

THE VIBRATIONAL SPECTRA OF THE FORMATE, ACETATE, AND OXALATE IONS¹

By K. ITO² AND H. J. BERNSTEIN

ABSTRACT

The infrared spectra of the formate, acetate, and oxalate ions have been obtained for both the solid and aqueous solution. The Raman spectra of these ions with depolarization ratios have been obtained in aqueous solution. Vibrational assignments have been made which differ slightly for the acetate ion and more markedly for the oxalate ion from earlier work. The depolarization ratios confirm Fonteyne's assignment for the formate ion.

INTRODUCTION

The Raman spectra of aqueous solutions of formate (4, 7), acetate (16), and oxalate (5, 8, 11) ions, and the infrared spectra of solid metal-formate (3), -acetate (10), and -oxalate (2) have been studied in the past but no reliable assignment has been made for the oxalate ion and in some respects the rather complete assignments for CH_3COONa and CD_3COONa in the solid state (10) and that for the formate ion merit reinvestigation.

Infrared spectra of solid sodium formate, light and heavy sodium acetate, and sodium oxalate, and their saturated solutions in H_2O and D_2O were obtained from 3–35 μ . The Raman spectra of the aqueous solutions with depolarization ratios were also obtained. From these more complete vibrational data and comparison of spectra with the isoelectronic molecules nitromethane and nitrogen tetroxide vibrational assignments have been made for acetate and oxalate ions. The depolarization ratios for the Raman bands of the formate ion confirmed the assignment of Fonteyne (7).

EXPERIMENTAL

The infrared spectra were obtained with a Perkin-Elmer Model 12C double pass spectrometer with CsBr, NaCl, and LiF optics. The Raman spectra were photoelectrically recorded on a White Raman spectrometer (18) and depolarization ratios measured by comparing Raman spectra obtained with polaroid film wrapped round the sample tube first with its axis in a direction parallel to the sample tube and then perpendicular to it (6). These ratios were corrected for convergence error in a manner previously described (1, 14).

The reported infrared spectra of the aqueous solutions are not as complete as those for the solids because of the strong H_2O and D_2O absorption. The solid infrared spectra were taken of films deposited from H_2O or CH_3OH on AgCl plates or polystyrene film. Raman spectra were obtained for the saturated aqueous solutions only and the depolarization ratios of all fundamentals measured.

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²National Research Laboratories Postdoctorate Research Fellow 1954–55.

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Acetate Ion

The Raman spectrum of a saturated solution of CH_3COONa in H_2O is shown in Fig. 1 and the Raman data for solutions of CH_3COONa and CD_3COONa given in Table I.

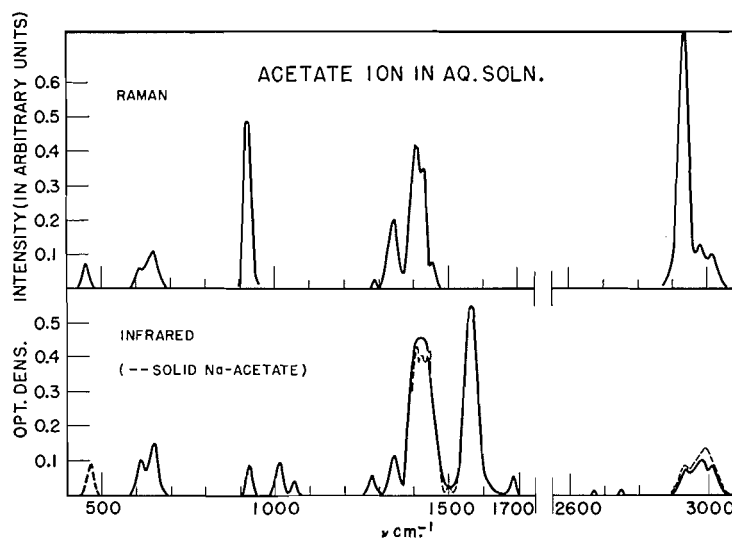


FIG. 1. The Raman and infrared spectra of the acetate ion.

