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Vibrational study of TIH_2AsO_4, TIH_2PO_4 and their deuterated analogues

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The Raman and infrared spectra of polycrystalline samples TIH_2AsO_4, TID_2AsO_4, TIH_2PO_4 and TID_2PO_4 have been investigated at 300 K in the frequency ranges 0 to 4000 and 200 to 4000 cm^{-1} respectively. The assignment of lattice, internal, and OH group vibrations has been approximated in terms of symmetry species. Although all the vibrations follow more or less the space group symmetry, the internal vibrations do not completely fulfill the requirements of the symmetry rule. The isotope effect was observed prominently on both compounds in Raman and infrared spectra. An attempt has been made to assign and explain the results.

1. Introduction

The KDP family is an extensively studied group [1]. One of the most widely used experimental techniques of study for both lattice and phase transition dynamics in these materials is inelastic light scattering [2, 3]. Extensive studies of Raman spectra of KDP-type compounds have been reported [2–9], but very little is known about TIH_2PO_4 (TDP), TIH_2AsO_4 (TDA) and their deuterated analogues (DTDP, DTDA) which may be regarded as the heaviest of the homologous series of alkali dihydrogen phosphates. The neutron diffraction study of TDP [10] shows that the high-temperature phase is centrosymmetric with a space group $P2_1/a$. The room-temperature X-ray diffraction studies of DTDP, DTDA and TDA [11–13] show that the heavy atom structures are also centrosymmetric with a space group $P2_1/c$. The Raman scattering studies of TDP has been reported [14] and confirmed that the compound has a slightly discontinuous phase transition at 230 K. Because no further literature on TDA, TDP, DTDA and DTDP was available, it was thought interesting to study the Raman and infrared spectra of the compounds. As a part of our systematic study of thallium(I) compounds of the KDP-family, we report here the vibrational spectra of TDA, TDP and their deuterated compounds to examine the symmetry and isotopic effect.

2. Experimental details

The TDP/TDA compounds were synthesized by the reaction

$$Tl_2CO_3 + 2H_3PO_4/H_3AsO_4 \rightarrow 2TIH_2PO_4/TIH_2AsO_4 + H_2O + CO_2$$

and their single crystals were grown from their aqueous solution by the slow evaporation method at room temperature. Needle-shaped transparent single crystals were grown. For their deuterated analogues, DTDP and DTDA, a similar procedure was followed at room temperature. To obtain a high deuteration level the compounds were repeatedly recrystallized by the same slow evaporation technique. The identity of the compound was confirmed by X-ray studies and the deuteration level was estimated by NMR studies and found to be 98%.

Raman spectra of TDA, DTDA, TDP and DTDP were recorded on a laser Raman spectrometer, model Cary-82 in the frequency range 0 to 4000 cm^{-1}. A 514.5 nm 200 mW Spectra-Physics argon-ion laser was used as the exciting source with a photon counting detector. Infrared spectra were studied using a Perkin-Elmer-598 spectrophotometer with the KBr pellet technique in the frequency range 200 to 4000 cm^{-1}.

3. Results and discussion

TIH_2AsO_4 and TIH_2PO_4 crystallize in the space group C_{2h}^5 ($P2_1/c$), and the factor group is therefore C_{2h}. All the heavy atoms are in general positions C_1 and are therefore invariant to the identity operation of the factor group. In order to determine the distribution of modes between types, we need to know the characters of the reducible representation for the total number of modes and also for acoustic, translational and rotational modes. The character table for the group C_{2h} is given in Table I. The table shows that in this centrosymmetric group, g-modes are Raman active and u-modes are infrared active.

There are four formula units per unit cell of both TDA and TDP, which gives splitting of each component of each internal fundamental into two infrared active ($A_u + B_u$) and two Raman active ($A_g + B_g$) components generating 2, 4, 6 and 6 lines for ν_1, ν_2, ν_3 and ν_4 frequencies, respectively, in each effect. It has been noticed [15] that all the active modes described in the correlation scheme are rarely observed in practice,

TABLE I Character table for the group C_{2h}

	I	C_2	σ_h	i	
A_g	1	1	1	1	α_{xx}, α_{yy}, α_{zz}; R_z
A_u	1	1	−1	−1	T_z
B_g	1	−1	−1	1	α_{yz}, α_{zx}; R_x, R_y
B_u	1	−1	1	−1	T_x, T_y

