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Lattice Vibrations in $M(CH_3COO)_2 \cdot 4H_2O/D_2O$, M = Mg, Co, and Ni

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Infrared and Raman spectra in the region 450–40 cm^{-1} are reported for the compounds $M(CH_3COO)_2 \cdot 4H_2O$, M = Mg, Co, and Ni and their deuterates at temperatures 300 and 95 K (130 K for Raman). The observed bands are assigned in the light of known crystal data and group theoretical analysis. It is shown that translations of H_2O, CH_3COO^-, and M^{2+} can be treated as internal vibrations of MO_6 complex having symmetry D_{4h}. © 1985 Academic Press, Inc.

Introduction

The salts $M(CH_3COO)_2 \cdot 4H_2O$ with M = Mg, Co, and Ni are isostructural (*1, 2*) and a comprehensive vibrational study by infrared and Raman (4000–400 cm^{-1}) in the temperature range 300 to 95 K (130 K for Raman) was undertaken to understand the dynamics of the system (*3, 4*). The earlier Raman study (*5*) of the region below 450 cm^{-1} was limited to the identification of a few lattice modes. Since no comprehensive study of the modes in this region has yet been reported, we present here our results with critical analysis and assignments in the light of known crystal structure and group theoretical predictions.

Experimental

The method of purifying the samples, preparation of their deuterates, and observing temperature-dependent infrared (450–200 cm^{-1}) and Raman (450–40 cm^{-1}) spectra have been described elsewhere (*3, 4*). The Co and Ni salts are highly absorbent in the concerned region. Hence the technique of rotating the samples with respect to the laser beam was used to obtain better quality Raman spectra. The far-infrared spectra were recorded on a Polytech FIR-30 spectrophotometer at the Regional Sophisticated Instrumentation Centre, IIT, Madras. This could only be done for the Co and Ni salts at room temperature. Typical infrared spectra of the hydrates and the deuterates at 95 K are shown in Fig. 1. The Raman spectra of the hydrates and deuterates at 300 K are shown in Fig. 2, where the 130 K spectra are also shown for the Mg salt. The wavenumbers of the observed bands and their assignments are given in Table I.

Crystal Structures of the Salts

The salt $Mg(CH_3COO)_2 \cdot 4H_2O$ was found (*1*) to be isostructural with the cor-

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TABLE I

WAVENUMBERS (cm^{-1}), QUALITATIVE INTENSITIES[a] AND ASSIGNMENTS OF THE LATTICE MODES (450–40 cm^{-1}) OBSERVED IN $M(CH_3COO)_2 \cdot 4H_2O$ (M = Mg, Co, AND Ni)

	ir/fir[b]				Raman					
	Hydrate		Deuterate		Hydrate		Deuterate			
M	300 K	95 K	300 K	95 K	300 K	130 K	300 K	130 K	Solution[c]	Assignments[d]
1	2	3	4	5	6	7	8	9	10	11
Mg	424 m	440 s	420 m	436 s	—	—	—	—	—	$\nu_3'(E_u)$
Co	358 m	368 s	354 m	364 s	—	—	—	—	—	
Ni	382 m	390 s	372 m	380 s	—	—	—	—	—	
Mg	384 m	394 m	374 s	382 s	—	396 vw	—	—	—	
Co	340 m	348 m	330 s	340 s	338 w,sh	—	—	—	—	
Ni	342 m	352 m	332 s	342 s	—	—	—	—	—	
Mg	338 m	340 m	334 m	338 s	—	—	—	—	—	$\nu_3''(A_{2u})$
Co	280 w	292 m	270 w	280 s	—	—	—	—	—	
Ni	294 m	305 s	280 m	292 s	—	—	—	—	—	
Mg	—	—	—	—	332 s	342 s	328 s	336 s	346 m(P)	$\nu_1'(A_{1g})$
Co	—	—	—	—	362 sh	372 sh	358 sh	—	—	
Ni	—	—	—	—	360 m	366 s	350 m	354 s	360 m(P)	
Mg	—	305 w	—	305 w	292 m	306 m	286 m	302 m	—	$R_z(A_2)$ Acetate libration (twist mode)
Co	—	—	—	—	318 w	320 w	316 w	—	—	
Ni	—	—	—	—	320 m	322 m	318 s	320 s	—	
Mg	278 m	280 m	272 m	274 m	—	—	—	—	—	$\nu_4'(A_{2u})$
Co	280 w,b	280 m,b	278 w,b	278 m,b	—	—	—	—	—	
Ni	280 m	282 m	280 m	280 m	—	—	—	—	—	
Mg	250 m,b	254 m 242 w	235 m,b	245 m 230 w	—	—	—	—	—	$\nu_4''(E_u)$
Co	240 w,b	252 w 240 w	236 w,b	252 w 232 w,sh	—	—	—	—	—	
Ni	250 m,b	266 m 254 m	246 m,b	264 m 250 m	—	—	—	—	—	
Mg	—	—	—	—	256 w,sh	272 w	258 vw	262 w	—	$\nu_5'(B_{2g})$
Co	—	—	—	—	300 m	318 sh	292 sh	—	—	
Ni	—	—	—	—	300 m	310 m	312 m	320 m	—	

