

65. *The Vibrational Spectra of Crystalline Dipotassium and Diammonium Hydrogen Phosphate, with Partial Assignments.*

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The infrared absorption spectra of crystalline dipotassium and diammonium hydrogen phosphate have been recorded from Nujol and Fluorube mulls and, in the case of diammonium hydrogen phosphate, from the dispersion in a thallos chloride pressed disc. Absorptions not previously observed have been recorded and partial assignments made on the assumption that the space group, C_{2h}^5 , of diammonium hydrogen phosphate is applicable to the dipotassium salt.

THE crystal structure of dipotassium hydrogen phosphate has not been determined and hence no complete analysis of the vibrational spectrum has been made. Smith *et al.*¹ have determined the space group of diammonium hydrogen phosphate, C_{2h}^5 , and the assumption is made here that this will be applicable to the potassium salt.

Ryskin and Stavitskaya² recorded the infrared spectrum of crystalline dipotassium hydrogen phosphate and noted that some band doublets occurred, but they neglected the symmetry of the crystal field; the present results agree well with those of Ryskin and Stavitskaya and additional band splitting is noted in the regions of ν_3 and ν_4 .

Ignoring the slight asymmetry caused by the O-H bond being non-colinear with the adjacent P-O bond, the free HPO_4^{2-} ion is of symmetry point group C_{3v} . This hexatomic ion has 18 degrees of freedom. Subtraction of the 6 degrees of translational and rotational motion leaves 12 degrees of vibrational freedom. Of these, 9 must be associated with the penta-atomic grouping, 3 will be doubly degenerate, and 3 nondegenerate. The remaining 3 will be associated with stretching, bending, and twisting motions of the O-H group. All are Raman- and infrared-active.

The Bravais unit cell is here identical to the crystallographic unit cell and contains four molecules. Halford's table³ shows that the site point symmetry for the space group C_{2h}^5 is C_i . There are 4 distinct sets of sites with 2 equivalent sites per set. Consequently, all degeneracy for the vibrations of the HPO_4^{2-} ion will be removed. Furthermore, resonance coupling may be expected between the 4 oscillators of the unit cell to give 18 vibrations which are symmetric, and 18 which are asymmetric, to the two-fold axis. Because there is a centre of symmetry, the rule of mutual exclusion applies and 18 of the 36 vibrations will be Raman- and eighteen infrared-active. The Table lists frequencies and probable assignments, taking into consideration the work of Ryskin and Stavitskaya.² The vibration $\nu_1'' a_1$, for example, could be split because of intermolecular coupling between phosphate ions. The crystal symmetry being considered, these vibrations would be two of symmetry species A_g and two of symmetry species A_u , Raman- and infrared-active, respectively.

Precise assignments of the component species of the formally degenerate vibrations cannot be made in the absence of detailed infrared and Raman polarisation data for single crystals.

The phosphate absorptions of diammonium hydrogen phosphate show similar behaviour, but here, hydrogen-bond formation between the ammonium ions and the hydrogen phosphate anions is indicated because the highest frequency P-O stretching absorption is *ca.* 42 cm^{-1} lower than the corresponding absorption in the potassium salt. The shifting of frequencies by hydrogen bonding may explain the apparent departure from the rule of mutual exclusion. It is not to be expected that hydrogen-bond formation will shift Raman and infrared frequencies by an identical amount; consequently, accidental

¹ Smith, Lehr, and Brown, *Acta Cryst.*, 1957, **10**, 709.

² Ryskin and Stavitskaya, *Optics and Spectroscopy*, 1960, **8**, 320.

³ Halford, *J. Chem. Phys.*, 1946, **14**, 8.