TABLE I
RAMAN SPECTRA OF CH_3COONa AND CD_3COONa IN H_2O

CH_3COO^-		CD_3COO^-	
$\nu(\text{cm}^{-1})$	ρ	$\nu(\text{cm}^{-1})^a$	ρ
3013	0.8 ₀ (D)	2264 (3.2)	0.7 ₄ (D)
2980	0.8 ₀ (D)	2231 (4.2)	0.7 ₄ (D)
2933	0.1 ₂ (P)	2185 ^b (6.4)	0.1 ₆ (P)
1456	D	2111 (10.0)	0.08 (P)
1429	D (?)	2068 ^c (2.3)	0.08 (P)
1414	0.4 ₉ (P)	1545 (0.61)	0.8 ₀ (D)
1344	0.5 ₆ (P)	1457 ^d (0.50)	0.5 ₇ (P)
1289	—	1432 ^e (1.5)	0.8 ₀ (D)
927	0.2 ₀ (P)	1405 (8.1)	0.3 ₆ (P)
649	0.5 (P)	1085 (3.6)	0.1 ₇ (P)
621	0.8 ₀ (D)	1049 (0.98)	0.8 ₀ (D)
471	D	1031 (8.6)	0.7 ₁ (D)
		883 (4.8)	0.1 ₂ (P)
		832 (0.61)	0.6 ₃ (D?)
		619 (2.6)	0.3 ₆ (P)
		526 (0.68)	0.7 ₁ (D)
		419 (0.61)	0.8 ₀ (D)

^a Values in brackets are the relative intensities referred to the 2111 cm^{-1} band.

^{b,c,d,e} Combination bands explained as $2\nu_2 = 2170$ (A_1), $2\nu_{13} = 2062$ (A_1), $\nu_{14} + \nu_{16} = 1466$ (A_1), or $\nu_9 + \nu_{11} = 1466$ (A_1) and $\nu_5 + \nu_{10} = 1451$ (B_1), respectively (see Table II).

The infrared spectrum of the saturated solution of CH_3COONa in H_2O and D_2O is shown also in Fig. 1. Only the part of the spectrum of the solid that differs sensibly from that of the solution is shown in Fig. 1. The band at 480 cm^{-1} in the spectrum of the solid is not found in solution because of the strong water absorption in this region. The spectrum of the solid agrees with that found by Jones and McLaren (10) and the band positions have been used in Table II in the column giving their assignment. The infrared spectrum of solid CD_3COONa is the same as that previously reported (10), and bands were observed at 2267 (m), 2288 (w), 1546 (s), 1408 (s), 1084 (w), 1043 (w), 940 (m), 883 (w), and 833 (m) cm^{-1} in the infrared spectrum of CD_3COONa in H_2O . In Table II the assignment for CH_3COO^- (solid) by Jones and McLaren

TABLE II
VIBRATIONAL ASSIGNMENT OF THE ACETATE ION

C_{2v}	$\begin{pmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{CH}_3 \end{pmatrix}^-$	CH_3COO^- (solid) ^a Jones, McLaren	CH_3COO^- (solution) This work	CH_3NO_2 (gas) Wells, Wilson	CD_3COO^- (solution) This work	Teller-Redlich product rule ratios	
						Obs.	Theor.
a_1	ν_1	C—H stretching	2936	2935 (P)	2965	2111 (P)	
	ν_2	CH_3 deformation	1430	1344 (P)	1413	1085 (P)	
	ν_3	C—O stretching	1414	1413 (P)	1384	1406 (P)	1.91
	ν_4	C—C stretching	924	926 (P)	921	883 (P)	
	ν_5	COO deformation	646	650 (P)	647	619 (P)	
a_2	ν_6	Torsion	—	—	—	—	
b_1	ν_7	C—H stretching	2989	3010 (D) or 2981 (D)	3048	2264 (D) or 2231 (D)	
	ν_8	C—O stretching	1578	1556	1582	1545 (D)	
	ν_9	CH_3 deformation	1443	1429 (D)	1449	1047 (D)	2.53
	ν_{10}	CH_3 rocking	1009	1020	1097	832 (D?)	
	ν_{11}	COO rocking (in-plane)	460	471 (D)	476	419 (D)	
b_2	ν_{12}	C—H stretching	2989	2981 (D) or 3010 (D)	3048	2231 (D) or 2264 (D)	
	ν_{13}	CH_3 deformation	1498	1456 (D)	1488	1031 (D)	2.49
	ν_{14}	CH_3 rocking	1042	1052	1153	940	
	ν_{15}	COO rocking (out-of-plane)	615	621 (D)	599	526 (D)	

