INFRARED VIBRATIONAL STUDIES OF SILVER AND AMMONIUM TRIHYDROGEN PERIODATES IN THE PARAELECTRIC AND ANTIFERROELECTRIC PHASES

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Infrared spectra (4000–200 cm^{-1}) of $Ag_2H_3JO_6$ and $(NH_4)_2H_3JO_6$ powder crystals have been obtained at room and liquid N_2-temperatures, i. e. for the paraelectric and antiferroelectric phases. The relative intensity temperature dependence for several bands in the $(NH_4)_2H_3JO_6$ spectrum was measured as well. The results have been discussed with relation to the crystallographic structure of the crystals studied.

1. Introduction

Silver trihydrogen periodate (STP), ammonium trihydrogen periodate (ADHP) and their deuterated analogues belong to the hydrogen bonded antiferroelectrics [1]. The crystal structure of these compounds [1–3] is very similar to that of KDP-type ferroelectrics [4] so far as hydrogen-bonded systems are concerned. Both the tetrahedral groups PO_4 in the KDP compound and the octahedral groups JO_6 in periodate compounds are joined together by means of hydrogen bonds in a way that each oxygen atom of PO_4 or JO_6 groups, respectively, is joined with an oxygen atom a neighbouring PO_4 or JO_6 group, respectively. The O...O distance in an ammonium trihydrogen periodate crystal is equal to 2.60 Å and is longer than that of KDP (2.48 Å) [4].

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In the present paper we have investigated the infrared spectra of paraelectric and antiferroelectric phases of STP, DSTP (silver trideuterium periodate) and ADHP in relation to the crystallographic structure. In addition the temperature dependence of the relative intensity of several bands (OH and JO_6 group vibrations) of ADHP has been studied in order to obtain more information of the possibility of phase transition studies of hydrogen bonded ferroelectrics by infrared spectroscopy.

The infrared spectra of the paraelectric phase of STP and ADHP compounds have been studied by several authors [5–10] but only Temme et al. [5, 6] have investigated all internal vibrations of the $H_3JO_6^{-2}$ ion in the paraelectric STP crystal. Blinc and Hadži [7, 8] have paid attention to the OH vibrations only and Siebert [9] recorded the spectrum of paraelectric ADHP in the region of NaCl transmission. The spectrum of STP recorded by Kyrki [10] is different from our results which may be due to refusing the sample by products of STP decomposition.

2. Experimental and results

The spectra of STP, DSTP and ADHP were recorded with a Perkin Elmer Model 621 infrared spectrophotometer. The substances were mulled with parafin oil and hexachlorobutadiene, respectively. The measurements have been carried out at room and liquid N_2 temperatures (i. e. in the para- and antiferro-electric phases) for STP and DSTP samples and at several different temperatures (below and above the transition point) for the ADHP sample.
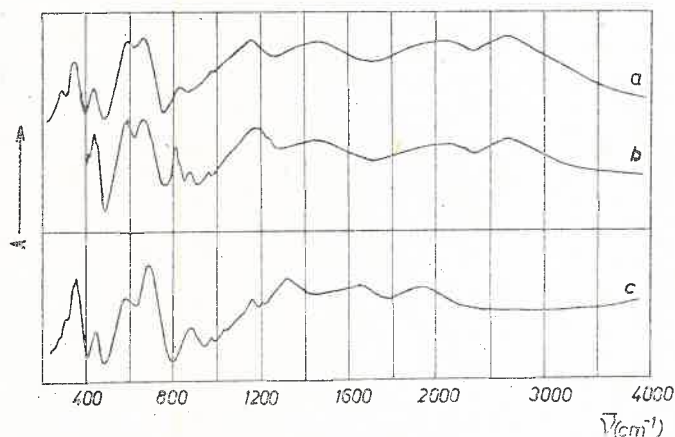

Fig. 1. Infrared spectra of $(NH_4)_2H_3JO_6$ at the room temperature — a; at liquid nitrogen temperature — b; and the infrared spectrum of $(ND_4)_2D_3JO_6$ at room temperature — c

