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Polarized Raman and Infrared Reflection Spectra of $Cu(HCOO)_2 \cdot 2(NH_2)_2CO \cdot 2H_2O$

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Polarized IR reflection and Raman spectra of $Cu(HCOO)_2 \cdot 2(NH_2)_2CO \cdot 2H_2O$ single crystals have been recorded. The reflection spectra have been analyzed by means of a four-parameter dielectric function. Vibrational bands due to $HCOO^-$, $(NH_2)_2CO$, and H_2O have been identified. The formate ions are found to be identical in the crystal. Fermi resonance between C–H symmetric stretching mode of $HCOO^-$ and combination bands in the region between 2800 and 3000 cm^{-1} is observed. The presence of large urea molecules between copper formate layers is responsible for the lowering of the wavenumber of out-of-plane CH bending and reduction in intensity of the CO asymmetric stretching of $HCOO^-$. © 1990 Academic Press, Inc.

Introduction

Copper formate tetrahydrate (CFT), $Cu(HCOO)_2 \cdot 4H_2O$, its deuterium analogue $Cu(HCOO)_2 \cdot 4D_2O$, and the anhydrous sample $Cu(HCOO)_2$ have been studied extensively because of its interesting antiferroelectric and antiferromagnet properties (*1*, *2*). The interlayer water molecules of CFT when substituted by larger urea molecules, the antiferromagnet copper formate bis-urea dihydrate (CFUH), $Cu(HCOO)_2 \cdot 2(NH_2)_2CO \cdot 2H_2O$, is obtained. Its structural analysis (*3*) has already been reported. A vibrational spectral analysis of the compound is expected to reveal the effect of substitution of two interlayer water molecules in CFT by large urea molecules and the distribution of vibrational energy levels in its crystal lattice.

Experimental

Single crystals of CFUH are grown from saturated aqueous solutions of CFT and urea by the evaporation method (*3*, *4*). Saturated aqueous solution of CFT is prepared by dissolving $CuCO_3 \cdot Cu(OH)_2$ in 30% aqueous formic acid. Due to the high optical density of the crystal, back scattering geometry is used to obtain the Raman spectra (Figs. 1 and 2). Spectra are recorded for the four orientations *c*(*bb*)*a*, *c*(*bc*)*a*, *c*(*ab*)*a*, and *c*(*ac*)*a* corresponding to the polarizations

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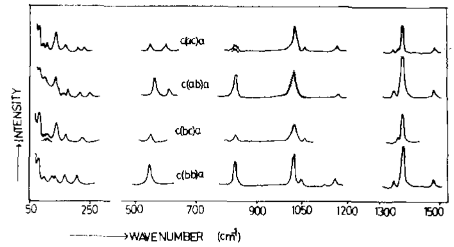

FIG. 1. Raman spectra of CFUH in the region from 50 to 1500 cm^{-1}.

α_{yy}, α_{yz}, α_{xy}, and α_{zx} in the Stokes region of the 5145 Å line using a Spex Ramalog 1401 double monochromator equipped with a Spectra Physics Model 165 Ar$^+$ laser (power 40 mW). Raman spectrum of polycrystalline CFT is also recorded for comparison. Infrared spectra of CFUH, CFT, and urea in the region 4000–200 cm^{-1} are obtained on a Perkin–Elmer 983G spectrophotometer with samples prepared as nujol and hostaflon mulls. Infrared spectra of partly dehydrated samples, prepared in a vacuum desicator over magnesium perchlorate, are also recorded. Polarized IR reflection spectra are obtained at 65° incidence using a Harrick VRA–VAA accessory and a wire-grid polarizer. A reflecting surface of about 15 × 10 mm parallel to the b c plane is formed by arranging several small crystals in an array along the b axis.

