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NEUTRON SPECTROSCOPY ON  
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ポリオキシメチレンの中性子分光

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中性子の非弾性散乱で配向したポリオキシメチレン結晶中での水素の振動数分布の軸方向に垂直な成分  $G_{perp}$  と平行な成分  $G_{para}$  を測定した。両者の強度比は北川，宮沢の計算と定理的に合っており，又スペクトルに出ているいくつかのピークも計算したスペクトルと大体合せることができる。

Neutron Spectroscopy on Polyoxymethylene

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The amplitude-weighted frequency distributions,  $G_{\text{perp}}$  and  $G_{\text{para}}$  of hydrogen atoms, in which the vibrational displacements of hydrogen atoms are perpendicular and parallel respectively to the chain axis in uniaxially oriented POM crystals, have been obtained by neutron inelastic scattering. Intensity ratio  $G_{\text{perp}}/G_{\text{para}}$  agrees qualitatively with the calculation of Kitagawa and Miyazawa. Several peaks observed in the spectra can be assigned possibly to singularities in the calculated frequency spectra.

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目 次 な し

## Neutron Spectroscopy on Polyoxymethylene

A polyoxymethylene (POM) molecule in the crystal lattice of the trigonal system has a helical conformation which contains nine monomer units of  $(-\text{CH}_2\text{O}-)$  and five turns in a fiber identity period. The molecular vibrations of POM have been investigated by the infrared absorption, Raman and neutron scattering measurements. The infrared spectra of POM were studied by Tadokoro et al.<sup>(1)</sup> who reported  $235\text{ cm}^{-1}$  and  $455\text{ cm}^{-1}$  lines in the low frequency region. Recently Sugeta et al.<sup>(2)</sup> observed a Raman line at  $64\text{ cm}^{-1}$  which was not reported previously. Trevino and Boutin<sup>(3)</sup> observed peaks at  $80\text{ cm}^{-1}$ ,  $180\text{ cm}^{-1}$  and  $430\text{ cm}^{-1}$  by neutron scattering. The neutron measurements of Trevino and LaGarde<sup>(4)</sup> also show peak at  $94\text{ cm}^{-1}$  in the low frequency region and those at  $462\text{ cm}^{-1}$ ,  $556\text{ cm}^{-1}$  and  $615\text{ cm}^{-1}$  in the high frequency region. The theoretical calculations of the normal vibrations of POM have been carried out to make the band assignments in some of these works. More advanced calculations of the lattice vibrations of POM crystals with the intra- and intermolecular force field by Kitagawa and Miyazawa<sup>(5)</sup> have shown that, in the frequency region below  $700\text{ cm}^{-1}$ , the amplitude-weighted frequency distributions of hydrogen atoms, in which the vibrational displacements of hydrogen atoms are parallel to the chain axis, is smaller than that of the displacements perpendicular to the chain axis, as shown in Fig. 2 (b). This result is in contrast with the neutron scattering spectra of Trevino and Boutin<sup>(3)</sup> and Trevino and LaGarde<sup>(4)</sup>.

In the present experiments the spectra of inelastic scattering of thermal neutrons from uniaxially oriented POM crystals have been obtained by the pulsed neutron spectrometer installed at JRR-2 reactor. The POM crystals prepared by the radiation induced polymerization of tetraoxane single crystals<sup>(6)</sup> were supplied from Dr. T. Kitagawa, Osaka University. The samples used in this work are thin plates with an effective thickness of about 2 mm, the chain axes are arranged along the surfaces of the plates. The time-of-flight method was used to analyze the energy of the scattered neutrons, which gained energy upon scattering through an angle of  $90^\circ$ . The energy of the incident neutrons was 8.1 mev. In the measurements we set up the crystal orientation so that the scattering vector was alternately parallel and perpendicular to the chain direction. The vibrational modes where the atomic displacements are perpendicular to the chain axis do not contribute to the scattering when the scattering vector is parallel to the chain axis. Similarly, the vibrational modes where the atomic displacements are parallel to the chain axis do not contribute to the scattering when the scattering vector is perpendicular to the chain axis. The observed spectra were corrected for background intensities, counter efficiency, scattering by air in the flight path and absorption in the samples. The intensities were then normalized to unity at the elastic peaks. The amplitude-weighted frequency distributions were obtained from the normalized data in the incoherent approximations. Since the cross section of a hydrogen atom is much larger than

that of a carbon or oxygen atom and almost incoherent, the obtained distributions reflect the vibrations of hydrogen atoms parallel or perpendicular to the chain axis.

