

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

| Acetate<br>absorption<br>band<br>(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}                               | $\rho_{\text{r}}\text{COO}$  |   |                              |
| 1050-1057}                               | $\rho_{\text{r}}\text{CH}_3$ | $\rho_{\text{r}}\text{CH}_3$                      |                              |
| 1010-1020}                               |                              |   |                              |
| 935-948                                  | $\nu_{\text{CC}}$            | $\nu_{\text{CC}}$                                 | $\nu_{\text{CC}}$            |
| 660-670                                  | $\delta_{\text{COO}}$        | $\delta_{\text{COO}}$<br>or<br>$\pi_{\text{COO}}$ | $\pi_{\text{COO}}$           |
| 606-620                                  |                              | $\pi_{\text{CH}}$                                 |                              |

  

| Formate<br>absorption<br>band<br>(range) | Assignments                             |                              |
|--|---|------------------------------|
|  | Nakamoto[4]                             | Saralidze <i>et al.</i> [5]  |
| 1585-1600                                | $\nu_{\text{asy}}\text{COO}$            | $\nu_{\text{asy}}\text{COO}$ |
| 1400-1440                                | $\rho_{\text{r}}\text{COO}$             | $\pi_{\text{CH}}$ in-plane   |
|  | $\delta_{\text{CH}}$                    |                              |
| 1360                                     | $\nu_{\text{sym}}\text{COO}$            | $\nu_{\text{sym}}\text{COO}$ |
| 1070                                     | $\pi_{\text{COO}}$ or $\pi_{\text{CH}}$ | $\pi_{\text{CH}}$            |
| 780                                      | $\delta_{\text{COO}}$                   | $\pi_{\text{COO}}$           |

\*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  $\nu$  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  $\text{Eu}(\text{OOCCH}_3)_3$ ,  $\text{Eu}(\text{OOC}(\text{CD}_3)_3$  and  $\text{La}(\text{OOCH})_3$ ,  $\text{La}(\text{OOC}(\text{CD}_3)_3$  based on deuteration studies

| $\text{Eu}(\text{OOCCH}_3)_3$ | $\text{Eu}(\text{OOC}(\text{CD}_3)_3$ | Assignment                  | $\text{La}(\text{OOCH})_3$ | $\text{La}(\text{OOC}(\text{CD}_3)_3$ | 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)}                              |                         |
| 1050(w)                       | 1088(w)                               | $\delta(\text{CD}_3)$ asym. | 779(s)                     | 1056(m)                               | $\nu(\text{CD})$        |
|                               |                                       |                             |                            | 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)}                        | $\nu_{\text{MO}}$       |
| 942(w)                        | 930(s)                                | $\nu_{\text{C-C}}$          | 238(vs)                    |                                       |                         |
|                               | 900(m)                                |                             |                            |                                       |                         |
|                               | 848(s)                                | $\rho_r\text{CD}_3$         | 167(vs)                    |                                       |                         |
|                               |                                       |                             | 150(m)                     |                                       |                         |
| 680(m)                        |                                       | $\pi_{\text{CH}}$           | 121(s)                     |                                       |                         |
| 668(m)                        |                                       |                             |                            |                                       |                         |
| 644(sh)                       | 640(s)}                               | $\delta_{\text{OCO}}$       |                            |                                       |                         |
| 614(m)                        | 620(s)}                               |                             |                            |                                       |                         |
|                               | 530(m)                                | $\pi_{\text{CD}}$           |                            |                                       |                         |
| 501(w)                        |                                       |                             |                            |                                       |                         |
| 473(vw)                       | 450(w), 430(w)                        |                             |                            |                                       |                         |
| 266(s)                        | 262(vs, v. br)}                       | $\nu_{\text{M-O}}$          |                            |                                       |                         |
| 220(m, sh)                    |                                       |                             |                            |                                       |                         |
| 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(vw)                   | 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.