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RAMAN CIRCULAR INTENSITY DIFFERENTIAL SPECTRA OF METHYL ORANGE INDUCED BY INCLUSION IN CYCLODEXTRIN

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Raman circular intensity differential spectra were measured for the aqueous dilute solution of methyl orange and α-cyclodextrin, making use of the resonance Raman effect. The obtained spectra were discussed in terms of the vibrational optical activity induced by the inclusion of methyl orange in α-cyclodextrin.

The measurement of vibrational optical activity is expected to have potential advantages for the molecular structural studies. It is due to the fact that it is applicable to chiral compounds having no UV or VIS absorption bands, and above all, it is based on the spectroscopic signals related directly to the details of molecular structures. Recently, for this purpose, Raman circular intensity differential (R-CID) spectroscopy[1)] has been developed and succeeded in the solution of stereochemical problems for some chiral compounds. At present, however, only a small number of examples of its applications can be found in literatures. Thus, it is significant for the development of the usefulness of this spectroscopy to increase the results of R-CID measurements. In the present note, we report a first experimental evidence of the vibrational optical activity induced in an achiral molecule placed in a chiral environment. We have attempted to measure the R-CID spectra of the inclusion compound of methyl orange (MO) with cyclodextrin (CD_x) and succeeded in obtaining the R-CID signals for the bands of MO.

The measurement arrangement is almost the same with the one described in the previous papers.[2,3)] The linearly polarized incident light (Ar^+ laser; 488.0 nm, 500 mW) is modulated to right and left circularly polarized light by a Pockels' cell (KDP, 370 Hz). By use of a synchronous photon counter, sum or difference counts for right (I_z^r) and left (I_z^l) circularly polarized light are obtained in up-down counting. The spectra consist of points in about 5 cm^{-1} intervals. The resolution of a monochromator is set at about 10 cm^{-1}. In the R-CID measurement, very careful adjustment of the optical elements is indispensable to minimize spurious signals (artifacts). The adjustment is carried out in such a way that the couplet signal of (+)-α-pinene in the 750-820 cm^{-1} region, which is regarded as a standard signal of R-CID, agrees both in the spectral pattern and Δ_z value ($\Delta_z=(I_z^r - I_z^l)/(I_z^r + I_z^l)$) with those in the literatures.[4)] In Fig.1 is shown this couplet signal obtained in the present study. The pattern of this couplet signal is similar to that reported, for example, by Barron[4)] and Δ_z values are about -3×10^{-3} for 770 cm^{-1} band and $+4 \times 10^{-3}$ for 790 cm^{-1} for the spectrum in Fig.1, while the corresponding values by Barron[4)] are about -2×10^{-3} and $+2 \times 10^{-3}$, respectively. At the present stage of R-CID spectroscopy, the above-mentioned data indicate that the Δ_z values obtained in our study agree well with those in the literature. As for the precision of measurements, the S/N ratios of our spectrum are comparable to or somewhat lower than those by Barron. From the above-mentioned examination, we considered that our measurement system has the accuracy and precision sufficient for carrying out the present experimental works. Moreover, since the R-CID spectra are based on the resonance Raman effect, the sample cell is rotated at 2500min^{-1}during the measurements.

In Fig.2 are shown the difference ($I_z^r - I_z^l$) spectrum and the depolarized Raman spectrum which corresponds to the sum ($I_z^r + I_z^l$) in the 1320-1480 cm^{-1} region. Δ_z values of significant signals in the difference spectrum are estimated to be in the order of 10^{-3}. This fact may indicate the validity of the R-CID signals shown in Fig.2. Furthermore, we adopted as the evidence of the validity of the signals the criterion that they have the sufficient reproducibility in the measurements of at least five times (In Fig.2, the signal marked with an asterisk has no reproducibility, thus,