^aIn this assignment the frequencies measured here have been used.

(but using our measured frequencies), that for CH_3NO_2 by Wells and Wilson (17), and the present assignments for CH_3COO^- and CD_3COO^- are given. The assignments are based on C_{2v} point group symmetry (17). The new information provided by the above spectra and comparison with the fundamentals of the isoelectronic CH_3NO_2 molecule have been the basis for the present assignment and as can be seen from Table II it differs from that of Jones and McLaren for CH_3COO^- in several respects. In particular, ν_2 , the fairly strong polarized Raman band at 1344 cm^{-1} , is taken as a fundamental here instead of the rather weak infrared band at 1498 cm^{-1} which is not observed in the Raman spectrum. This band at 1498 cm^{-1} is then to be interpreted as a difference tone (see Table III). The present assignments for ν_2 and ν_3 were confirmed from the depolarization ratios and comparison of the Raman spectra of CH_3COO^- and CD_3COO^- . Other changes are to assign the band at 1429 cm^{-1} , which is found to be depolarized, as ν_9 and the band at 1443 cm^{-1} in the infrared spectrum of the solid as ν_{13} . One other small

modification is introduced by the fact that three bands in the CH stretching region are observed in the infrared and Raman spectra of the solution whereas there are only two in the infrared spectrum of the solid (see Fig. 1). Assuming all three to be fundamentals, ν_1 is readily assigned because of its depolarization ratio but a choice is left for ν_7 and ν_{12} as indicated in Table II.

Of the two COO rocking modes ν_{11} and ν_{15} the higher was taken as the out-of-plane mode ν_{15} , since it was expected that the π electron cloud in the COO⁻ group accumulating in the direction perpendicular to the COO⁻ plane gives rise to more repulsion in the potential energy function for the out-of-plane mode than for the in-plane mode. The moment of inertia argument used by Wells and Wilson for the corresponding assignment in CH₃NO₂ leads to this result also (which was recognized also by Jones and McLaren in their assignment).

Our assignment for CD₃COO⁻ is essentially the same as that reported by Jones and McLaren except for the CD stretching modes. From Raman spectrum and depolarization ratios (see Table I) the band at 2231 cm.⁻¹

TABLE III
COMBINATION AND DIFFERENCE FREQUENCIES FOR INFRARED BANDS OF CH₃COO⁻

Aqueous solution		Solid (Na salt)		Assignment	Irred. representation
Obs.	Calc.	Obs.	Calc.		
2746	2757	2740	2752	$\nu_2 + \nu_3$	A ₁
2668	2688	2653	2676	$2 \times \nu_2$	A ₁
2583	2576	2605	2587	$\nu_8 + \nu_{10}$	A ₁
		2557	2550	$\nu_7 - \nu_{11}$	A ₁
2486	2482	2495	2499	$\nu_8 + \nu_4$	B ₁
2416	2433	2424	2423	$\nu_3 + \nu_{10}$	B ₁
1911	1915		1927	$\nu_1 - \nu_{10}$	B ₁
1693	1702		1688	$\nu_5 + \nu_{14}$	B ₂
		1498	1506	$\nu_1 - \nu_2$	A ₁
			1493	$\nu_1 - \nu_9$	B ₁
1289*	1300	1300	1292	$2 \times \nu_5$	A ₁
1277	1271	1254	1261	$\nu_5 + \nu_{15}$	B ₂

*Observed in the Raman spectrum.

assigned by the above authors to ν_1 must be either ν_7 or ν_{12} . In Table III the combination bands for CH₃COO⁻ observed in the infrared spectrum are given with plausible assignments.

