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RAMAN CIRCULAR INTENSITY DIFFERENTIAL SPECTRA OF SOME OPTICALLY ACTIVE SECONDARY ALCOHOLS

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Raman circular intensity differential spectra of (+)-2-butanol, (+)-2-pentanol, and (+)-2-octanol are presented. The same spectral patterns are observed in the 700-1000 cm^{-1} region, and several correlations are pointed out for the bands characteristic of secondary alcohols, which are assigned to the symmetric stretching of the C_3O skeleton.

The measurement of vibrational optical activity was expected to have potential advantages for chiral compounds having no UV or VIS absorption bands. Recently, for this purpose, Raman circular intensity differential (R-CID) spectroscopy[1] has been developed and succeeded in the solution of stereochemical problems of some chiral compounds. In the present investigation, we are interested in (S)-(+)-sec-alcohols with a C_3O ($CH_3CH(OH)CH_2$-) structural unit, and examine the correlations between the R-CID spectra and the unit structure.

The samples were (S)-(+)-2-butanol, (S)-(+)-2-pentanol, and (S)-(+)-2-octanol (Tokyo Kasei Co. Ltd.) and used without prior purification. The experimental arrangement was almost the same with the one described previously[2]. A linearly polarized incident light (Ar^+ laser; 488.0 nm, 500 mW) was modulated to right and left circularly polarized light by the pockels' cell (KDP, 370 Hz), which was driven by a quasi-square wave high voltage instead of a sinusoidal one which is usually used. By use of the synchronous photon counter (PC 1), sum or difference counts for right and left circularly polarized light were obtained in up-down counting. In the present system, sum spectra consists of points in ca. 5 cm^{-1} intervals, and their apparent features become more ambiguous than those in usual Raman spectra. The gate time can be spread about twice in the quasi-square modulation, when compared with the case using

sinusoidal one, and set at 0.7 msec, which was about 1/2 of the half cycle of the modulation frequency.

Figure 1 shows the R-CID spectra of (+)-α-pinene observed as a standard sample by using both sine (A) and quasi-square (B) wave modulations. As was expected, the counts of sum and difference spectra in (B) are larger by a factor of 2 than those in (A). Furthermore, since the instrument used previously had a divider of electronic circuits, the Δ_z spectrum in (A) was obtained by dividing electrically the difference signals by the sum signals which was the output from the second photon counter (PC 2, maximum count capacity; ca. 4000 counts). Therefore, the fluctuation of each point was observed because of the noise of PC 2. On the other hand, the Δ_z spectrum in (B) is obtained by dividing numerically the difference spectrum by the sum spectrum, both of which are the output from PC 1, with the data processor (JASCO Model DP 500). It can be seen that, in the latter case, the fluctuation disappears.

Figures 2-4 show the R-CID spectra in the ca. 700-1000 cm^{-1} region of (+)-2-butanol, (+)-2-pentanol, and (+)-2-octanol, respectively. In these figures the Δ_z spectra are omitted, since the band separations, which are clear in the difference spectra, become indistinguishable in the Δ_z spectra because of the large back ground scatterings, as the circumstances pointed out by Barron[3]. According to the Raman study for (+)-2-butanol by Berman and Mcketta[4], the band at 780 cm^{-1} is assigned to the CH_2 rocking mode, and the band at 910 cm^{-1} to the CH_3 rocking mode. One of the bands characteristic of sec-alcohols is also observed around 820 cm^{-1}, which arises from the symmetric stretching of the C_3O skeleton[5].

Comparing with the R-CID spectrum of (+)-2-butanol, it can be assumed that the CH_2 rocking bands are observed at 790 cm^{-1} for (+)-

