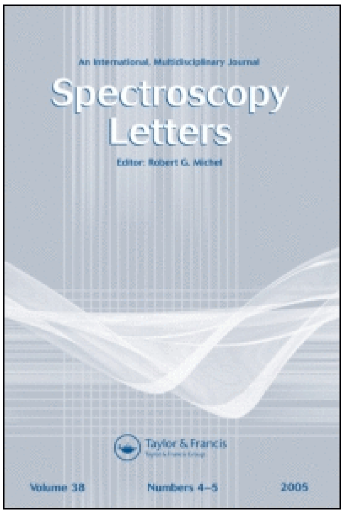

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VIBRATIONAL SPECTRA OF AND ISOTOPE EFFECT IN HYDROGEN BONDED POTASSIUM HYDROGEN OXALATE

Key words : Infrared spectra, Raman spectra, Isotope effect, Hydrogen bond

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The crystal structure of potassium hydrogen oxalate, KHC_2O_4, has been determined by Pedersen[1]. There are infinite chains of hydrogen oxalate ions held together by short (2.534 Å) hydrogen bonds. The O-D..O distance of KDC_2O_4 derived from lattice constant changes is estimated to be about 0.005 Å larger than the O-H..O distance which means that the isotope effect is small[1]. We believe, however, on the ground of the infrared and Raman spectra of KHC_2O_4 and KDC_2O_4 reported in this paper, that the isotope effect in these crystals is much larger.

EXPERIMENTAL AND RESULTS

KHC_2O_4 and KDC_2O_4 were prepared by the method described by Pedersen[1]. Infrared spectra from 4000 to 200 cm^{-1} and from 200 to 33 cm^{-1} were made with a Perkin-Elmer 225 and a Beckman IR 11 spectrophotometer respectively. All the spectra were of the solid state as emulsions in Nujol and Fluorolube. Raman spectra of crystal powders sealed in glass tubes were obtained on a Coderg PH 1 instrument using the 4880 Å line of an Ar$^+$ laser (C. R. L. model 52) and the 6328 Å line of a He-Ne laser (Spectraphysics Model 125).

The infrared spectra of KHC_2O_4 and KDC_2O_4 at room and liquid nitrogen temperature are shown in Fig. 1. The room temperature spectra are practically the same as those recorded by Pedersen[1] for the 4000-650 cm^{-1} region except for the water bands shown in his spectra. The Raman spectra of acid oxalates are shown in Fig. 2. The frequencies, relative intensities and the assignments of the corresponding bands are given in Tables 1 and 2.