The present assignments for light and heavy acetate ion (solution) are consistent with the product rule as shown in the last column of Table II. The theoretical ratios are taken from the paper of Jones and McLaren (10) which were calculated using dimensions of the solid ion. Since these ratios are very insensitive to small changes in molecular dimensions they will be very nearly the same for the solid ion and the ion in solution.

Oxalate Ion

The Raman spectrum of a saturated solution of potassium oxalate in H₂O is shown in Fig. 2 and the Raman data given in Table IV. The infrared spectrum of saturated solutions of potassium and cesium oxalate in H₂O

and D_2O is shown also in Fig. 2. The frequencies of the fundamentals are given in Table IV and those of the combination bands in Table V. The infrared spectrum of solid sodium oxalate is listed in Table IV (fundamentals) and

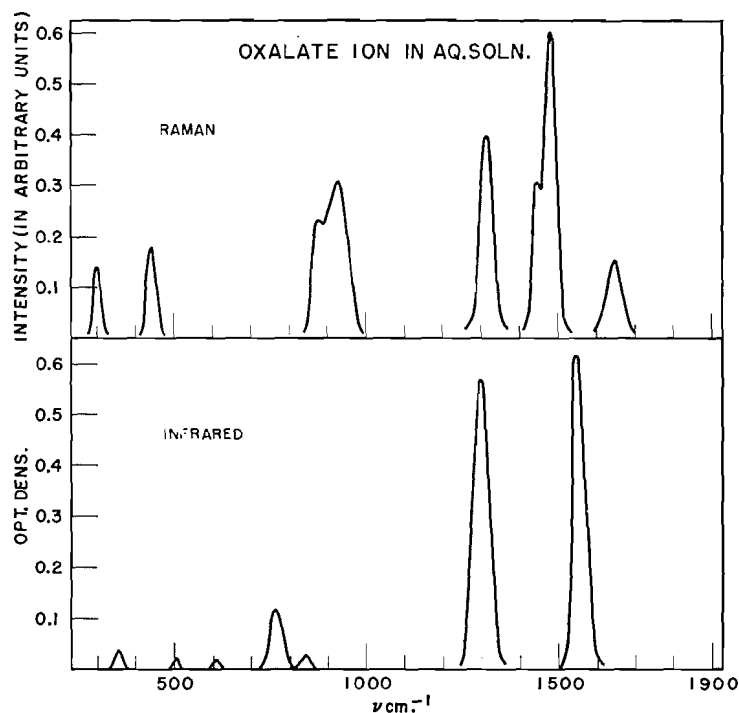


FIG. 2. The Raman and infrared spectra of the oxalate ion.

Table V (combination tones). The principal difference between the solid and solution infrared spectra is that the band at 507 cm^{-1} in the solid is by

TABLE IV
VIBRATIONAL ASSIGNMENT OF THE OXALATE ION

Irrad. rep. (D_{2h})	$\begin{pmatrix} \text{O} & \text{C} & \text{O} \\ \diagdown & & \diagup \\ \text{O} & \text{C} & \text{O} \end{pmatrix}^{--}$	$\text{C}_2\text{O}_4^{--}$			Na_2O_4 gas	Previous assignment for $\text{C}_2\text{O}_4^{--}$ by Lecomte <i>et al.</i>	
		Solid Na salt	Aq. soln.	Dep. ratio			
a_{1g}	ν_1 C—O stretching		1488	0.3 (P)	1360	~ 1480	Raman active
	ν_2 COO deformation		904	0.1 (P)	813	~ 900	
	ν_3 C—C stretching		445	0.5 (P)	283	~ 320	
b_{1g}	ν_4 C—O stretching		1660	0.8 (D)	1724	~ 1640	
	ν_5 COO rocking (in-plane)		300	0.8 (D)	500	525–575	
b_{2g}	ν_6 COO rocking (out-of-plane)		1305	0.8 (D)	(1480)	~ 450	Infrared active
a_{1u}	ν_7 Torsion		—	—	—	—	
b_{1u}	ν_8 COO rocking (out-of-plane)	507	500	—	(680)	665	
b_{2u}	ν_9 C—O stretching	1640* 1405 }	1555	—	1749	1500–1600	
	ν_{10} COO rocking (in-plane)		(160)	—	380	~ 370	
b_{3u}	ν_{11} C—O stretching	1319	1300	—	1265	1200–1300	
	ν_{12} COO deformation	766	766	—	752	750–800	