Data (in cm.^{-1}) and probable assignments for the infrared (i.r.) and Raman spectra of dipotassium and diammonium hydrogen phosphate. Headings: 1, i.r. spectrum (mull); 2, i.r. spectrum (TlCl disc); 3 Raman spectrum (crystalline solid).⁴

Ion or group	I.r. assignments	K_2HPO_4	$(\text{NH}_4)_2\text{HPO}_4$			Raman symmetry species
			1	2	3	
PO_4	$\nu_1'' A_u$	{ 836s 850s-vs	860m 902m	858w-m 903m	905	A_g
	$\nu_2'' A_u$	{ 428w 444w, sh	< 400?	< 400?	380s	A_g
	$\nu_3'' A_u, B_u, B_u$	{ 955s 980s 1069vs 1086vs 1125vs	959s 1030s 1057vs 1068vs 1083vs	958s 1030s ? 1068vs 1086vs	956vs 1002m 1059w 1068m	A_g, B_g, B_g
OH	$\delta(\text{OH})$	{ 517s 537vs 544vs	537m-s 558m-s	531m-s 557s	526pol.	A_g
	$\nu(\text{OH})$	{ 1281w 1300w 2500m	1201w 1213w ca. 2200w-m	1200w 1213w 2230w-m	1410m-s sharp 1412w	?
NH_4	$\nu_4'' A_u, B_u, B_u$	{	1417s 1464vs	1417m-s 1465s-vs 1478s-vs	1412w	
	$\nu_2'' A_u, B_u$ or $\nu_4'' + \nu_6''$	{	1524m-s 1705w-m inf. 1722m	1518m-s 1676vw? 1705w, inf. 1717w-m	1680vw 1701w	A_g, B_g or $\nu_4'' + \nu_6''$

agreement between the two spectra may occur in some regions. The O-H deformation vibrations, according to Ryskin and Stavitskaya,² appear in the region 1200–1300 cm.^{-1} ; in the present work, these occur at 1281 and 1300 cm.^{-1} for the dipotassium salt and at 1201 and 1213 cm.^{-1} for the diammonium salt. It is reported² that these bands disappear on deuteration, in favour of a single new absorption at 940 cm.^{-1} in dipotassium deuterium phosphate. However, the possibility exists that a second O-D absorption is masked by strong absorption at 940 cm.^{-1} in this salt.

Assignment of the $\delta(\text{OH})$ vibrations to the above region means that the Raman frequency at 1059 cm.^{-1} , assigned to a $\delta(\text{OH})$ vibration,⁴ can now be assigned to one of the ν_3'' components of the penta-atomic PO_4 group. The OH twisting frequency will then be the 400 cm.^{-1} absorption, associated⁴ with an OH vibration. OH stretching frequencies occur at 2500 cm.^{-1} , in the dipotassium salt, and at 2200 cm.^{-1} , in the diammonium salt, as broad absorptions, but Ryskin and Stavitskaya² associate a band near 2940 cm.^{-1} and a very broad absorption in the 1950 cm.^{-1} region with $\nu(\text{OH})$. Hydrogen bonding undoubtedly complicates matters.

The ammonium ions of diammonium hydrogen phosphate give rise to the appropriate number of infrared bands for the crystal site symmetry C_i , but from the Nujol no further resolution of bands occurs. However, dispersion of this diammonium salt in a thallos chloride pressed disc⁵ gives a much improved spectrum showing five bands in the ammonium ion ν_3'' region. Displacement of ammonium ions by thallos ions in the lattice of the diammonium salt is not indicated, because the frequencies of the phosphate absorptions are identical with those of the crystalline diammonium salt. In addition, thallos phosphate dispersed in thallos chloride absorbs strongly at 900, 938, and 992 cm.^{-1} . There is some evidence that grinding for more than 30 min., when preparing the disc, gives rise to some decomposition.

⁴ Taurel and Delain, *Compt. rend.*, 1958, **246**, 260.

⁵ Thompson, *J.*, 1963, 998.

EXPERIMENTAL

Spectra were recorded from Nujol and Fluorube mulls on polyethylene and polytetrafluoroethylene films, respectively. Thallous chloride discs were prepared as described in a previous paper.⁵ The infrared spectrophotometer was a Unicam S.P. 100 instrument fitted with sodium chloride and potassium bromide prisms; it was calibrated with polystyrene and water vapour.

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