Table 2. Previous assignments of mid i.r. absorptions in rare-earth acetates and formates*

Acetate absorption band (range)	Assignments Moeller[1]	Patel[3], Nakamoto[4]	Grigor'ev[2]
1545–1565	$\nu_{asy}COO$	$\nu_{asy}COO$	$\nu_{asy}COO$
1440–1462	$\nu_{sym}COO$	$\delta_{asy}CH_3$	$\nu_{sym}COO$
1425–1430		$\nu_{sym}COO$	$\nu_{sym}COO$
1375–1377	ν_{C-C}	$\delta_{sym}CH_3$	
1338–1345	$\rho_r COO$		
1050–1057	$\rho_r CH_3$	$\rho_r CH_3$	
1010–1020			
935–948	ν_{CC}	ν_{CC}	ν_{CC}
660–670	δ_{COO}	δ_{COO}, or π_{COO}	π_{COO}
606–620		π_{CH}	

Formate absorption band (range)	Assignments Nakamoto[4]	Saralidze *et al.*[5]
1585–1600	$\nu_{asy}COO$	$\nu_{asy}COO$
1400–1440	$\rho_r COO$ δ_{CH}	π_{CH} in-plane
1360	$\nu_{sym}COO$	$\nu_{sym}COO$
1070	π_{COO} or π_{CH}	π_{CH}
780	δ_{COO}	π_{COO}

*Note – Nakamoto's results based on sodium salts.

parison the absorptions for the sodium salts are included. It may be observed that the heavier rare-earth acetates and formates manifest absorptions at higher frequencies than the absorptions of the sodium salts, which have been assigned as ionic lattice modes. This is similar to the observations made in the low-frequency region for the anhydrous rare-earth carbonates[9] and nitrates[10]. The trend in the position of the strong vibrations appears to shift with increasing mass of the rare-earths (e.g., Eu < Tb < Er in the acetates and La < Nd in the formates) as expected for a metal–oxygen bond of high covalent character. These absorptions were found to be unaffected upon application of high external pressures and thus, demonstrated non-lattice like behavior. As a consequence, these absorptions are assigned to the metal–oxygen stretching vibrations. At least two such absorptions occur for each salt as would be expected for ν metal-oxygen vibrations in a chelated-type structure. Contributing evidence comes from the separation of $\nu_{asym}COO$ and $\nu_{sym}COO$ vibrations. It would be expected that this

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10. A. Walker and J. R. Ferraro, *J. chem. Phys.* **43**, 2689 (1965).

Table 3. Assignments for $Eu(OOCCH_3)_3$, $Eu(OOCCD_3)_3$ and $La(OOCH)_3$, $La(OOCD)_3$ based on deuteration studies

$Eu(OOCCH_3)_3$	$Eu(OOCCD_3)_3$	Assignment	$La(OOCH)_3$	$La(OOCD)_3$	Assignment
2980(w)		ν(CH)	2856(w)		ν(CH)
2930(w)					
	2265(w)	ν(CD)		2208(w)	ν(CD)
	2230(w)				
1542(vs)	1542(vs)	δ(COO) asym.	1605(vs)	1585(vs)	ν(COO) asym.
1430(vs)		$\delta(CH_3)$ asym.	1580(vs)	1550(vs)	
1410(sh)	1410(vs)	δ(COO) sym.	1428(vs)		δ(CH)
			1405(vs)		
1340(m)		$\delta(CH_3)$ sym.	1358(s)	1334(s)	ν(COO) sym.
1230(w)				1328(s)	
				1056(m)	ν(CD)
	1088(w)	$\delta(CD_3)$ asym.	779(s)	770(m)	δ(OCO)
1050(w)					
	1030(w)	$\delta(CD_3)$ sym.			
1018(m)		$\rho_r CH_3$			
950(w)			262(s)	280(s, v. br)	ν_{MO}
942(w)	930(s)	ν_{C-C}	238(vs)		
	900(m)				
	848(s)	$\rho_r CD_3$	167(vs)		
			150(m)		
680(m)		π_{CH}	121(s)		
668(m)					
644(sh)	640(s)	δ_{OCO}			
614(m)	620(s)				
	530(m)	π_{CD}			
501(w)					
473(vw)	450(w), 430(w)				
266(s)					
220(m, sh)	262(vs, v. br)	ν_{M-O}			
205(vvw)	205(vvw)				
185(m)					
154(m)					

Table 4. Low-frequency absorptions for several rare-earth acetates and formates

$Y(OAc)_3$	$Eu(OAc)_3$	$Tb(OAc)_3$	$Er(OAc)_3$	Na(OAc)	$La(OOCH)_3$	$Nd(OOCH)_3$	Na(OOCH)
315(vs)							
			292(sh)		262(s)	282(vs)	
260(m)	266(s)	276(s)	280(s)		238(vs)	240(vs)	
		258(w, sh)	260(w, sh)			183(w, sh)	
217(m)	220(sh)	225(w)	229(w)		167(s)		195(v. br)
	205(vvw)	205(vvw)		200(v. br)	150(m)	163(vs)	
165(sh)	185(m)	192(m)	194(m)				
156(m)	154(m)	160(m)	166(m)		121(m)	133(m)	
123(w)		133(w)	138(m)				
116(vw)		110(vw)					

Abbreviations: s = strong; m = medium; w = weak; v = very; br = broad; sh = shoulder.