The IR reflectivity data in the αth polarization are analyzed by means of a dielectric function (*5*) of the type

$$\varepsilon_\alpha(\omega) = \varepsilon_{\alpha\infty} \prod_{j=1}^{n_\alpha} \frac{\omega^2_{\alpha j\mathrm{LO}} - iT_{\alpha j\mathrm{LO}}\omega - \omega^2}{\omega^2_{\alpha j\mathrm{TO}} - iT_{\alpha j\mathrm{TO}}\omega - \omega^2},$$

which is found to give better fits than the classical dispersion relation in the case of broad bands (*5*, *6*). In the above expression $\omega_{\alpha j\mathrm{TO}}$, $\omega_{\alpha j\mathrm{LO}}$, $T_{\alpha j\mathrm{TO}}$, and $T_{\alpha j\mathrm{LO}}$ are the wavenumbers and the related damping factors of the jth TO and LO optical modes; $\varepsilon_{\alpha\infty}$ in the high-frequency dielectric constant. The IR reflectivity is calculated according to the relations derived from the Fresnel's equations (*7*). The mode strength is calculated according to the equation

$$S_k = (\omega^2_{\alpha k\mathrm{LO}} - \omega^2_{\alpha k\mathrm{TO}})(\varepsilon_{\alpha\infty}|\omega^2_{\alpha k\mathrm{TO}}) \times \prod_{j=1\neq k}^{n_\alpha} \frac{(\omega^2_{\alpha j\mathrm{LO}} - \omega^2_{\alpha k\mathrm{TO}})}{(\omega^2_{\alpha j\mathrm{TO}} - \omega^2_{\alpha k\mathrm{TO}})}$$

The results of the analysis are shown in Figs. 3a and 3b; the values of the parameters are reported in Table I.

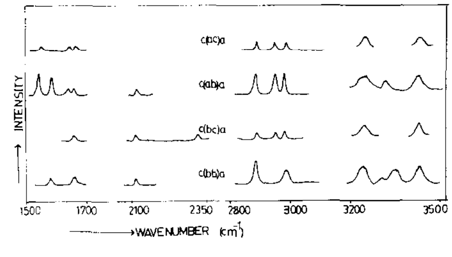

FIG. 2. Raman spectra of CFUH in the region from 1500 to 3500 cm^{-1}.

Discussion

CFUH crystallizes in the monoclinic system $P2_1/c$ (C^5_{2h}) with two formula units in the unit cell (*3*). Cu atoms are in the centrosymmetric site. All the formate ions and urea and water molecules are in general sites. The factor group analysis (*8*) gives the distribution of irreducible representations at $k = 0$ as

$$\mathrm{CFUH} = 45A_g(\mathrm{R}) + 45B_g(\mathrm{R}) + 47A_u(\mathrm{IR}) + 46B_u(\mathrm{IR})$$

Correlation scheme shows that all the internal modes of $HCOO^-$ give components of A_g, B_g, A_u, and B_u species in the crystals.

In CFUH, the copper formate layers are held together by hydrogen bonds formed by $(NH_2)_2CO$ and H_2O molecules. The carbonyl oxygen atom of the formate ion is involved in hydrogen bond with water mole-