Mg	—	—	—	—	246 s	258 s 236 w	240 m	248 s	260 w(D)	$\nu_5''(E_{2g})$
Co	—	—	—	—	250 sh	258 w	240 sh	—	—	
Ni	—	—	—	—	270 b	280 w	280 w 264 vw	280 w 264 v,w	262 w(D)	
Mg	—	222 v,w	—	222 v,w	206 m	216 s	204 m,b	210 m	212 w(P)	$\nu_2'(A_{1g})$
Co	—	—	—	—	222 w	—	—	—	—	
Ni	—	222 v,w	—	—	230 w	232 w	228 w	230 w	—	
Mg	—	—	—	—	—	208 m	204 m,b	204 m	—	$\nu_2''(B_{1g})$
Co	—	—	—	—	202 v,w	202 v,w	—	—	—	
Ni	—	—	—	—	207 m	212 m	198 m	204 m	—	
Mg	b	—	—	—	182 b	184 b	166 b	168 b	—	$\nu_6'(E_{1u})$
Co	182 w	—	—	—	184 b	184 b	164 b	—	—	
Ni	180 w	—	—	—	188 w 174 w	180 b	180 sh 164 w	180 sh 164 w	—	
Mg	b				—	—	—	—	—	$\nu_6''(B_{2u})$
Co	156 m				—	—	—	—	—	
Ni	162 m				158 w	—	—	—	—	
Mg	b				130 sh	130 sh	130 sh	130 sh		$R_y(B_1)$ Acetate libration
Co	126 m				—	—	—	—	—	
Ni	130 m				132 m	132 m	132 m	132 m		
Mg	b				112 s	112 s	112 s	112 s		$\nu_6(A_2)$ (Internal mode of acetate)
Co	112 sh				112 sh	112 sh	112 sh	—		
Ni	118 sh				118 m	118 m	118 m	116 m		
Mg	b				64 w	64 w	64 w	64 w		$R_x(B_2)$ Acetate libration
Co	56 w				60 sh	60 sh	60 sh	—		
Ni	58 sh				58 w	58 w	58 w	58 w		
Mg	b				44 w	44 w	44 w	44 w		Eternal mode of MO_6
Co	46 w				44 w	44 w	44 w	—		
Ni	46 w				44 w	44 w	44 w	44 w		

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[a] Strong (s), medium (m), weak (w), very weak (vw), broad (b), shoulder (sh).

[b] Wavenumbers below 200 cm^{-1} are from far-infrared (fir) data and these could not be obtained for the Mg salt.

[c] (P) and (D) indicate polarized and depolarized nature of bands in solution spectra.

[d] Primes on ν refer to splitting due to D_{4h} symmetry of $MO_6(O_h)$. The ν without prime is internal mode of CH_3COO^-, R_x, R_y, and R_z are the three acetate librations along respective axes.