The spectra obtained for all studied compounds are shown in Figs. 1, 2. The frequencies are presented in Table I. In Fig. 3 the relative integrated intensity against temperature is plotted for several bands of ADHP; namely $\bar{\nu}_{JO_6}$ (700 cm^{-1}), δ_{OH}(1175 cm^{-1}) and γ_{OH}(850,900 cm^{-1}) bands. The area between the band contour and the straight line connect-

TABLE I

Frequencies (in cm^{-1}) of the observed IR absorption spectra of $Ag_2H_3JO_6$, $Ag_2D_3JO_6$ and $(NH_4)_2H_3JO_6$ compounds

$Ag_2H_3JO_6$ room temperature	$Ag_2H_3JO_6$ liquid N_2 temperature	$Ag_2D_3JO_6$ room temperature	$(NH_4)_2H_3JO_6$ room temperature	$(NH_4)_2H_3JO_6$ liquid N_2 temperature	Assignment
			3200 s 3060 s	3310 s 3230 s 3210 s 3100 s	ν_{NH_4}
2600 vs, b 2340* 2200 vs, b 1700* 1550 vs, b	2600 vs, b 2340* 2200 vs, b 1700* 1550 vs, b		2650 s, b 2250 s, b 2100 s, sh 1750 s, b	2650 s, b 2300 s, b 1700 s, b	ν_{OH}
			1700 m	1700 s	δ_{NH_4}
		1950 s, b 1700 s, b 1370 vs 1150 s			ν_{OD}
			1430 s 1410 s	1490 s 1430 s 1410 s	δ_{NH_4}
1200 ? m, sh 1160 vs	1250 ? m, sh 1190 vs	1160 w	1175 s 1130 s	1210 s	δ_{OH}
970 w, sh	965 vw	970 w, sh			?
		880 m			δ_{OD}
840 w	885 m 870 m 835 m 810 s		900 w 850 m	970 w 925 s 880 s 870 s	γ_{OH}
715 m, sh 670 vs	715 m, sh 670 vs	715 m, sh 680 vs	765 m, sh 700 vs	765 m 740 s	ν_3 (F_{1u})

TABLE I (continued)

$Ag_2H_3JO_6$ room temperature	$Ag_2H_3JO_6$ liquid N_2 temperature	$Ag_2D_3JO_6$ room temperature	$(NH_4)_2H_3JO_6$ room temperature	$(NH_4)_2H_3JO_6$ liquid N_2 temperature	Assignment
				720 vs	
				700 vs	
				670 m, sh	
590 vs	610 vs	575 s	610 s	610 s	
	595 vs		590 s	590 s	
	580 vs			575 s	
				560 m	$\nu_1(A_g)+$
				540 w	$+\nu_2(E_g)$
				470 m	
	460 s			460 s	
450 m	440 s	440 m	440 m		$\nu_4(F_{1u})$
	415 s			430 s	
360 s		340 vs	350 vs		$\nu_5(F_{2g})$
300 m		300 m, sh	260 m		$\nu_6(F_{2u})$

* minima in the trio system.

ing two minima was estimated and regarded as a measure of the integrated intensity at the defined temperature. The ratio of this quantity to the quantity measured at 300 K was regarded as the relative intensity of the band. The intensity at maximum was also measured
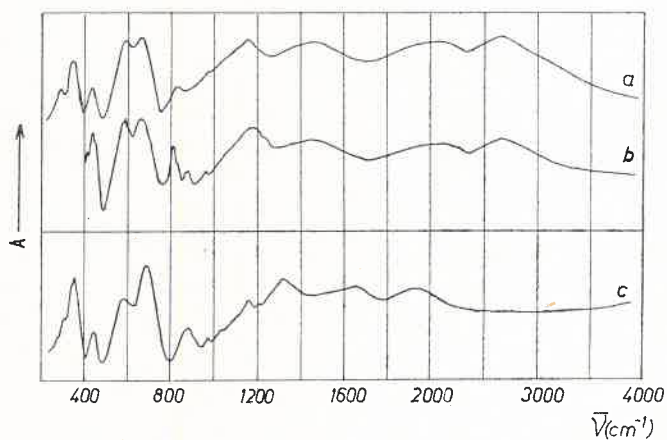