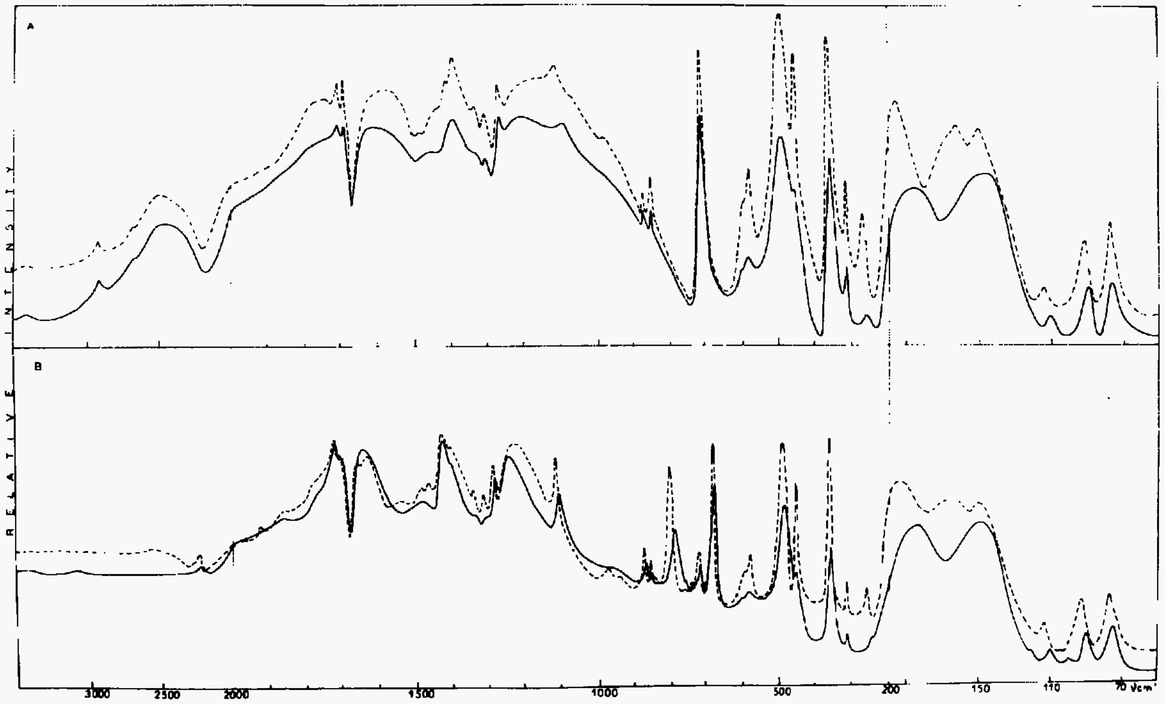

FIG. 1 : Infrared spectra of (a) KHC_2O_4 and (b) KDC_2O_4. Solid line and dotted line correspond to room and liquid nitrogen temperature spectra respectively.

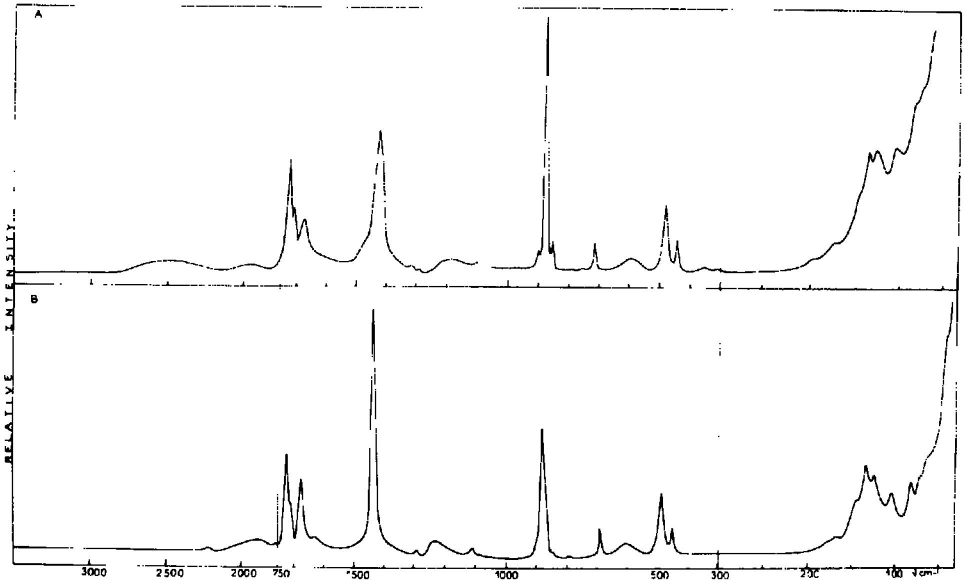

FIG. 2 : Raman spectra of (a) KHC_2O_4 and (b) KDC_2O_4.

TABLE 1

Infrared and Raman frequencies of potassium hydrogen oxalate

KHC_2O_4			KDC_2O_4			Assignment
IR 300 K	IR 90 K	Raman	IR 300 K	IR 90 K	Raman	
2680 sh	2680		2220 w	2230	2214 (4)	(α)
		2540 (5)	1985 sh	1985		
2440 m, b	2460		1845 sh	1853	1882 (8)	
1975 sh	2000	1950 (4)	1770 sh	1773	1775 (6)	
1800 sh						
1720 s	1719	1717 (44)	1722 s	1724	1717 (42)	ν C=O
1701 s	1702	1703 (25)	1704 s	1707	1703 (23)	
1678	1678		1680	1681		ν COO
		1667 (22)			1669 (32)	
1610 s, b	1580		1643 s, b	1658		(α)
			1623 sh	1630	1626 (9)	
1468 sh	1490	1470 sh				δ OH
	1445		1478 w	1486		comb
				1465		
	1422	1423 (55)	1429 s	1433	1430(100)	ν_s COO
1403 vs	1404		1406 sh	1408		
1340 sh	1342		1338 w	1341		comb
1310 m	1317	1313 (4)	1309 w	1315		
1270 s	1278	1292 (3)	1282 m	1288	1287 (3)	ν C-O
1200 s, b	1170	1191 (6)	1244 s, b	1228	1227 (7)	(α)
1103 sh	1121	1108 (5)				γ OH
			1110 m	1120	1102 (4)	δ OD
	985		955 sh	975		comb
				942		
		901 (9)				
879 w	882	882(100)	874 w	879	870 (53)	ν C-C
859 w	860	859 (13)	857 w	860	856 (17)	
			793 ms	807	783 (4)	γ OD
719 s	722	719 (14)	683 s	687	681 (13)	δ COO (H)
605 m	605	611 (11)	600 m	600	595 (7)	ρCOO
590 ms	590	588 (6)	587 ms	586		
498 s	498	491 (28)	490 s	497	480 (27)	δ COO
462 sh	462	452 (15)	457 s	457	443 (13)	ρCOO
364 s	370	364 (4)	360 s	367	349 (2)	w COO
320 m	321		315 w	316		
267 m	274		251 sh	257		

(α) Subbands of the OH or OD stretching band centered near 1500 ± 100 cm^{-1}.

