^{-1} , 1000 to 1100 cm^{-1} , and 800 to 950 cm^{-1} . The two higher frequency regions are appropriate for CH_2 wag, twist, and rock modes,⁶ whereas the lower-frequency region is appropriate for some of the corresponding CD_2 modes. Although isotopic substitution has

generated CH_2 and CD_2 groups in 'enantiomeric' environments, it is naive to expect the two corresponding Raman optical activity band structures to be mirror-images: the CH_2 and CD_2 deformation frequencies are sufficiently different that they will mix to different extents with other modes so that the normal modes in the two regions are not enantiomeric.

The Raman optical activity spectra of several deuteriated camphors have also been obtained. However, the effects of deuterium substitution are much harder to discern because camphor itself has a rich Raman optical activity spectrum,⁵ whereas adamantanone itself is not chiral so that all optical

activity effects in deuteriated adamantanones are attributable to isotopic substitution. The deuteriated camphor spectra are not reproduced here, but it is worth reporting that, in (+)-3,3-dideuteriocamphor, the most noticeable changes [relative to (+)-camphor] occur between 800 and 900 cm^{-1} , the region where CD_2 effects occur in the dideuterioadamantanone.

We thank the S.R.C. for an equipment grant.

(Received, 5th December 1977; Com. 1239.)

¹ L. D. Barron and A. D. Buckingham, *Ann. Rev. Phys. Chem.*, 1975, **26**, 381.

² G. Holzwarth, E. C. Hsu, H. S. Mosher, T. R. Faulkner, and A. Moscovitz, *J. Amer. Chem. Soc.*, 1974, **96**, 251.

³ L. D. Barron, *J.C.S. Chem. Comm.*, 1977, 305.

⁴ H. Numan and H. Wynberg, *J. Org. Chem.*, in the press.

⁵ L. D. Barron, *J.C.S. Perkin II*, 1977, 1074.

⁶ F. R. Dollish, W. G. Fateley, and F. F. Bentley, 'Characteristic Raman Frequencies of Organic Compounds,' Wiley, New York, 1974.