Fig. 2. Infrared spectra of $Ag_2H_3JO_6$ at the room temperature — a, at the liquid nitrogen temperature — b and the infrared spectrum of $Ag_2D_3JO_6$ at the room temperature — c

for all studied bands assuming the position of the chosen minimum as the position of the base line. The transmission minimum at 790 cm^{-1} was chosen for 700 and 850 cm^{-1} bands and at 980 cm^{-1} for 900 and 1175 cm^{-1} bands. The relative intensity at maximum was determined in the same way as the relative integrated intensity. The temperature dependence of the
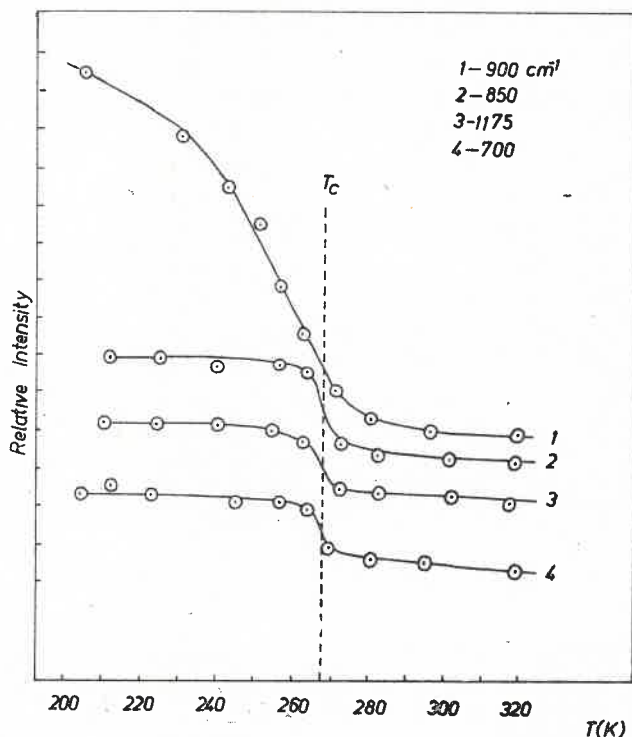

Fig. 3. Temperature dependence of the intensities of the 900 cm^{-1} -1, 850 cm^{-1} -2, 1175 cm^{-1} -3, and 700 cm^{-1} -4, bands in $(NH_4)_2H_3JO_6$ spectra. The coordinate is different for each curve

relative integrated intensity and the relative intensity at the maximum have the same character for all studied bands and only the first one is presented in Fig. 3.

ADHP crystals were prepared by crystallization from a periodic acid solution with the addition of an excess of concentrated ammonia.

STP was prepared according to two methods; namely using Stephenson and Adams' method [11] and by precipitation of an aqueous $AgNO_3$ solution with a solution of periodic acid. Identical spectra were recorded for the two obtained samples. DSTP was prepared by precipitation of a solution of $AgNO_3$ in D_2O with a similar solution of previously deuterated periodic acid. The discoloration of the obtained sample showed that decomposition had occurred during a few hours. This was why we have not succeeded in obtaining the low temperature spectrum of this compound. It was partly decomposed during preparation of the sample to the low temperature measurements.

3. Discussion

3.1. Crystal structure and selection rules

ADHP exhibits antiferroelectric properties below 251 K [12], STP below 227 K [13] and their deuterated analogues below 266 K, 267 K [12, 14], respectively.

In the paraelectric phase both compounds have rhombohedral symmetry and belong to the space group C_{3i}^2 [1–3]. The periodate group has an octahedral arrangement of oxygen atoms around the iodine and each oxygen atom is linked by the hydrogen bond to an oxygen atom of a neighboring JO_6 group. The primitive unit cell of the ammonium compound contains three ADHP molecules [1, 2] and that of the silver compound one STP molecule [3].

Below T_c, ADHP exhibits a superperiod only along the hexagonal c-axis [15], whereas silver trihydrogen periodate gives rise to a superlattice along two axes [14]. The symmetry of the antipolar phase is trigonal for the ammonium compound and monoclinic (pseudo-trigonal) for the silver compound [1].

The three different distributions of protons along the O...O bond, the same as in the KH_2PO_4 crystal [16], are possible and the site symmetry of the JO_6 group is S_6 or C_3 and depends upon the protons distribution. It must be noted that if the JO_6 group has the C_3 site symmetry the hydrogen bond is not centrosymmetric and the space group of the paraelectric phase is lower than that indicated by X-ray studies.