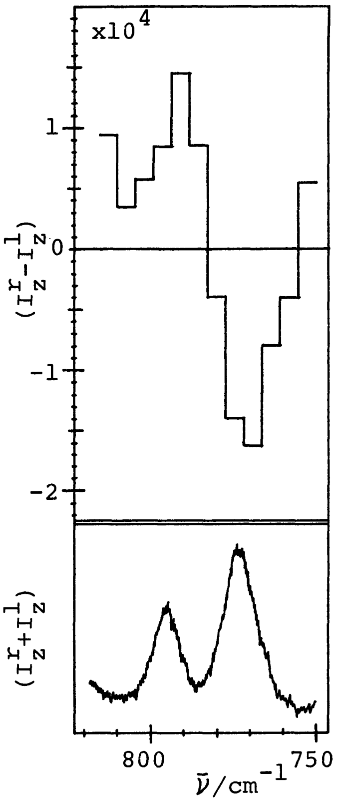

Fig.1 R-CID and depolarized Raman spectra of (+)-α-pinene inthe 750-820 cm^{-1} region.

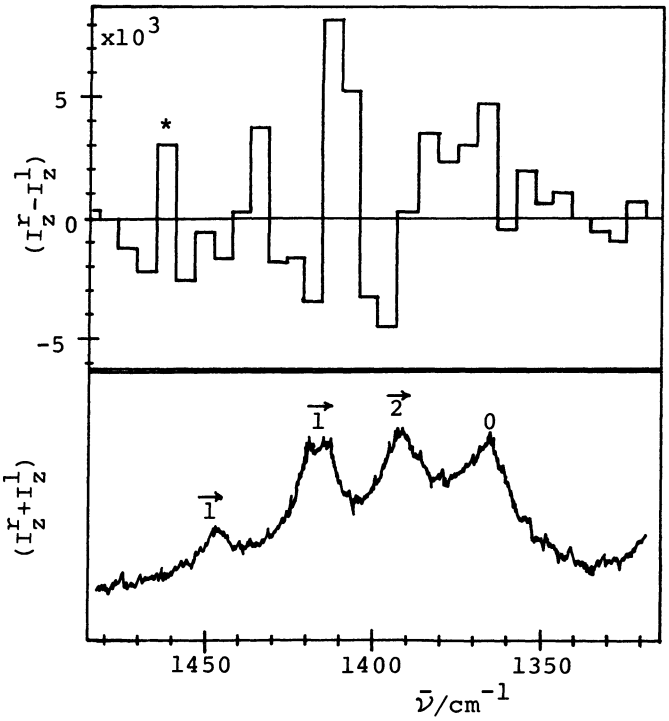

Fig.2 R-CID and depolarized Raman spectra of MO-α-CD$_x$ in the 1320-1480 cm^{-1} region.
concentration of MO:3.5x10^{-5} M,
concentration of α-CD$_x$:3.5x10^{-3} M.
for the sample at room temperature.

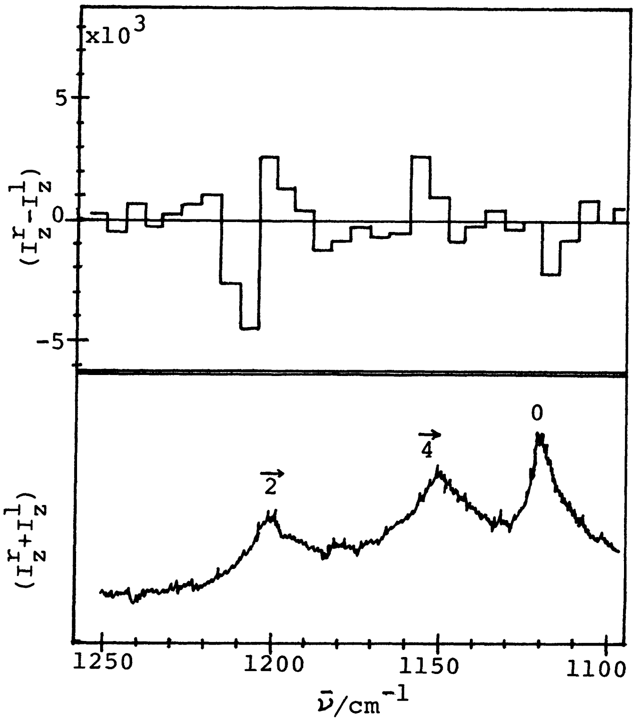

Fig.3 R-CID and depolarized Raman spectra of MO-α-CD$_x$ in the 1100-1250 cm^{-1} region.
concentration of MO:3.5x10^{-5} M,
concentration of α-CD$_x$:3.5x10^{-3} M.
for the sample at room temperature.