The observed time-of-flight spectra for both parallel and perpendicular settings are shown in Fig. 1. The amplitude-weighted frequency distributions,  $G_{\text{para}}$  and  $G_{\text{perp}}$  obtained from data in Fig. 1 are shown in Fig. 2. It is noted in these figures that in the energy range below about  $200 \text{ cm}^{-1}$  the intensities for parallel setting are appreciably less than those for the perpendicular setting. This fact agrees with the results of the corresponding calculations by Kitagawa and Miyazawa<sup>(5)</sup>, in contrast with the neutron scattering spectra of Trevino et al.<sup>(3,4)</sup>

The broad peaks around  $450 \text{ cm}^{-1}$  should be compared with the peaks at  $480 \text{ cm}^{-1}$  in the frequency distributions calculated by Kitagawa and Miyazawa<sup>(5)</sup>, and the band of  $455 \text{ cm}^{-1}$  from the infrared measurements<sup>(1)</sup>, which is the optical active mode due to the C-O-C bending vibrations. The spectra in the low frequency region below about  $200 \text{ cm}^{-1}$  are expected to be sensitive to intermolecular parameters as well as intramolecular ones. In that energy region, the well defined peaks are observed at  $90 \text{ cm}^{-1}$  both for  $G_{\text{perp}}$  and  $G_{\text{para}}$  distributions, and at  $130 \text{ cm}^{-1}$  for  $G_{\text{perp}}$ , and  $120 \text{ cm}^{-1}$  for  $G_{\text{para}}$ . These observed peaks should be compared with the peaks at  $70 \text{ cm}^{-1}$  and  $120 \text{ cm}^{-1}$  obtained from the Kitagawa and Miyazawa's crystal structure model<sup>(5)</sup> with the intermolecular potentials determined by a rather simplified assumption.



The calculation of Kitagawa and Miyazawa has shown a sharp peak at  $160 \text{ cm}^{-1}$  for  $G_{\text{perp}}$ , weak peaks at  $200 \text{ cm}^{-1}$  and prominent peaks at  $235 \text{ cm}^{-1}$  both for  $G_{\text{perp}}$  and  $G_{\text{para}}$  distributions, as shown in Fig. 2 (b). Although not well resolved, the peaks are also observed around  $160 \text{ cm}^{-1}$  and  $200 \text{ cm}^{-1}$  for both distributions. Though it is not easy to identify the observed peaks and the calculated ones, it seems that there are peaks which correspond to the calculated ones mentioned above. The intensities around  $300 \text{ cm}^{-1}$  are probably due to the combinations of multiple phonon scattering effects.

It can be concluded that the intensity ratio  $G_{\text{perp}}/G_{\text{para}}$  agrees with that obtained by Kitagawa and Miyazawa and the crystal structure or the intermolecular potentials assumed in their work are valid for phonon distribution in the low frequency region.

The authors would like to thank Dr. T. Kitagawa and Prof. T. Miyazawa for kindly providing the POM samples and for their valuable comments, and their thanks are also to Dr. Y. Hamaguchi for his continuous interest and encouragement.

## References

- (1) H. Tadokoro, M. Kobayashi, Y. Kawaguchi, A. Kobayashi and S. Murahashi, J. Chem. Phys., 38, 703 (1963).
- (2) H. Sugeta, T. Miyazawa and T. Kajiura, J. Polymer Sci., B, 7, 251 (1969).
- (3) S. Trevino and H. Boutin, J. Chem. Phys., 45, 2700 (1966).
- (4) S. Trevino and V. E. LaGarde, "Molecular Dynamics and Structure of Solid", National Bureau of Standards Special Publication 301, p.533 (1969).
- (5) T. Kitagawa and T. Miyazawa, SPSJ 20th Symposium on Macromolecules, 631 (1971), (in Japanese).
- (6) T. Kitagawa, A. Tanaka and M. Nishii, J. Polymer Sci., B, 9, 579 (1971).