In Table II the correlation diagram for JO_6 fundamentals is given.

TABLE II

Correlation diagram for JO_6 fundamentals
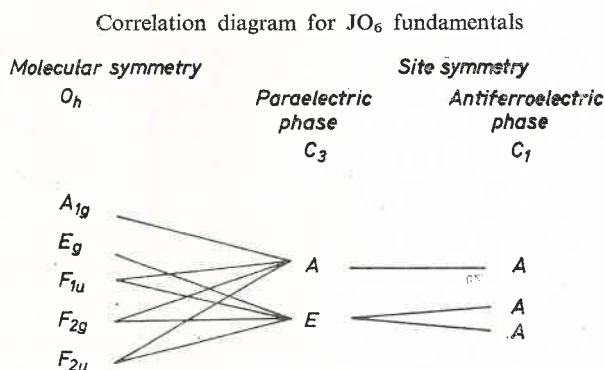
3.2. JO_6 Group frequencies assignment

The JO_6 group in periodic acid is known to have octahedral symmetry from infrared and the Raman studies. Its five fundamental modes have the following frequencies [17]:

$$\nu_1 = 632\ A_{1g} \quad \nu_4 = 426\ F_{1u}$$
$$\nu_2 = 594\ E_g \quad \nu_5 = 387\ F_{2g}$$
$$\nu_3 = 700\ F_{1u}$$

The sixth (F_{2u}) mode is inactive both in the infrared and the Raman spectrum. In the crystals studied all the vibrations are infrared active both in the para- and antiferroelectric phases which indicates C_3 site symmetry for the JO_6 group. To a broad feature appearing at 590 cm^{-1} in the room temperature spectrum of STP we have assigned coinciding bands of v_1 and v_2 type vibrations. When the temperature is decreased three components of the broad band are observed at 610, 595, 580 cm^{-1} one of which may be due to a separated A_{1g} vibration, two to a split E_g type vibration. In the room temperature spectrum of ADHP the broad band in this region is split into two components (590, 610 cm^{-1}) one of which is assigned to the $v_1(A_{1g})$ vibration (610 cm^{-1}) and the second to $v_2(E_g)$ vibration (590 cm^{-1}). So the bands appearing at 670, 715 cm^{-1} in the spectrum of STP and at 700, 765 cm^{-1} in the spectrum of ADHP belong to the two components of the split v_3 (F_{1u}) vibration. This assignment is different from that made by Temme et al. [6] who ascribed the bands appearing at 670, 590 cm^{-1} in the spectrum of STP to v_1, v_2 vibrations and the band at 715 cm^{-1} to v_3 vibration. The $v_1(A_{1g})$, $v_2(E_g)$ frequencies observed in the spectrum of ADHP molecule are the same as those observed for $Na_2H_3JO_6$, $Na_3H_2JO_6$ molecules [18] which confirms our assignment. Besides, the relative intensity of all three bands is also in agreement with such an assignment.

One band only is observed in the region of the $v_4(F_{1u})$ vibration (450 cm^{-1} – STP, 440 cm^{-1} – ADHP) and one in the region of the $v_5(F_{2g})$ vibration (360 cm^{-1} – STP, 350 cm^{-1} – ADHP) in the paraelectric spectra of both compounds. The $v_6(F_{2u})$ mode has been assigned to the feature at 300 cm^{-1} in STP spectrum and at 260 cm^{-1} in ADHP spectrum. This is in agreement with the studies of Temme et al. [6].

In the low temperature spectra of both compounds the bands are split into several components. This is due to a lowering of crystal symmetry and an increase in the number of molecules in the primitive unit cell. Lower local symmetry may remove the degeneration of E type vibration and the dynamical coupling of molecules in the primitive unit cell can lead to dynamical splitting. The low temperature spectrum of STP can be interpreted assuming the C_1 local symmetry for the JO_6 group. Then the splitting of the E type vibration into two components and F vibrations into three components is expected just as it is observed for v_2 and v_4 modes in the STP spectrum (see Table I). But in the case of the ADHP molecule the interaction of molecules in a primitive unit cell leading to dynamical splitting must play an important role. Only in this way the appearance of five components in the region of $v_1 + v_2$ and three in the region of v_4 vibrations might be explained.