TABLE 2

Infrared and Raman frequencies of lattice vibrations of potassium hydrogen oxalate

KHC_2O_4 IR 300K	KHC_2O_4 IR 90K	KHC_2O_4 Raman	KDC_2O_4 IR 300K	KDC_2O_4 IR 90K	KDC_2O_4 Raman	Assignment
186 s	196	193 wv	185 s	195		
	172 sh	170 sh		170 sh	173 sh	T'
150 s, b	163		150 s, b	165		
	150	145 sh		150	143 sh	
		135 ms			133 ms	R'
		125 ms			125 ms	
112 w	115		109 w	113		
		104 m			105 w	
90 m	93		90 m	93		
		82 sh			83 sh	
76 m	78		76 m	78		
		73 sh				
					61 sh	
					43 sh	

DISCUSSION

Potassium hydrogen oxalate crystallizes in the monoclinic system, space group $P2_1/c$ (C^5_{2h}) with Z = 4. The crystal is built of infinite chains of non planar $HC_2O_4^-$ ions held together by short hydrogen bonds[1]. The results of the corresponding factor-group analysis are shown in Table 3.

TABLE 3

Symmetry species and selection rules for factor group C_{2h} and the number of internal and lattice vibrations of KHC_2O_4 crystal

C^5_{2h}	IR	R	n	n_i	T	T'	R'
Ag	f	a	24	15	0	6	3
Bg	f	a	24	15	0	6	3
Au	a	f	24	15	1	5	3
Bu	a	f	24	15	2	4	3

IR : infrared, R : Raman, n_i : internal vibrations, T' : translational and R' : rotational vibrations, f : forbidden, a : active

The hydrogen oxalate ions are in general positions and each of the fifteen intramolecular modes is expected to have four components, two infrared and two Raman active. An approximate description of the internal modes in terms of OH group vibrations and skeletal stretching and bending motions is based on the analogy with the spectra of $NaHC_2O_4$[2].

The 4000-800 cm^{-1} region. The most characteristic feature of the infrared spectrum of KHC_2O_4 is a very strong and broad absorption, between 2800 and 800 cm^{-1}, on which other bands are superimposed (Fig. 1). This absorption centered at about 1500 ± 100 cm^{-1} is assigned to the OH stretching vibration of the strongly hydrogen bonded acid oxalate. Two OH bending and five skeletal stretching frequencies are expected in this region and are identified as follows.

The skeletal stretching frequencies appear near 1720-1701, 1667, 1423, 1290,and 882 cm^{-1} and are approximately described as ν C=O, ν_a COO, ν_s COO, ν C-O and ν C-C motions respectively. All of them give rise to strong and narrow Raman bands, except the ν C-O mode, the intensity of which is low, and their frequencies vary relatively little on deuteration (Fig. 2). Four of their infrared counterparts are readily identified as well-defined bands or doublets while the assignment of the ν_a COO vibration poses a problem. There is a broad absorption maximum near 1580 cm^{-1} and a narrow "transmission peak" at 1678 cm^{-1}. The former is not likely to be due to the ν_a COO vibration since it shifts by about 80 cm^{-1} towards higher frequencies on deuteration while the Raman ν_a COO band does not shift. The ν_a COO mode is thus believed to correspond to the deuteriation insensitive "transmission peak". The explanation of such transmission peaks in terms of a resonance interaction between a narrow and a broad vibrational level was already given by Evans[3]. In our case the narrow and broad levels would correspond to the ν_a COO and ν OH vibrations respectively.

The OH bending frequencies, which are deuteration and temperature sensitive, are identified at 1103 and 1470 cm^{-1}. The assignment of the former to a γ OH motion is straightforward since it shifts to 793 cm^{-1} on deuteration ; the corresponding band is strong in absorption and very weak in Raman. The δ OH Raman band, on the other band, is identified as the shoulder at 1470 cm^{-1} which does not appear in the spectrum of KDC_2O_4. The infrared δ OH band is difficult to locate in the 1500-1400 cm^{-1} region because of overlapping with other bands while its δ OD analog is readily observed at 1110 cm^{-1}.

