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Far Infrared Spectra of Potassium Oxalate Monohydrate and Its Deutero Analog

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The far infrared spectra of potassium oxalate monohydrate and its deutero analog in their crystalline state were measured. Assignment of the infrared absorption bands was made on the basis of frequency shift associated with deuterium substitution of hydrogen atoms in water of crystallization and also on the basis of comparison of neutron scattering spectra of the compounds with the infrared spectra.

Molecules of the water of crystallization form various types of bondings with surrounding atoms and ions through hydrogen bond and lone-pair coordination. Chidambaram *et al.* classified molecules of the water of crystallization on the basis of their coordination to ions and electron accepter groups.[1] In the present study, potassium oxalate monohydrate (p.o.m.), which belongs to type A,[1] was chosen as a representative of crystals containing molecules of the water of crystallization whose lone pairs are not specifically directed to any of the surrounding atoms and ions. A spectroscopic investigation in the region of 4000—60 cm^{-1} was carried out. The IR spectra of p.o.m. and its deutero analog (*d*-p.o.m.) have been observed by several investigators.[2-4] In the lower frequency region, measurement of Raman spectra of metal oxalate in aqueous solution was made.[5] However, no measurement of far IR spectra has been reported so far. In the present investigation, far IR spectra of p.o.m. and *d*-p.o.m. were measured in order to obtain optically active lattice vibration frequencies and to assign several IR absorption bands.

Experimental

The far IR spectra of p.o.m. in Nujol mull were measured in the region of 400—60 cm^{-1} with a Hitachi FIS-3 Far IR Spectrometer. Sample for the measurement was obtained by recrystallization of a special grade reagent p.o.m. of Koso Chemical Co., Ltd. from aqueous solution. The measurement was made for the sample in Nujol mull, sealed in a thin polyethylene sack. *d*-p.o.m. was prepared by vacuum distillation of p.o.m.-heavy water solution and vacuum drying of the residue. The far IR spectra of the Nujol mull were measured. The far IR spectra are shown in Figs. 1 and 2. IR spectra of the same samples in the region of 4000—400 cm^{-1} were measured with a Perkin-Elmer 521 Spectrophotometer and a Hitachi EPI-L Spectrophotometer. The spectra are shown in Figs. 3 and 4.

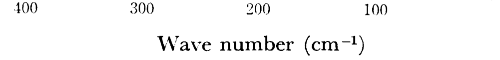

Fig. 1. Far infrared spectra of potassium oxalate monohydrate crystal in Nujol mull.

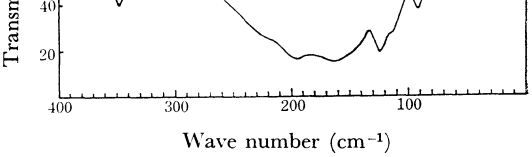

Fig. 2. Far infrared spectra of deuterated potassium oxalate monohydrate crystal in Nujol mull.

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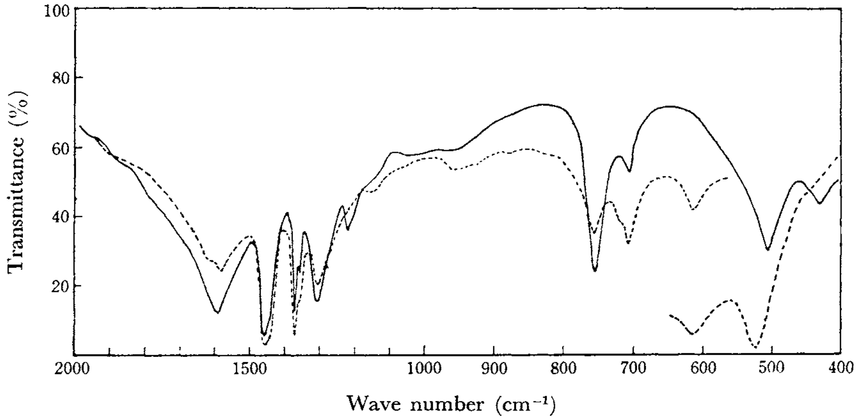

Fig. 3. Infrared spectra of deuterated potassium oxalate monohydrate crystal in Nujol mull (solid line) and potassium oxalate monohydrate crystal in Nujol mull (dotted line).