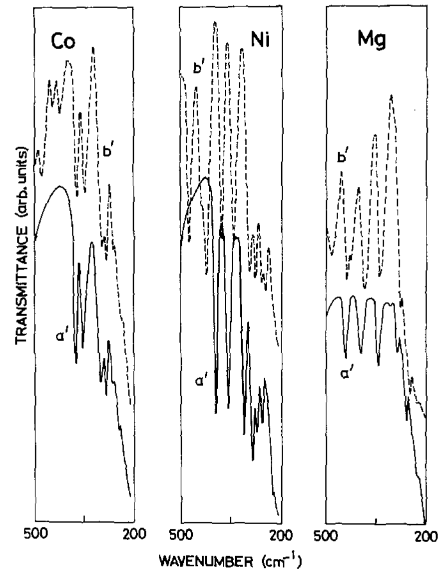

FIG. 1. Infrared spectra (200–500 cm^{-1}) of $M(CH_3COO)_2 \cdot 4H_2O/D_2O$, M = Mg, Co, and Ni, at 95 K (a') hydrate and (b') deuterate.

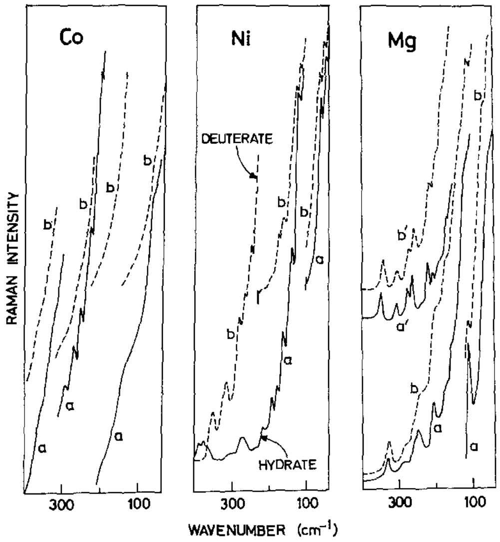

FIG. 2. Raman spectra (40–400 cm^{-1}) of $M(CH_3COO)_2 \cdot 4H_2O/D_2O$, M = Mg, Co, and Ni (a) hydrate and (b) deuterate at 300 K, and (a') hydrate and (b') deuterate at 130 K (400–180 cm^{-1}).

responding Co and Ni salts (*2*). The unit cell is monoclinic and contains two molecules related by the operations of the space group $P2_1/C$ (C^5_{2h}). Two types of crystallographically inequivalent water molecules are identified differing in their hydrogen bonding scheme and HOH angles. The cation (M^{2+}) is at the center of an inversion symmetry and is surrounded by a distorted octahedron of six oxygen atoms—four from two symmetry-related water dipoles and two from different but symmetry-related acetate groups. The distances of six oxygen ligands linked to M^{2+} in these compounds are given in Table II. In the Mg salt the water oxygens form an approximate square, while the acetate oxygens lie above and below this square. In the Co and Ni salts, on the other hand, H_2O(I) oxygens lie above and below the square formed by the oxygens of two H_2O(II) and two carbonyl groups. However, in all the three cases the MO_6 octahedron, which is ideally supposed to have symmetry O_h, appears from our spectral data to have a symmetry D_{4h}. The correlations of the species of the point

TABLE II

METAL–OXYGEN DISTANCES AND IONICITY OF M–O BOND IN $M(CH_3COO)_2 \cdot 4H_2O$ (M = Mg, Co, AND Ni) COMPOUNDS

Compounds	M–OH_2(I) (Å)	M–OH_2(II) (Å)	M–O_{Ac} (Å)	Ref.	Degree of ionicity, Ref. (*10*) (%)
$Mg(CH_3COO)_2 \cdot 4H_2O$	2.07	2.08	2.11	(*1*)	73.4
$Co(CH_3COO)_2 \cdot 4H_2O$	2.06	2.11	2.12	(*2*)	55.5
$Ni(CH_3COO)_2 \cdot 4H_2O$	2.06	2.11	2.12	(*2*)	51.4

groups with those of site and factor group symmetries are given in Tables III and IV.