## Figure Captions

- Fig. 1 The observed time-of-flight spectra both for the parallel and perpendicular settings in the scattering conditions.
- Fig. 2 (a) The amplitude-weighted frequency distributions of POM derived from the time-of-flight spectra of the scattered neutrons for the oriented samples.  
(b) The calculated frequency distributions after Kitagawa and Miyazawa<sup>(5)</sup>.

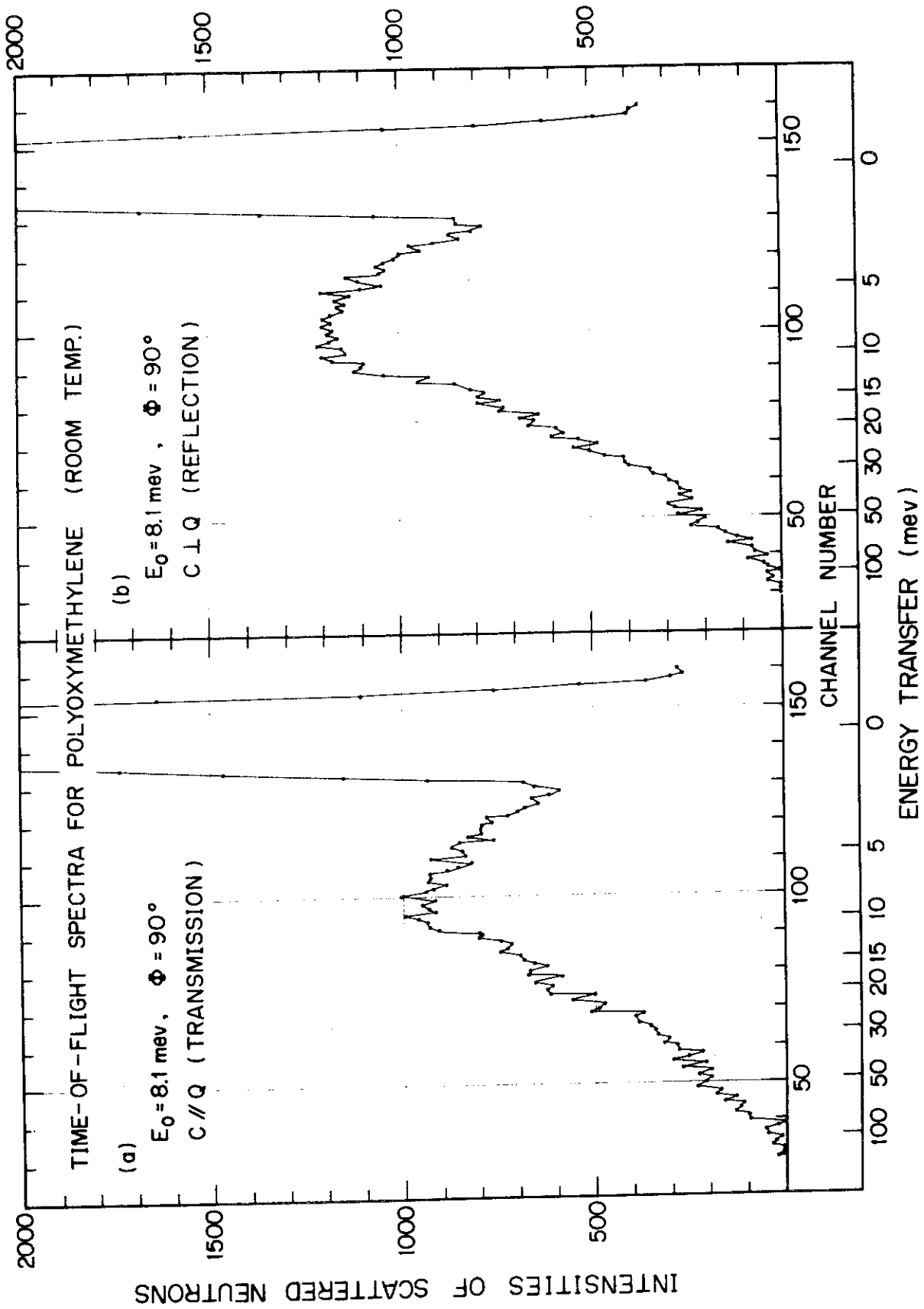


Fig. 1

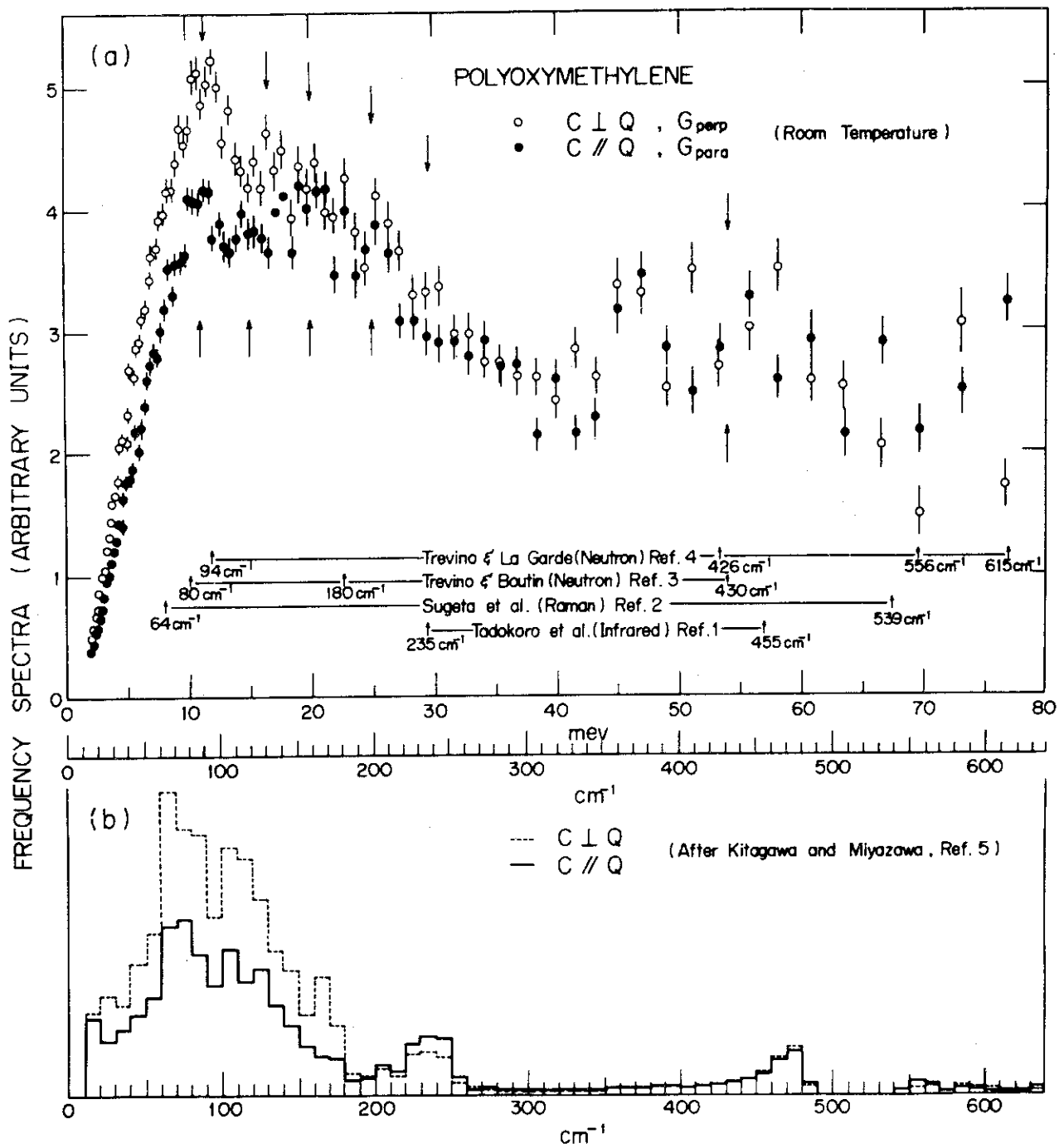


Fig. 2