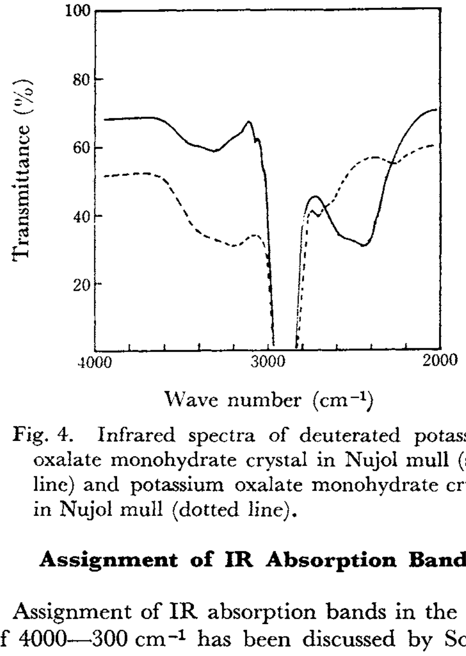

Fig. 4. Infrared spectra of deuterated potassium oxalate monohydrate crystal in Nujol mull (solid line) and potassium oxalate monohydrate crystal in Nujol mull (dotted line).

Assignment of IR Absorption Bands

Assignment of IR absorption bands in the region of 4000—300 cm^{-1} has been discussed by Schmelz *et al.*[3] and also by Pedersen.[4] However, several new experimental facts found in the present study suggest the following assignment of some IR absorption bands.

As the relative intensities of O–H and O–D stretching bands of the residue show that deuteration was carried out almost perfectly, IR spectra of the residue may be interpreted as those of deuterate. (see Figs. 2, 3 and 4).

Schmelz *et al.* and Pedersen did not point out the presence of a shoulder band at the higher frequency side of the strong band at 1580 cm^{-1} of p.o.m.[3,4] In their studies, IR spectra were recorded with a spectrometer equipped with prism optics. In the present study, IR spectra were obtained with grating spectrometers having higher resolving power. From the result the presence of a shoulder band at 1608 cm^{-1} and the shift of shoulder band to lower frequency on deuteration were confirmed. A band corresponding to the shoulder band appears at 1225 cm^{-1} in the spectra of *d*-p.o.m. Therefore, the two bands at 1608 cm^{-1} and 1225 cm^{-1} are assigned to H_2O bending and D_2O bending vibration, respectively. Schmelz *et al.* and Pedersen found a shift of frequency of the band at 710 cm^{-1} associated with deuteration.[3,4] In accordance with their results, the band of p.o.m. at 718 cm^{-1} shifts to lower frequency on deuteration as shown in Fig. 3, and the corresponding band appears at 505 cm^{-1} for *d*-p.o.m. It was also found that the band of p.o.m. at 614 cm^{-1} shifts to lower frequency on deuteration and two bands appear at 432 cm^{-1} and 358 cm^{-1} for *d*-p.o.m. as shown in Figs. 2 and 3. The results along with the observed neutron scattering peaks, 700 cm^{-1}, 605 cm^{-1}, 500 cm^{-1} (p.o.m.) and 505 cm^{-1}, 450

TABLE 1. OBSERVED FREQUENCIES (cm^{-1})

IR		Neutron scattering*	
$K_2C_2O_4\cdot H_2O$	$K_2C_2O_4\cdot D_2O$	$K_2C_2O_4\cdot H_2O$	$K_2C_2O_4\cdot D_2O$
718	505	700	505
614	432	605	450
524	358	500	370
351	348		
210	215		
190	195	195	190
160	165		
129	125		136
115	115	110	
92	93	95	94
56	54		

* Taken from Ref. 6

cm^{-1}, 370 cm^{-1} (*d*-p.o.m.),[6] confirm assignment of the IR absorption bands at 718 cm^{-1}, 614 cm^{-1}, 524 cm^{-1} (p.o.m.) and the bands at 505 cm^{-1}, 432 cm^{-1}, 358 cm^{-1} (*d*-p.o.m.) to the rotational lattice vibrations primarily associated with molecules of the water of crystallization and with those of the heavy water of crystallization, respectively. This assignment is consistent with the fact that the IR absorption bands due to molecules of the water of crystallization and of the heavy water of crystallization molecules were observed in the region of 900—300 cm^{-1} in the case of aquo complexes.[7] No shift of frequency of the band at 524 cm^{-1} (p.o.m.) on deuteration may be explained by overlapping of CO_2 wagging band. The band at 710 cm^{-1} (p.o.m. and *d*-p.o.m.) is considered to be due to Nujol.

Far IR absorption bands in the region of 250—60 cm^{-1} (Figs. 1 and 2) may be due to translational lattice vibrations. Assignment of these bands will have to be discussed on the basis of calculation of lattice vibrations and other experimental data. In this paper, only the correspondence of frequencies of IR absorption bands with those of neutron scattering peaks[6] is pointed out for the bands at 190 cm^{-1}, 115 cm^{-1}, 92 cm^{-1} (p.o.m.) and 195 cm^{-1}, 125 cm^{-1}, 115 cm^{-1}, 93 cm^{-1} (*d*-p.o.m.) as shown in Table 1.

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