TABLE III

CORRELATIONS OF THE SPECIES OF THE POINT GROUP WITH THOSE OF SITE AND FACTOR GROUP SYMMETRIES OF H_2O AND CH_3COO^-

	Symmetry species of CH_3COO^- and H_2O [C_{2v}]	Site symmetry (C_1)	Factor group (C_{2h})
Librations	A_2(R) B_1(R,ir) B_2(R,ir)	A(R,ir)	A_g(R) B_g(R) A_u(ir) B_u(ir)
Translations	A_1(R,ir) B_1(R,ir) B_2(R,ir)	A(R,ir)	A_g(R) B_g(R) A_u(ir) B_u(ir)

Results and Discussion

The acetate group in these salts can be assumed to have the symmetry of free water (C_{2v}) as the reorientational barrier about the C–C bond is very low (~114 cm^{-1}) (*6*). The 15 internal modes of the acetate ion fall well above 450 cm^{-1}, except ν_6 which has been assigned at 118 cm^{-1} in the Ni salt (*3*). The internal and librational modes of water also fall above 450 cm^{-1}. Therefore, the modes expected below 450 cm^{-1} are (i) librations of the acetate group, (ii) translations of acetate ion and water, and (iii) translations of M^{2+}. Since the internal modes of acetate and water and the librations of water were assigned in the point group symmetry, the acetate ion librations may also be assigned in its point group symmetry.

TABLE IV

CORRELATION OF THE SPECIES OF O_h GROUP TO THAT OF D_{4h}, SITE (C_i) AND FACTOR GROUP (C_{2h})

Symmetry species of $MO_6(O_h)$ internal modes	Symmetry species (D_{4h})	Site symmetry (C_i)	Factor group (C_{2h})
A_{1g}(R), ν_1	A_{1g}(R), ν'_1	A_g(R)	A_g(R) B_g(R)
E_g(R), ν_2	A_{1g}(R), ν'_2	A_g(R)	A_g(R) B_1(R)
	B_{1g}(R), ν''_2	A_g(R)	A_g(R) B_g(R)
F_{2g}(R), ν_5	B_{2g}(R), ν'_5	A_g(R)	A_g(R) B_g(R)
	E_g(R), ν''_5	$2A_g$(R)	$2A_g$(R) $2B_g$(R)
F_{1u}(ir), ν_3	A_{2u}(ir), ν''_3	A_u(ir)	A_u(ir) B_u(ir)
	E_u(ir), ν''_3	$2A_u$(ir)	$2A_u$(ir) $2B_u$(ir)
F_{1u}(ir), ν_4	A_{2u}(ir), ν'_4	A_u(ir)	A_u(ir) B_u(ir)
	E_u(ir), ν''_4	$2A_u$(ir)	$2A_u$(ir) $2B_u$(ir)
F_{2u}, ν_6	B_{2u},ν'_6	A_u(ir)	A_u(ir) B_u(ir)
	E_{1u}(ir), ν''_6	$2A_u$(ir)	$2A_u$(ir) $2B_u$(ir)

Note. R and ir within parentheses indicate Raman and infrared activities.

Treated as an individual translation, each mode of water is expected to show a frequency shift ratio ~1.05 on deuteration, whereas the observed ratios are much below this in all the observed bands. That would indicate strong coupling of the translations of H_2O (D_2O), CH_3COO^-, and M^{2+}, so that their translations are best treated as the vibrations of the MO_6 moiety, with four oxygens from water (O_w) and two from the acetate group (O_{Ac}). The large number of observed bands would indicate that the symmetry of the MO_6 is lower than O_h and in view of known crystal data (*1*, *2*) it can be taken to be D_{4h}. The correlation of Table III indicates that each translation/libration of the acetate/H_2O group in C_{2v} symmetry generates four phonons $A_g + B_g + A_u + B_u$; the $A_g + B_g$ being Raman active and the other two ($A_u + B_u$) infrared active. The fact that our observations (cf. Table I) show several frequencies occurring exclusively either in Raman or in infrared would mean that the departure of the MO_6 moiety from O_h to D_{4h} symmetry is only marginal.

Although this model is sufficient to interpret the nonpolarized infrared and Raman spectra of polycrystalline samples involving translatory vibrations, it will be insufficient to interpret the polarized vibrational spectra for single crystals where a full factor group analysis has to be carried out considering the Bravias unit cell and its symmetry.