The remaining bands in the 2800-800 cm^{-1} region cannot be considered as fundamentals. In the infrared spectrum of KHC_2O_4 most of them appear as strong and broad bands or shoulders such as the absorptions near 2440, 1975, 1800, 1600, and 1200 cm^{-1}. In the Raman spectrum, similar broad bands are observed near 2540, 1950, 1600, and 1190 cm^{-1}, their peak intensity, however, being very low. In the infrared spectrum of KDC_2O_4 the broad absorption weakens and narrows down to the 2100-1000 cm^{-1} region. The absorption pattern is different and the infrared maxima near 1985, 1853, 1640, and 1230 cm^{-1} appear sharper. The same is true of the 1882, 1630, and 1227 cm^{-1} Raman bands. The center of gravity of the main ν OD absorption, however, does not seen to change considerably and the ν OD frequency is thus roughly the same as the ν OH frequency. The maxima and the shoulders may be interpreted as subbands of the OH (OD) stretching band in much the same way as the well-known acetic acid subbands in the 3000 cm^{-1} region[4]. No assignment of the submaxima is given except for the 2440 cm^{-1} band. This absorption, assigned to a ν OH fundamental by Pedersen[1], is likely to be due to a δ OH + γ OH combination since it shifts to 2460 cm^{-1} on cooling and disappears on deuteration.

The 800-200 cm^{-1} region. There are eight infrared and six Raman bands in this region where skeletal bending vibrations are expected (Table 1). All of them are assigned to intramolecular modes either on the ground of their position or, in the case of the low frequencies at 320 and 267 cm^{-1}, because of their isotopic shifts which appear too large for lattice modes.

The frequencies near 719 and 498 cm^{-1} can be assigned to δ COO vibrations of the carboxylic and carboxylate groups respectively since the former shifts to 683 cm^{-1} on deuteration and the latter gives rise to a strong Raman band[2]. The 605-590 cm^{-1} correlation field doublet and the 462 cm^{-1} band are described as rocking vibrations by analogy with the spectra of $NaHC_2O_4$[2] while the frequencies near 364, 320 and 267 cm^{-1} may correspond mainly to wagging and torsional motions.

The 200-33 cm^{-1} region. There are fifteen infrared (9T' + 6 R') and eighteen Raman active (12 T' + 6 R') lattice modes (Table 3). Seven infrared and eight Raman lattice frequencies are observed in the 200 to 33 cm^{-1} region and as expected their frequencies do not coincide (Table 2). We have no experimental criteria for assigning them in terms of symmetry species. It can be argued on general grounds, however, that strong infrared bands near 196, 163 and 150 cm^{-1} are due mainly to translational vibrations and that strong Raman bands near 135, 125 and 105 cm^{-1} are due mainly to rotational vibrations. The external vibrations of acid oxalate chains necessarily include the hydrogen bond motions. There are eight hydrogen bond vibrations for a chain with a repeat unit comprising two $HC_2O_4^-$ ions and it was shown for similar systems that there are two hydrogen bond stretching vibrations one of translational and one of rotational origin[5]. The former could thus be sought in the 200-160 cm^{-1} and the latter in the 150-135 cm^{-1} regions. A linear triatomic O-H..O model calculation indicates that the symmetric stretching frequency is not expected above 250 cm^{-1} for a system with the antisymmetric frequency at about 1500 cm^{-1}.

Isotope effect. There is a strong positive isotope effect in the $NaHC_2O_4$ crystal containing infinite chains of $HC_2O_4^-$ ions, the O-H..O and O-D..O distances being 2.571 and 2.593 Å respectively[6]. An analysis of the infrared spectra has shown that the center of gravity of the very broad OH stretching band near 1800 ± 100 cm^{-1} almost does not shift on deuteration while the δ OH and γ OH bands near 1440 and 1042 cm^{-1} yield the isotopic ratios of 1.33 and 1.38 respectively[2]. This was interpreted by assuming that the expected ν OH/νOD isotopic shift is roughly compensated by the weakening of the hydrogen bond on deuteration[2]. We believe that much the same occurs for KHC_2O_4. The hydrogen bond in this compound is even shorter (2.534 Å) and accordingly the ν OH frequency is lower (1500 ± 100 cm^{-1}) and the δ OH (1470 cm^{-1}) and γ OH (1103 cm^{-1}) frequencies are higher. The isotopic ratio for the ν OH frequency is close to unity and those of the OH bending frequencies equal to 1.34 and 1.39. The lengthening of the hydrogen bond distance is thus expected to be at least as big as that in the sodium acid salt, i. e., of about 0.020 Å instead of 0.005 Å[1].

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