we have concluded it to be a noise.). In the R-CID spectrum in Fig.2, the double couplet between 1380 and 1430 cm^{-1} is especially noticeable. Machida et al.$^{5)}$ pointed out the strong coupling between the vibrations corresponding to the bands at 1393 and 1420 cm^{-1}. It is consistent with the fact that in the R-CID spectrum, the signals for these bands appear as a couplet. Moreover, the couplet signal centered at about 1415 cm^{-1} is also observed. This signal may come from the fact that the Raman band at 1420 cm^{-1} consists of two bands, which suggests the possibility of the coupling between another pair of two different vibrational modes. Under such an assumption, the double couplet in question can be satisfactorily explained.

Previously, we examined the Raman spectra of aqueous solutions of MO-CD$_x$ complex in terms of band shifts accompanied with the inclusion phenomena.$^{6)}$ The numbers and arrows in the Raman spectra in Figs.2 and 3 indicate the magnitudes (in cm^{-1}) and the directions of band shifts. From the comparisons of R-CID signals and band shifts, it has been made clear that the bands which give rather strong R-CID signals accompany distinct band shifts, and the ones which show no shift give no significant R-CID, or at most, relatively weak ones. However, the interesting fact is that the band exhibiting a large shift does not always correspond to a strong R-CID. Such an example is shown in Fig.3. As is seen from Fig.3, the R-CID signal corresponding to the Raman band at 1150 cm^{-1}, which exhibits the greatest band shift, is only a very weak one. This fact suggests the possibility that the R-CID may yield new information on the states of inclusion complexes in water.

The strong R-CID signals suggest that the moieties of MO molecule corresponding to the vibrations giving those signals are fixed in the strongly chiral field in the cavity of α-CD_x. On the other hand, the band shifts may occur as a result of various circumstances. That is, the changes of wavenumbers may be caused not only by the direct interaction between the vibrating moiety of the molecule and α-CD_x, but also by other factors. For example, they can be realized when MO molecule is fixed to α-CD_x at the part of the molecular structure other than the vibrating moieties. Under such an assumption, it is supposed from the results in Figs.2 and 3 that the N=N group (1420 cm^{-1}) and the benzene ring with SO_3^- group (1393 cm^{-1}) are fixed in the cavity close to the field with strong chirality, and the moiety from the benzene ring to the azo group (1150 cm^{-1}) is considered at least not to be fixed in the favorably dissymmetric configuration in the cavity. The above-mentioned image for the MO-α-CD_x complex in water is consistent with the structure of a MO-α-CD_x solid sample, determined with X-ray diffraction method by Harata.[7] At present, however, the structural considerations such as described above are only speculations. Further investigations for various sample systems, including the studies by other methods, are required to obtain the more definite conclusion. The experimental study from such viewpoint is now proceeding in our laboratory.

References

1) L.D.Barron, Adv. Infrared Raman Spectrosc., 4, 271(1978).
2) H.Waki, S.Higuchi, S.Tanaka, and N.Sakayanagi, Bunko Kenkyu, 29, 381(1980).
3) H.Waki, S.Higuchi, and S.Tanaka, Chem. Lett., 1981, 147.
4) For example, L.D.Barron, Acc. Chem. Res., 13, 90(1980).
5) K.Machida, H.Lee, and A.Kuwai, J. Raman Spectrosc., 9, 198(1980).
6) H.Sato, S.Higuchi, N.Teramae, and S.Tanaka, Chem. Lett., 1979, 299.
7) K.Harata, Bull. Chem. Soc. Jpn., 49, 1493(1976).

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