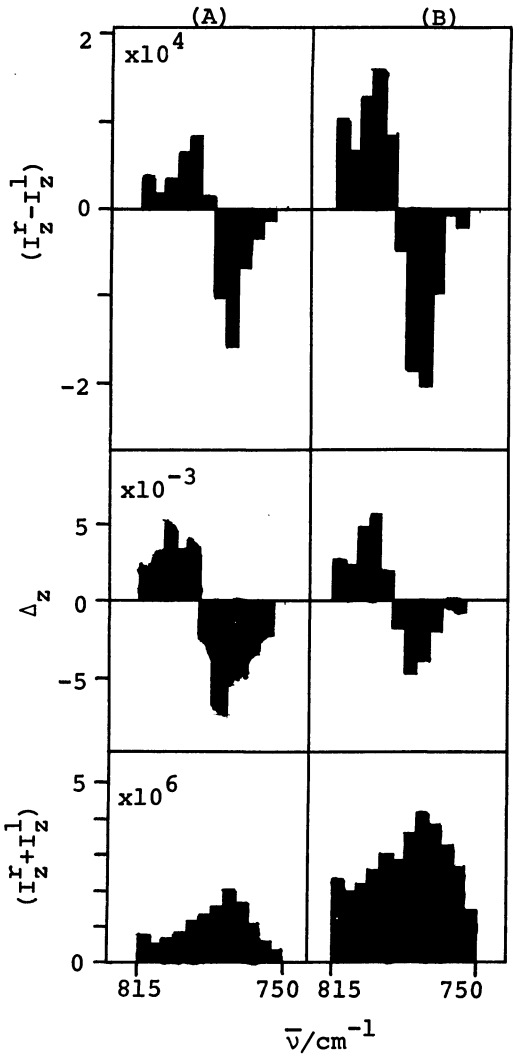

Fig.1 R-CID spectra of (+)-α-pinene
(A) sinusoidal modulation
(B) quasi-square modulation

2-pentanol and 800 cm^{-1} for (+)-2-octanol. Although the number of CH_2 groups increases for these compounds, these bands may be attributed to the CH_2 group adjacent to the asymmetric carbon atoms since the distinct R-CID signals with negative sign are observed. The relative intensity for this CH_2 rocking band in (+)-2-pentanol is rather small than in the others, but detailed interpretations of this problem cannot be made at present. The R-CID signals corresponding to the CH_3 rocking bands seem to be also observed at the wave numbers from 900 to 930 cm^{-1}, but with positive signs. However, it is difficult to regard these bands as a key band of sec-alcohol, because they are obscure in each Raman spectrum in order to be affected by the length of carbon chain and to differ considerably in their wave numbers.

On the other hand, the C_3O stretching bands characteristic of sec-alcohols, which have considerably strong intensities in each polarized Raman spectrum and are easily distinguished from others, are observed at the wave numbers from 820 to 840 cm^{-1} for these three compounds. Their R-CID signals have all the same sign. The absolute configurations of these compounds are all expressed as S in the (R,S) term system, and correlated with their negative R-CID signals. The C_3O stretching mode directly reflect the chirality of optically