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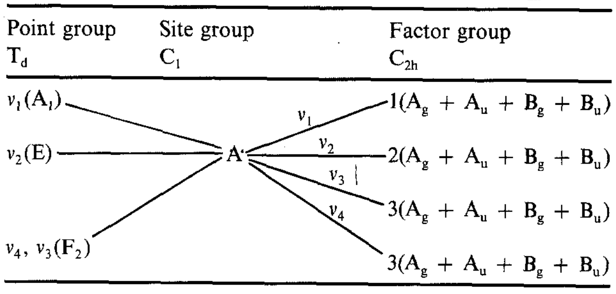
TABLE II Correlation diagram for AsO_4 or PO_4 in C_{2h}



particularly under the normal conditions of examining a polycrystalline sample at room temperature. The interactions between the molecules are, of course, very weak compared to those within molecules.

The isolated AsO_4^{3-} or PO_4^{3-} ions belong to the point group T_d, but in TDA and TDP, the symmetry of these ions reduced to C_1. In order to facilitate the analysis of the vibrational behaviour of the species investigated, Table II presents the complete correlation diagram between the point group, the site group and the factor group. It can be seen that because of the symmetry reduction from T_d to C_1, total removal of the degeneracies and total activation of all infrared bands occurs. Additionally, as a consequence of the coupling possibilities, all the active bands can further split under the factor group symmetry. The factor group analysis leads to the optional vibrations

$$\Gamma_T = 18A_g + 18B_g + 17A_u + 16B_u$$

Further, some other bands are also included here because of the OH group vibrations in these compounds.

All the active internal vibrations of TDA, TDP and their deuterated crystals can be described in terms of group vibrations as bending, stretching and OH group motions. The Raman spectra of tetrahedral AsO_4^{3-} oxoanions in solution gives their bands at $\nu_1 = 810$, $\nu_2 = 342$, $\nu_3 = 810$ and $\nu_4 = 398\,cm^{-1}$ and similarly for the PO_4^{3-} ions, the bands are at $\nu_1 = 938$, $\nu_2 = 420$, $\nu_3 = 1017$ and $\nu_4 = 567\,cm^{-1}$. According to the frequencies of the vibrations of the free ions, the internal modes in TDA and TDP have been assigned. The assignments and vibrational modes for TDA and TDP are given in Tables III and IV respectively. The tables show that the frequencies are between 300 and $600\,cm^{-1}$ for bending, 600 and $1000\,cm^{-1}$ ($1200\,cm^{-1}$ for TDP) for stretching and 1000 and $3000\,cm^{-1}$ for OH group vibrations. We shall examine these regions of TDA, TDP and their deuterated polycrystalline samples. Raman and infrared spectra of these are given in Figs 1 to 4.

In the bending region, the motions may be derived from the degenerated F_2 and E modes of the free arsenate or phosphate ions. A careful analysis of the spectra in Fig. 1 shows clearly that in the bending regions of the AsO_4^{3-} ion, the number of bands is greater than those of the stretching region, whereas a reverse trend observed for PO_4^{3-} ions in TDP is shown in Fig. 3. However, the number of bands should be more in both the regions as predicted by the simple site symmetry analysis. This implies that factor group effects are prominent in the bending region of AsO_4^{3-} ions in TDA and the stretching region of PO_4^{3-} ions in TDP. Furthermore, only five Raman active and three (five in TDP) infrared active lines available in the bending region do not appear to fulfill completely the predictions of factor group (C_{2h}) analysis because of the smaller number of observed A_g, B_g, A_u and B_u modes. Hence, they do not obey the centre of symmetry completely.

These bending frequencies of (Tables I and II) shift more or less on deuteration and the maximum shift is found to be $40\,cm^{-1}$ in TDA. This type of shift may be attributed to the mass effect and some coupling with –OD vibrations. The infrared couterpart of the Raman band at $437\,cm^{-1}$ was not available in TDA. However, a decrease in Raman frequency of $10\,cm^{-1}$ was observed when going from hydrogenated to deuterated TDA. All the modes in this bending region of TDA and TDP shift towards the low wavenumber side with a decrease of frequency of more than $10\,cm^{-1}$ in most of the bands on deuteration. Generally, a high-frequency shift is not observed in this region. Thus this effect may be concerned with different geometries of corresponding $H_2AsO_4^-$, $D_2AsO_4^-$, $H_2PO_4^-$ and $D_2PO_4^-$ ions.