*Split by the Fermi resonance into two bands with equal intensity.

far the strongest band in this region, whereas in solution it is weak (at 500 cm^{-1}) and comparable in intensity to the bands at 361 and 605 cm^{-1} . Because of its strong absorption in the solid this band was chosen as a fundamental. Another feature in the infrared spectrum of the solid is the doublet

TABLE V
COMBINATION AND DIFFERENCE FREQUENCIES FOR THE INFRARED BANDS OF $\text{C}_2\text{O}_4^{--}$

Aqueous solution		Solid Na salt, obs.	Assignment	Irred. rep.
Obs.	Calc.			
		3134		
		3054		
	2960	2935	$\nu_4 + \nu_{11}$	B_{2u}
2860		2862	?	
2782	2788	2767	$\nu_1 + \nu_{11}$	B_{3u}
2604	2605		$\nu_6 + \nu_{11}$	B_{1u}
2474		2479	?	
		1885	?	
1452*	1460		$\nu_{10} + \nu_{11}$	B_{1g}
	1255	1249	$\nu_9 - \nu_5$	B_{3u}
		1029	?	
	894	898	$\nu_4 - \nu_{12}$	B_{2u}
		873	?	
888*	890		$2\nu_3$	A_{1g}
846	855	854	$\nu_{11} - \nu_3$	B_{3u}
605	605	611	$\nu_3 + \nu_{10}$	B_{2u}
	539	533	$\nu_6 - \nu_{12}$	B_{1u}
361	360	363	$\nu_4 - \nu_{11}$	B_{3u}

*Observed in the Raman spectrum.

1405 and 1640 cm^{-1} which may be explained on the basis of Fermi resonance of ν_9 (b_{2u}) with $\nu_{11} + \nu_5$ (B_{2u}). In solution, only one strong band at 1555 cm^{-1} is observed. The oxalate ion has D_{2h} symmetry in the solid sodium salt (9) and is assumed to have the same symmetry in solution. This is borne out by the infrared and Raman spectra which exhibit the character of mutual exclusion. In Table IV the assignment for $\text{C}_2\text{O}_4^{--}$ is given for the solid and solution made on the basis of the selection rules, depolarization ratios, and comparison with the spectrum of isoelectronic N_2O_4 (15). In the last column of the table the previous assignment of Lecomte *et al.* (2) is given for comparison. Since our infrared investigation covered a larger region than that investigated previously (2) and since our depolarization data are more complete than those of an earlier investigation (8), several differences between the present and the earlier (2) assignments are not unexpected. In particular the depolarization ratio of the band at 445 cm^{-1} established it as ν_3 . By analogy with N_2O_4 the other low lying Raman band is ν_5 and the high one at 1305 cm^{-1} is then ν_6 . The band at 665 cm^{-1} reported by Lecomte *et al.* (2) occurring in the region of CO_2 absorption was not observed here. As ν_8 we choose the strong infrared band (solid) at 507 cm^{-1} . The ν_{10} mode was calculated here as $\sim 160 \text{ cm}^{-1}$ and estimated previously (2) to be $\sim 370 \text{ cm}^{-1}$. The calculation for ν_{10} follows from the Urey Bradley treatment by Shimanouchi *et al.* (12) for D_{2h} molecules. Here it was shown that the ratio of the product of the two b_{1g} frequencies to

that of the two b_{2u} frequencies is a function of masses and geometry only and independent of force constants if the interaction between COO groups on different C atoms is neglected. The structural parameters used to calculate this ratio are given below (9):

$$\nu_{CC} = 1.56 \text{ \AA}, \nu_{CO} = 1.24 \text{ \AA}, \angle OCO = 125^\circ.$$