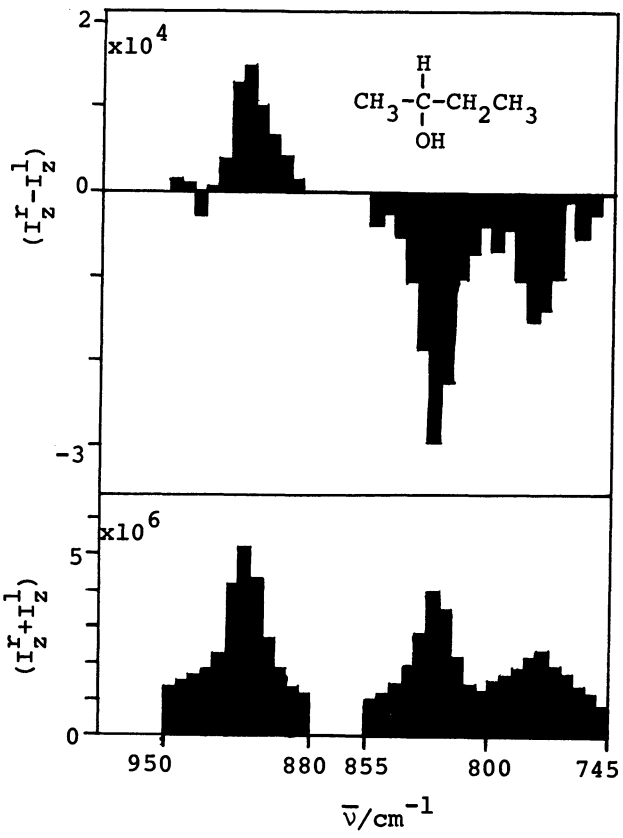

Fig.2 R-CID spectrum of (+)-2-butanol

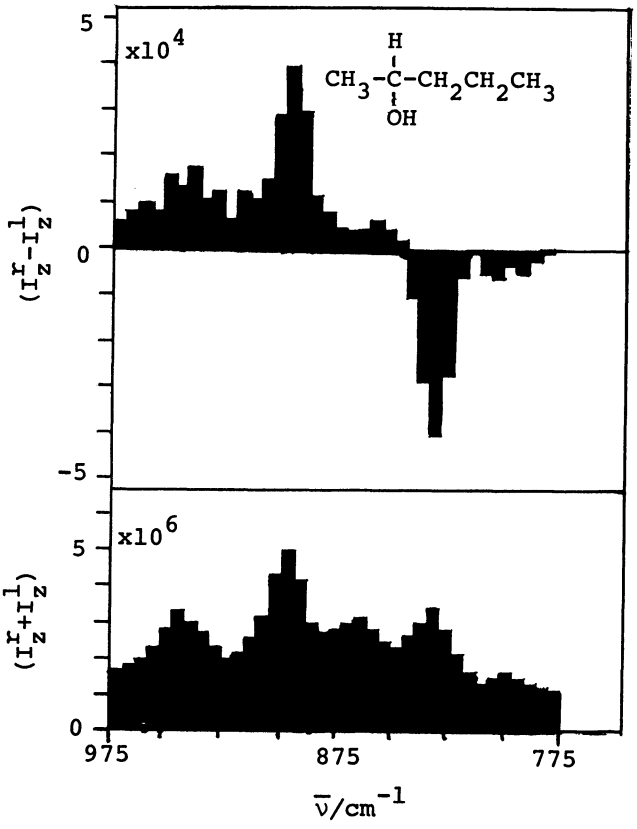

Fig.3 R-CID spectrum of (+)-2-pentanol

active sec-alcohols and can be distinguished easily in their Raman spectra. Thus, it may be concluded that the C_3O stretching band in the R-CID spectrum is regarded as the best indicator of the absolute configuration for sec-alcohols. In order to confirm the present results, the measurements for the compounds having the different configuration are desirable, and the examinations are now proceeding in our laboratory.

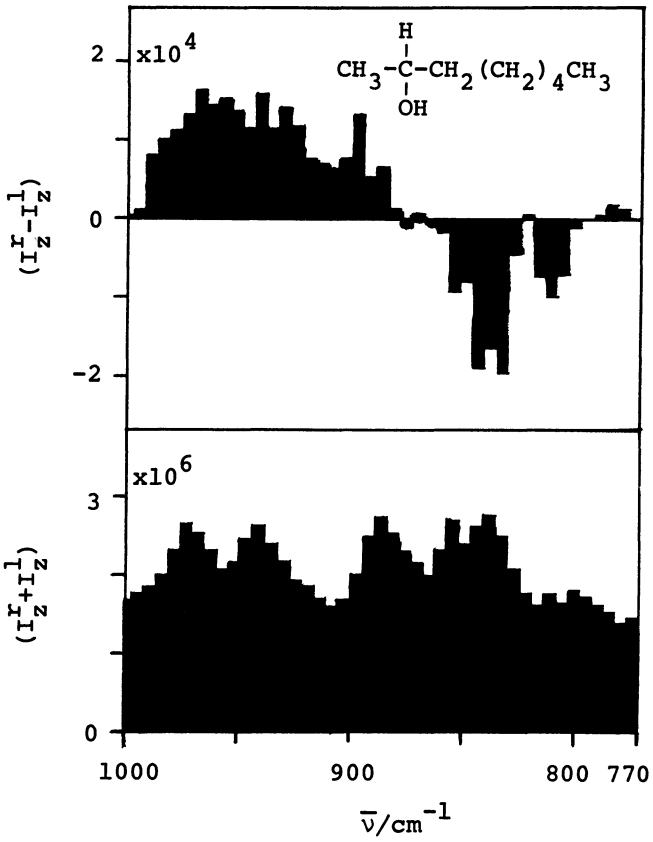

Fig.4 R-CID spectrum of (+)-2-octanol

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