In the stretching region, only two Raman and four

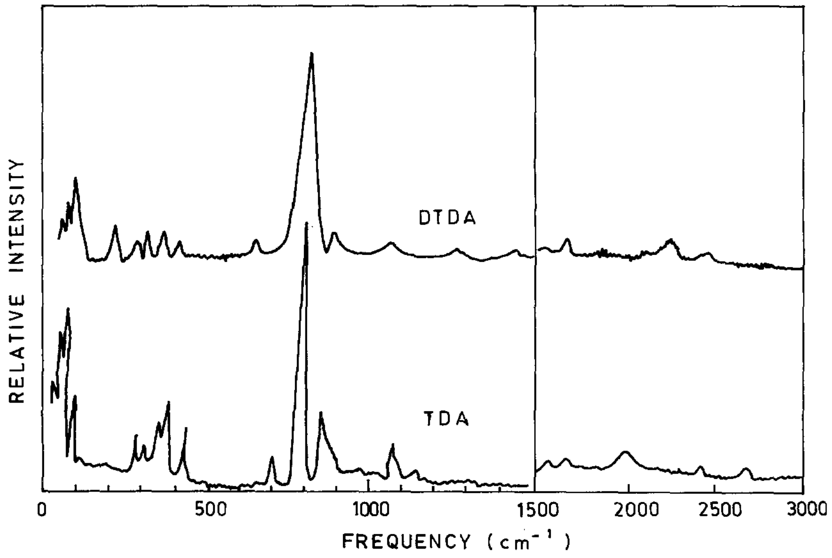


Figure 1 Raman spectra of TlH_2AsO_4 (TDA) and TlD_2AsO_4 (DTDA) at 300 K on polycrystalline samples.

TABLE III Raman and infrared frequencies of TlH_2AsO_4 and TlD_2AsO_4 at 300 K

TlH_2AsO_4			TlD_2AsO_4		
Raman (cm^{-1})	Infrared (cm^{-1})	Raman assignment	Raman (cm^{-1})	Infrared (cm^{-1})	Raman assignment
2700	2700	A_g	–	2680	
–	2640		–	2650	
2440	2440	A_g	2480	–	A_g
–	2330		2350	2375	A_g
–	2275		–	2260	–
2000	1950	A_g	–	1790	–
	1910		1690	1700	A_g
1770	–	A_g	1470	1480	A_g
1700	–	A_g	1270	–	A_g
1595	–	–	1075	1010	B_g
1155	1220	A_g		1065	–
1070	1100	B_g	–	990	–
	1060		870	870	A_g, ν_1
865	865	A_g, ν_1	805	810	
800	790			840	A_g, ν_3
	820	A_g, ν_3	670	650	B_g
700	720	B_g	427	–	B_g
437	–	B_g	345	370	A_g, ν_4
385	390	A_g, ν_4		337	
370	370	A_g	320	290	B_g, ν_2
			275	237	B_g
320	305	B_g, ν_2	200	–	B_g
285	290	B_g	93	–	A_g
–	240	–	45	–	B_g
90	–	A_g	35	–	B_g
65	–	B_g	31		B_g
44	–	B_g			
34	–	B_g			
26	–				

TABLE IV Raman and infrared frequencies of TlH_2PO_4 and TlD_2PO_4 at 300 K

TlH_2PO_4			TlD_2PO_4		
Raman (cm^{-1})	Infrared (cm^{-1})	Raman assignment	Raman (cm^{-1})	Infrared (cm^{-1})	Raman assignment
2720	2730	A_g	–	2300	
2650	2660	A_g	2070	2110	A_g
2340	2310	A_g	1980	2000	A_g
1700	1700	A_g	1710	1710	A_g
1250	1270	A_g	–	1690	
1140	1150		1150	1180	A_g
	1120	A_g	–	1160	
1080	–	B_g	1090	1080	B_g
960	950	A_g, ν_3	980	975	A_g, ν_3
920	930	A_g, ν_1	920	925	A_g, ν_1
–	880		912	–	
850	850	A_g	855	865	A_g
–	830		735	–	
–	790		520	520	A_g, ν_4
–	770		–	500	–
525	530	A_g, ν_4	412	415	A_g, ν_2
–	450		318	–	B_g
–	460				
418	420	A_g, ν_2	102	–	A_g
–	380		43	–	B_g
–	360		30	–	B_g
325	320	B_g			
250	270	B_g			
140	–	A_g			
44	–	B_g			
35	–	B_g			
26	–	B_g			