The value of $\nu_{10} = 160 \text{ cm}^{-1}$ is further supported by the assignment of two observed combination tones at 1452 cm^{-1} in the Raman spectrum and 605 cm^{-1} (solution), 611 cm^{-1} (solid) in the infrared spectrum. Other interpretations of these bands are not readily forthcoming.

In Table V the combination bands observed in the infrared spectrum are listed with plausible assignments. The bands at 2862 , 2479 , 1885 , 1029 , and 873 cm^{-1} in the infrared spectrum of the solid cannot be interpreted in terms of binary combinations of the listed fundamentals.

Formate Ion

The Raman spectrum of a saturated solution of potassium or sodium formate in H_2O is shown in Fig. 3 and the frequencies and depolarization ratios

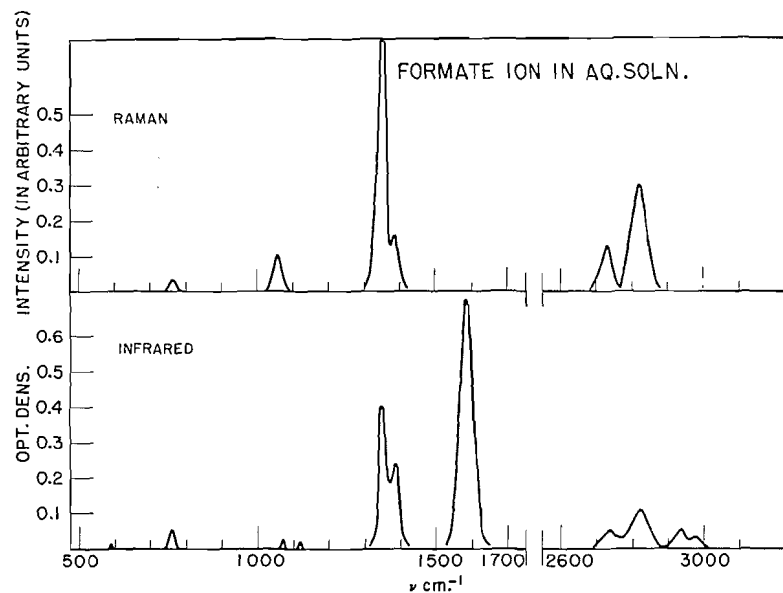


FIG. 3. The Raman and infrared spectra of the formate ion.

given in Table VI. The infrared spectrum of a saturated solution of these salts in H_2O and D_2O is given also in Fig. 3 and the frequencies in Table VI (fundamentals) and Table VII (combination tones). The infrared spectrum of solid sodium formate is given in Table VI (fundamentals) and in Table VII (combination tones).

The present assignment for the formate ion made on the basis of C_{2v} symmetry and the measured depolarization ratios is given in Table VI.

Of the two rocking frequencies, ν_5 and ν_6 , the higher one might be expected to be the out-of-plane mode analogous to the acetate and oxalate ions but these were assigned as shown in the table because of the results of Newman (13) obtained from the polarized infrared spectra of solid sodium formate. The present assignment for the aqueous solution is the same as that by

TABLE VI
VIBRATIONAL ASSIGNMENT OF THE FORMATE ION

Irrad. repta.	$\left(\begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{C}-\text{H} \end{smallmatrix}\right)^{-}$	Raman $\Delta\nu$	Infrared			
			Dep. ratio (aq. soln. of K salt)	ν (aq. soln. of K salt)	ν (solid Na salt) This work	ν (solid Na salt) Newman
a_1	ν_1 C—H stretching	2803	0.37 (P)	2803	2841	2870
	ν_2 C—O stretching	1349	0.29 (P)	1351	1366	1377
b_1	ν_3 COO deformation	762	0.43 (P)	760	772	784
	ν_4 C—O stretching			1585	1567	1620
b_2	ν_5 COO rocking (C—H bending, in-plane)	1380	0.80 (D)	1383	1377	1365
	ν_6 COO rocking (C—H bending, out-of-plane)	1066	0.83 (D)	1069	1073	1070

