

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	$\nu_{\text{asy}}\text{COO}$	$\nu_{\text{asy}}\text{COO}$	$\nu_{\text{asy}}\text{COO}$
1440-1462	$\nu_{\text{sym}}\text{COO}$	$\delta_{\text{asy}}\text{CH}_3$	$\nu_{\text{sym}}\text{COO}$
1425-1430		$\nu_{\text{sym}}\text{COO}$	$\nu_{\text{sym}}\text{COO}$
1375-1377}	$\nu_{\text{C}-\text{C}}$	$\delta_{\text{sym}}\text{CH}_3$	
1338-1345}	$\rho_r\text{COO}$		
1050-1057}	$\rho_r\text{CH}_3$	$\rho_r\text{CH}_3$	
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 <i>et al.</i> [5]	
1585-1600	$\nu_{\text{asy}}\text{COO}$	$\nu_{\text{asy}}\text{COO}$	
1400-1440	$\rho_r\text{COO}$	π_{CH} in-plane	
	δ_{CH}		
1360	$\nu_{\text{sym}}\text{COO}$	$\nu_{\text{sym}}\text{COO}$	
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., $\text{Eu} < \text{Tb} < \text{Er}$ in the acetates and $\text{La} < \text{Nd}$ 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 $\nu_{\text{asy}}\text{COO}$ and $\nu_{\text{sym}}\text{COO}$ vibrations. It would be expected that this

9. J. R. Ferraro, A. Quattrochi, K. C. Patil and C. N. R. Rao, *J. inorg. nucl. Chem.* **31**, 3667 (1969).
 10. A. Walker and J. R. Ferraro, *J. chem. Phys.* **43**, 2689 (1965).

Table 3. Assignments for $\text{Eu}(\text{OOCCH}_3)_3$, $\text{Eu}(\text{OOC}^2\text{D}_3)_3$ and $\text{La}(\text{OOCH})_3$, $\text{La}(\text{OOC}^2\text{D})_3$ based on deuteration studies

$\text{Eu}(\text{OOCCH}_3)_3$	$\text{Eu}(\text{OOC}^2\text{D}_3)_3$	Assignment	$\text{La}(\text{OOCH})_3$	$\text{La}(\text{OOC}^2\text{D})_3$	Assignment
2980(w)		$\nu(\text{CH})$	2856(w)		$\nu(\text{CH})$
2930(w)					
	2265(w)	$\nu(\text{CD})$		2208(w)	$\nu(\text{CD})$
	2230(w)				
1542(vs)	1542(vs)	$\delta(\text{COO})$ asym.	1605(vs)	1585(vs)}	$\nu(\text{COO})$ asym.
1430(vs)		$\delta(\text{CH}_3)$ asym.	1580(vs)	1550(vs)}	
1410(sh)	1410(vs)	$\delta(\text{COO})$ sym.	1428(vs)		$\delta(\text{CH})$
			1405(vs)		
1340(m)		$\delta(\text{CH}_3)$ sym.	1358(s)	1334(s)}	$\nu(\text{COO})$ sym.
1230(w)				1328(s)}	
	1088(w)	$\delta(\text{CD}_3)$ asym.	779(s)	1056(m)	$\nu(\text{CD})$
1050(w)				770(m)	$\delta(\text{OCO})$
	1030(w)	$\delta(\text{CD}_3)$ sym.			
1018(m)		$\rho_r\text{CH}_3$			
950(w)			262(s)	280(s, v. br)	} ν_{MO}
942(w)	930(s)	$\nu_{\text{C}-\text{C}}$	238(vs)		
	900(m)				
	848(s)	$\rho_r\text{CD}_3$	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)		} $\nu_{\text{M}-\text{O}}$			
220(m, sh)	262(vs, v. br)}				
205(vvw)	205(vvw)				
185(m)					
154(m)					

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

$\text{Y}(\text{OAc})_3$	$\text{Eu}(\text{OAc})_3$	$\text{Tb}(\text{OAc})_3$	$\text{Er}(\text{OAc})_3$	$\text{Na}(\text{OAc})$	$\text{La}(\text{OOCH})_3$	$\text{Nd}(\text{OOCH})_3$	$\text{Na}(\text{OOCH})$
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.