Neglecting the possible correlation field splittings, the $M(CH_3COO)_2 \cdot 4H_2O$ molecule has a total of $81 - 6 = 75$ vibrations. Out of these the internal modes of the acetate ion (15×2) and water (3×4), and water librations (3×4) have been identified earlier (*3*, *4*). Thus only 21 modes are expected in the region below 450 cm^{-1}. The translations of water, acetate ion, and M^{2+} constitute the 15 internal model of MO_6 and the rest, six (3×2), are acetate ion librations. The external modes of MO_6 moiety are expected to fall below 40 cm^{-1}.

The MO_6 moiety having symmetry O_h would have six normal vibrations designated as ν_1(A_{1g}totally symmetric), ν_2(E_{2g}—doubly degenerate), and ν_5(F_{2g}—triply degenerate) active in Raman only, $\nu_3(F_{1u})$ and $\nu_4(F_{1u})$ active in infrared only, while $\nu_6(F_{2u})$ is inactive (*7*). However, in symmetry D_{4h} the degeneracies of the modes are expected to be lifted as shown in Table IV. The site symmetry for MO_6 in the crystal is C_i in which the degeneracy is completely lifted, though the mixing of Raman and infrared active modes is prohibited.

In order to assign the observed bands, we consider the representative example of Mg salt. The assignments of the bands in other salts will follow accordingly. As seen from Table III, except for the infrared inactive twist mode (A_2), all other librations of the acetate group are expected in both the infrared and Raman spectra. The Raman bands at 292, 130, and 64 cm^{-1} are assignable to acetate librations because these bands remain practically undisplaced on deuteration. The small shift (6 cm^{-1}), shown by the band at 292 cm^{-1} may be attributed to the coupling of this acetate libration with the mode of water, since the acetate group is intramolecularly bonded to one of the waters (*1*, *2*). The band at 292 cm^{-1} is absent in the infrared at 300 K, and hence it is assigned to the infrared-forbidden twist mode (R_z, A_2). Its appearance in the infrared spectrum at 95 K as a weak band indicates a distortion in the symmetry, which is consistent with crystal data where C–O distances for the two carbonyl groups in acetate differ substantially (O_1–C_1 = 1.33 Å and O_2–C_1 = 1.25 Å). These distances are almost equal in both the Co and Ni salts (*2*) where this band does not appear in infrared even at 95 K. We also note that the degree of ionicity for Mg–O is 73.4% against 55.5% for Co–O and 51.4% for Ni–O (*10*). Since the M–O_{Ac} bond has the main contribution in the R_z mode, we would expect the large ionicity for Mg–O to reflect in

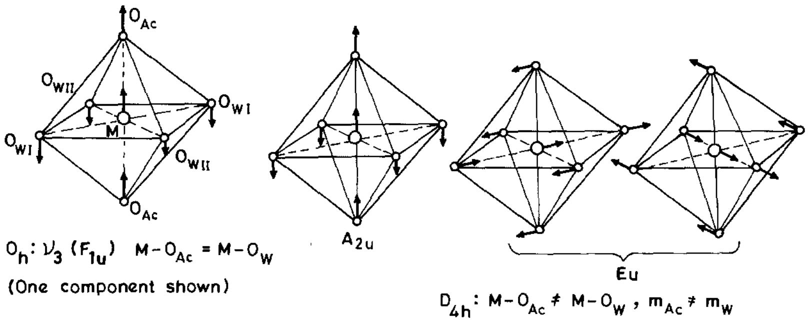

FIG. 3. The splitting of the triply degenerate vibration $\nu_3(F_{1u})$ under O_h into E_u and A_u when symmetry is lowered to D_{4h} [Distance M–O_w < M–O_{Ac}; $\nu(E_u) > \nu(A_u)$].

the lowest frequency of the R_z mode in the Mg salt. This is in agreement with the data, the Co and Ni salts showing R_z at 318 and 320 cm^{-1}, respectively, as against 292 cm^{-1} for Mg salt.

Since the acetate groups are planar and are held together by normal hydrogen bonds (*1, 2*), the out-of-plane libration $R_y(B_1)$ should have higher frequency than the in-plane libration $R_x(B_2)$. This decides the assignments of the 130- and 64-cm^{-1} bands as R_y and R_x, respectively. That none of the acetate librations shows splitting even at low temperature indicates their equivalence in the unit cell with respect to the external field.