Fonteyne (7) which was made on the basis of the Raman spectrum of the light and heavy formate ion in aqueous solution without measuring the depolarization ratios. Newman's assignments (last column of Table VI) of

TABLE VII
COMBINATION AND DIFFERENCE FREQUENCIES FOR THE INFRARED BANDS OF HCOO^-

Aqueous solution				Solid (Na salt)		
Obs.	Calc.	Assign-ment	Irrad. rep.	Obs.	Calc.	Assignment
				4313	4319	$2953 + \nu_2$
4180	4186	$\nu_1 + \nu_5$	B_1	4200	4218	$\nu_1 + \nu_5$
4091	4111	$2728 + \nu_5$	A_1	4085	4097	$2720 + \nu_5$
				3611	3613	$\nu_1 + \nu_3$
3181	3178	$2\nu_4$	A_1	3190	3194	$2\nu_4 + 60$
				3070	3074	$2\nu_4 - 60$
2974	2972	$\nu_4 + \nu_5$	A_1	2953	2944	$\nu_4 + \nu_5$
				2791	2781	$\nu_1 - 60$
2728	2734	$\nu_2 + \nu_5$	B_1	2720	2743	$\nu_2 + \nu_5$
				2599	2600	$2720 - 2 \times 60$
2415	2420	$\nu_2 + \nu_6$	B_2	2435	2439	$\nu_2 + \nu_6$
				2134	2138	$\nu_2 + \nu_3$
				1700	1707	$\nu_4 + 140$
				1620	1627	$\nu_1 + 60$
				1514	1517	$\nu_5 + 140$
				1226	1237	$\nu_5 - 140$
				1013	1013	$\nu_5 - 60$
				958	953	$\nu_6 - 2 \times 60$
				923	930	$\nu_6 - 140$
				898	892	$\nu_3 + 2 \times 60$
				840	832	$\nu_3 + 60$

the a_1 C—O stretching and the b_1 COO rocking were reversed as shown in the seventh column of Table VI because of the analogy with the corresponding fundamentals in the aqueous solution.

The infrared spectra of solid sodium formate were obtained of the solid films deposited from H_2O , a mixture of H_2O and CH_3OH , or a mixture of H_2O and acetone, on AgCl and NaCl plates. All solid samples were dried over P_2O_5 in a desiccator and had no absorption band in the O—H stretching region, $3100\text{--}3800\text{ cm}^{-1}$, showing that the samples were indeed anhydrous. The infrared spectra of these samples seemed to change slightly from sample to sample depending on the method of preparation, in contrast to the infrared spectra of the acetate and oxalate salts. In particular the ν_1 C—O stretching mode shows a rather complicated behavior and has two bands at 1567 cm^{-1} and 1514 cm^{-1} in some samples. The intensity of the latter band was increased by dehydration in a desiccator and was even stronger in some cases than that at higher wave numbers. However, the band at 1567 cm^{-1} was assigned as a fundamental by analogy with the fundamentals for the aqueous solution. The band at 1620 cm^{-1} which was assigned as a fundamental by Newman was observed only in some samples as a weak band or a small shoulder.

Table VII shows the combination and difference bands observed in the infrared spectrum and a possible assignment. In the case of the infrared spectrum of the solid, it is necessary to assume lattice vibrational modes coupling with the internal vibrational modes of the formate ion in order to explain the observed combination bands satisfactorily. Two lattice frequencies at 140 cm^{-1} and 60 cm^{-1} have been assumed in the seventh column of Table VII which are used to interpret 13 of the 21 combination tones. There are several possible choices of the assignments for some bands in the solid infrared spectrum but only one is shown rather arbitrarily.

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