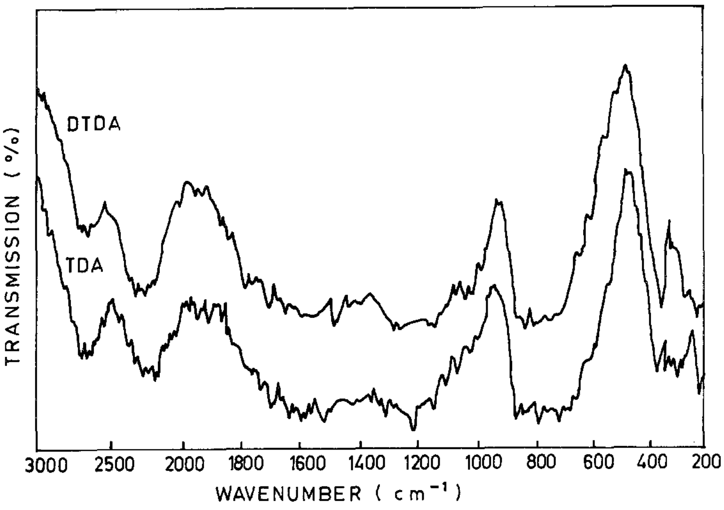


Figure 2 Infrared spectra of TIH$_2$AsO$_4$ (TDA) and TID$_2$AsO$_4$ (DTDA) at 300 K on polycrystalline samples.

infrared lines are active in TDA (Table III). One band at 800 cm^{-1} of the TDA Raman spectra (790 or 820 cm^{-1} in Raman spectra) is well-defined. Some of the lines of TDA in the stretching region are masked by other strong lines or simply missed. The Raman and infrared band at 865 cm^{-1} is due to the symmetric stretching vibrations of AsO$_4^{3-}$ ions. In TDP, the observed A$_g$ bands at 1140, 960, 920, 1080 cm^{-1} can be assigned to the stretching vibrations. The bands at 800 cm^{-1} in TDA, and 850 cm^{-1} in TDP can be assigned to the OH mode on the grounds of their isotopic shift. The OH bands are very weak in Raman spectra and there may be a possibility of overlapping by other strong bands. In the powder spectra, it is very difficult to separate those modes because of their very weak interaction. However, the above bands at 865 and 920 cm^{-1} can be assigned to the expected As–O and P–O stretching vibrations, respectively, of the A$_g$ (A$_u$) species. All other bands, except 966 cm^{-1}, are identified as the stretching modes of their ions in that region. The band at 966 cm^{-1} in TDP can be also assigned to OH vibrations because of its large frequency shift in DTDP. The intensity of all the modes decreases on deuteration. From Tables III and IV, it can be seen that most of the bands in the stretching region shift to the higher wavenumber side on deuteration. The OD vibrations in DTDA and DTDP were also found to be coupled more or less with the stretching motions.

The groups AsO$_4^{3-}$ and PO$_4^{3-}$ keep their characteristic tetrahedral structure in the crystal phase of all compounds; therefore, it is expected that the site group predictions for both the groups will be useful in explaining the number of Raman and infrared bands. They satisfy, more or less, the predicted values for the groups. The characteristic modes for PO$_4^{3-}$ are higher than that of AsO$_4^{3-}$ modes which were also observed in the present spectra. The infrared band at 990 cm^{-1} for DTDA is ambiguous and could not be assigned. This may be the multiphonon combinations or due to mixed modes of stretching and OD vibrations. Raman frequencies of TDA at 1155 and 1075 cm^{-1} shift towards the higher wavenumber side on deuteration. A similar trend is also exhibited by their corresponding infrared frequencies. In TDP and DTDP, the Raman frequencies (stretching) at 1140, 1080 and 960 cm^{-1} and their infrared counterparts also behave in a similar manner to TDA. In this region, OH and OD frequencies are more or less coupled with stretching motions. Hence, the above trend is exhibited.