3.3. The hydrogen bond frequencies

On the basis of deuteration shift five bands are attributed to hydrogen-bond vibrations (see Table I).

Trio (A, B, C) has been assigned as previously to overtones of the bending vibrations ($2\delta_{OH}$, $2\gamma_{OH}$) coupled with the stretching vibration by the Fermi resonance mechanism. The overtones $2\delta_{OH}$ and $2\gamma_{OH}$ correspond approximately to the minima in the A, B, C system which is in agreement with Claydon and Sheppard's postulate [19] regarding the nature of the observed trio and the broadness of the v_{OH} stretching band. The trio bands

of ADHP overlaps with the bands corresponding to the NH_4^+ group vibrations. A broad, asymmetric band (with a shoulder) corresponds, in the spectra of the paraelectric phase of both compounds, to the δ_{OH} vibration. The γ_{OH} vibration appears as a weak, broad band in the STP spectrum and as a band doublet in the ADHP spectrum.

The trio bands practically do not change after cooling the sample to liquid N_2 temperature. The bands corresponding to δ_{OH} in the plane bending mode shift towards lower frequencies in both studied compounds. The temperature dependence intensity studies show the abrupt increase of intensity of the δ_{OH} band (1175 cm^{-1}) in the spectrum of ADHP (see Fig. 3) at the Curie point. The intensity does not change very much over a wide range of temperature below and above the Curie point. The same behaviour is observed for the studied ν_{JO} band (700 cm^{-1}) indicating the observed changes are characteristic both for vibrations due to JO_6 and OHO groups. They are connected with the structure rearrangement during antiferroelectric transition.

The most sensitive to the transition is the γ_{OH} out-of-plane bending mode. The weak and broad band observed in the spectrum of the paraelectric phase of STP splits into two components in the antiferroelectric phase (810, 870 cm^{-1}) and becomes more intensive. One can distinguish several peaks which are probably due to correlation field splitting. Similar changes are observed for the γ_{OH} doublet (900, 850 cm^{-1}) in the ADHP spectrum. Very interesting is the different shape of intensity-vs-temperature curves for both components of the γ_{OH} mode. The feature observed at 850 cm^{-1} behaves in the same way as the studies δ_{OH}, ν_{JO} bands except that the intensity change is larger for the γ_{OH} component. The intensity of the second component remains almost constant up to the Curie point and then increases continuously over a large temperature range. This difference can be explained only if the origin of the doublet is known. The appearance of the γ_{OH} doublet is in agreement with C_3 site symmetry of the JO_6 group but it can be due as well to the existence of two types of hydrogen bonds in the crystal. The unequivocal types of hydrogen bonds are, for example, responsible for the several components of the γ_{OH} band in the spectra of the ferroelectric phase of $NH_4D_2PO_4$ and $NH_4H_2AsO_4$ compounds [20].

The broadness and weakness of the γ_{OH} components in the room temperature spectra may be due to disorder in the paraelectric phase of the studied crystals. Different γ_{OH} frequencies of nonequivalent OH groups should give rise to a relatively weak and broad band. A disorder in the paraelectric phase may be due to several reasons including:

(1) Static disorder of hydrogen atoms in crystal lattice
(2) Dynamic disorder of hydrogen atoms
(3) Tunneling proton motion
(4) Strong thermal motion causing a breaking of the hydrogen bond during torsional OH vibration (an identical effect was observed in alanine crystal [21]).

If the appearance of the γ_{OH} doublet in the ADHP spectrum was due to the existence of two types of hydrogen bonds then their different behaviour could be connected with complete ordering of hydrogen atoms at the Curie point in one type of hydrogen bond (to which the band at 860 cm^{-1} corresponds) and gradual ordering of hydrogen atoms in the ferroelectric phase in the second type of hydrogen bond (to which the band at 900 cm^{-1}

corresponds). The different shape of the intensity versus temperature curve for both γ_{OH} components is difficult to explain when we assume that only one type of hydrogen bond exists in the ADHP crystal.

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