The assignments of the 15 internal modes of MO_6 are guided by theoretical calculations of frequencies of the various modes (*7*). In the case of split components of any given mode the detailed designation are based on the expected relative positions and intensities. Accordingly, $\nu_3(F_{1u})$ is expected around 370 cm^{-1}; so that the infrared bands at 424, 384, and 338 cm^{-1}, which gain intensity and show hypsochromic shift in going to 95 K, are assigned as the split components of $\nu_3(F_{1u})$ mode. As seen from Table IV, triply degenerate F_{1u} vibration under O_h splits into doubly degenerate E_u and A_{2u}, both infrared active. Since in these salts MO_6 has two oxygens from the acetate group and four from water, such that M–O_w is smaller than M–O_{Ac} (2.07 Å against 2.12 Å, cf. Table II) the doubly degenerate vibration E_u which involves the stretching of M–O_w (shorter bond) more dominantly shall have higher frequency than A_{2u} which has dominant contribution from M–O_{Ac}. Figure 3 shows the situation. Therefore, the two upper bands at 440 and 395 cm^{-1} in the 95 K infrared spectrum of Mg salt are assigned to $\nu_3'(E_u)$ and the lower band at 340 cm^{-1} to A_{2u}. The Raman band at 332 cm^{-1} is strong and is therefore assigned to the totally symmetric mode $\nu_1'(A_g)$. We notice that there is a corresponding polarized band at 346 cm^{-1} in the solution spectra, where MO_6 is expected to exist even in solutions. That the 332-cm^{-1} band is not the counterpart of the 338-cm^{-1} band in infrared becomes clear by looking at the corresponding cases of Co and Ni salts. If we assign the band at 332 cm^{-1} for the Mg salt to the totally symmetric stretching mode ($\nu_1'(A_g)$), we would expect its wavenumber to be the lowest for the three investigated isostructural compounds. This trend is expected because the M–O bonds are most ionic for M = Mg and the related bands involve M–O stretching.

The $\nu_4(F_{1u})$ mode is expected around 270 (cm^{-1}) (*7*) and would be infrared active (cf. Table IV). Therefore, the infrared bands at 278 and 250 cm^{-1} are assigned to the $\nu_4'(A_{2u})$ and $\nu_4''(E_u)$ split components of ν_4; the doubly degenerate band (E_u) is distinguished from the nondegenerate A_{2u} band because E_u band shows splitting. The MO_6 unit interactions in the unit cell may lift the degeneracy but the splittings may not be observable due to large inherent width of the bands. The sample cooling reduces the half-widths and the split components are observed. The triply degenerate Raman active mode $\nu_5(F_{2g})$ is expected around 251 cm^{-1} and the doubly degenerate $\nu_2(E_g)$ mode around 205 cm^{-1} (*7*). Therefore, the Raman bands at 256 and 246 cm^{-1} are assignable to $\nu''_5(B_{2g})$ and $\nu''_5(E_g)$ components. These assignments are supported by the appearance of the corresponding bands in the solution Raman spectra at 260 cm^{-1}. The $\nu_2(Eg)$ mode shows only one member (206 cm^{-1}) at 300 K, but has split components $\nu'_2(B_{1g})$ and $\nu''_2(A_{1g})$ at 216 and 208 cm^{-1} in the 130 K Raman spectra. The individual assignments to A_{1g} and B_{1g} bands is guided by the relative Raman intensities of the two bands; moreover the solution Raman spectrum shows a polarized band at 212 cm^{-1} corresponding to $\nu''_2(A_{1g})$. Similar basis has been used by Johnson *et al.* (*9*) in assigning vibrations of MO_4 group in various compounds.

The triply degenerate $\nu_6(F_{2u})$ is expected at ~134 cm^{-1} (*7*) and therefore far-infrared bands at 180 and 182 cm^{-1} in Ni salt are assigned to $\nu'_6(E_{1u})$ and $\nu''_6(B_{2u})$ split components, respectively. The Raman band at 112 cm^{-1} has already been identified as ν_6 internal mode of the acetate ion (*3*) and the weak Raman band at 44 cm^{-1} is assigned to the external mode of MO_6. The other external modes are expected below 40 cm^{-1}.

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