Raman frequencies of TDA (Table III) at 2000 and 2440 cm^{-1} and their infrared counterpart at 1950, 2330, 2440 and 2640 shift to the higher frequencies on deuteration. The bands at 2720, 2650 and 2340 in TDP are not producd by DTDP. The number of bands are less in both the deuterated spectra of TDA and TDP in comparison to their hydrogenated one. These may be associated with OH group vibrations and those

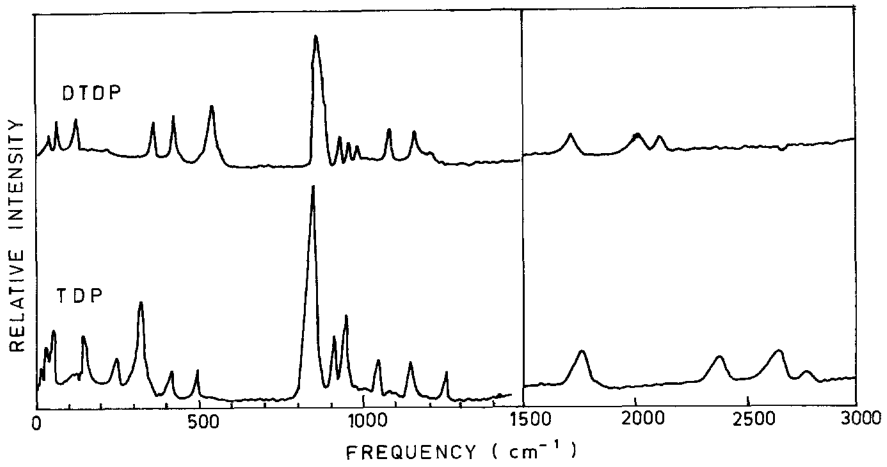


Figure 3 Raman spectra of TIH$_2$PO$_4$ (TDP) and TID$_2$PO$_4$ (DTDP) at 300 K on polycrystalline samples.

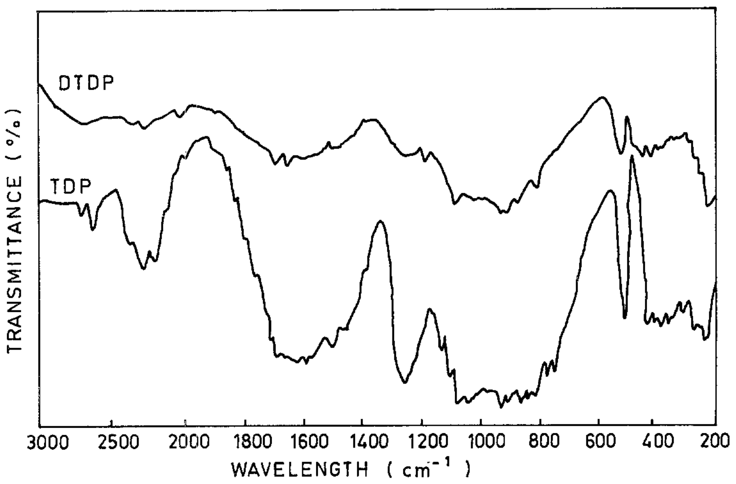


Figure 4 Infrared spectra of TlH_2PO_4 (TDP) and TlD_2PO_4 (DTDP) at 300 K on polycrystalline samples.

bands not prominent or missed in Raman and infrared spectra may be due to the strain or weak effect produced in them. It is notable that a Raman band at 1700 cm^{-1} decreases on deuteration (Table III and IV) whereas a band at 1595 cm^{-1} in TDA has a corresponding band at 1470 cm^{-1}. This much shift may be connected with an anion distortion due to hydrogen and deuterium bondings.

The modes below 300 cm^{-1} are considered to be due to lattice vibrations. The intensity of the Raman bands in the 20 to 100 cm^{-1} region was carefully measured. Except 90 cm^{-1} in TDA, all its other bands, together with all bands of TDP, decrease on deuteration in this lattice vibration region. One band at 26 cm^{-1} in both compounds may be a doublet of 34 cm^{-1} (TDA) or 35 cm^{-1} (TDP) which was not available in their deuterated compounds. This shifting of bands to lower frequencies on deuteration may be ascribed to the condensation in the crystal lattice. The Raman frequencies, which appear in the 100 to 30 cm^{-1} range, may be due to predominantly (OH) . . . O bending modes derived from rotational or translational motions. In particular, an infrared band at 240 cm^{-1} and one Raman band at 200 cm^{-1} of TDA and DTDA, respectively, are associated with the vibrational frequencies. Similarly, the band at 250 cm^{-1} and its infrared frequency at 270 cm^{-1} in TDP are also due to the same vibrational motions. However, these frequencies were found to be very less in number as expected. The vibrations in these compounds are very similar to those of CsH_2PO_4 [16] and KH_2PO_4 [17].

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