TABLE I

DIELECTRIC FUNCTION PARAMETERS

Polarization	ω_{LO}	Γ_{LO}	ω_{TO}	Γ_{TO}
$\parallel b$ $\varepsilon_\infty = 1.581$	3440.8	40.3	3435.3	40.2
	3321.2	36.8	3320.3	41.7
	3259.4	45.1	3258.1	44.7
	3125.3	52.1	3124.3	45.2
	3078.5	35.2	3076.5	34.2
	3033.6	31.6	3032.5	30.6
	2922.5	30.5	2919.3	34.3
	2871.1	26.1	2870.3	33.8
	1692.6	29.1	1688.5	32.6
	1670.0	29.0	1668.7	30.2
	1602.7	45.8	1598.2	45.2
	1481.2	61.7	1480.0	56.9
	1457.7	59.9	1453.1	61.9
	1371.9	40.9	1368.6	43.3
	1214.4	65.5	1211.4	60.8
	1144.8	79.8	1143.3	63.1
	1094.4	42.8	1092.5	38.6
	1075.2	99.3	1057.8	78.4
	1015.7	63.9	1009.1	55.5
	951.7	87.9	944.5	68.2
	902.3	71.4	896.3	60.9
	794.0	71.0	792.6	46.5
	751.4	99.4	749.1	59.9
	727.0	82.7	703.8	45.7
	698.2	55.9	654.8	71.2
	638.5	35.5	620.1	60.7
	592.7	75.0	584.0	64.1
	569.9	65.1	528.0	58.2
	494.8	50.4	461.7	26.1
	456.4	50.9	410.3	41.8
	424.4	36.5	385.5	79.9
$\parallel c$ $\varepsilon_\infty = 1.889$	3423.7	52.4	3420.0	48.4
	3324.8	49.1	3323.3	47.3
	3260.3	45.6	3258.5	44.2
	3204.7	53.3	3201.3	50.6
	3126.7	43.3	3124.7	41.3
	3083.2	42.4	3081.0	44.3
	3034.7	40.0	3033.4	41.5
	2922.1	54.1	2920.6	47.6
	2849.7	30.9	2846.6	26.2
	1679.5	32.5	1665.5	33.6
	1588.4	42.8	1573.4	41.3
	1492.1	60.9	1491.2	64.6
	1455.6	48.3	1453.4	48.1
	1362.3	25.9	1355.7	28.5
	1219.5	73.7	1217.2	67.9
	1152.6	75.0	1150.0	65.7
	1095.3	48.1	1093.4	45.1
	1074.7	84.6	1063.4	67.9
	1018.5	59.5	1012.9	47.1
	952.2	71.8	947.2	55.6
	900.4	64.3	898.5	51.2
	821.1	45.5	819.1	40.7
	795.2	55.6	794.4	43.0
	755.1	82.6	749.3	59.4
	743.7	72.6	736.8	57.2
	719.8	69.2	704.8	43.9
	694.6	64.1	671.9	55.5
	628.9	32.2	612.9	28.9
	600.3	65.4	585.1	64.5
	574.2	72.9	542.1	62.7
	522.0	60.0	513.0	59.0
	478.1	57.5	467.5	33.7
	437.6	72.9	415.5	36.4
	422.9	53.5	377.7	59.3

cule. The other oxygen atom is bonded to the copper atom (*3*). The layer structure of the compound, the presence of large interlayer urea molecules, hydrogen bonds of water molecules with carbonyl oxygen atom, and the lower site symmetry of the formate ions may affect the vibrational

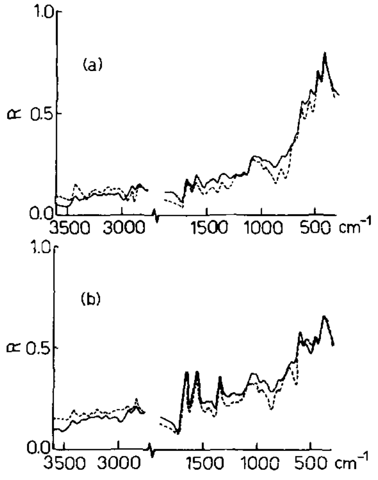

FIG. 3. Analysis of the IR reflection spectra of CFUH, R_{CFUH} along *b c* crystal plane. (a) $E \parallel b$. (b) $E \parallel c$. Solid line, experimental spectra; dashed line, calculated spectra.

TABLE II

RELATIVE ABSORPTION INTENSITIES ALONG THE CRYSTAL AXES

Molecule	Symmetry species	Relative intensities $a^*(\perp bc)$	b	c
Urea	A_1	0.330	0.190	0.480
	B_2	0.132	0.800	0.068
	B_1	0.538	0.010	0.452
Formate ion	A_1	0.285	0.286	0.429
	B_2	0.001	0.580	0.419
	B_1	0.714	0.134	0.152
Water	A_1	0.864	0.124	0.012
	B_2	0.010	0.003	0.987
	B_1[a]	0.126	0.873	0.001

[a] Libration.

modes of formate ions. The relative intensities of the IR active components derived from the internal modes can be evaluated, in the limits of the oriented gas model, using the atomic coordinates given in the X-ray work (*3*). In Table II the relative intensities along the $a^*(\perp b\ c)$, b, and c axes are given for the vibrations associated to the C_{2v} urea, formate ion and water. For a complete identification of the bands due to $HCOO^-$, $(NH_2)_2CO$, and H_2O the vibrational spectra of CFT and urea are also used.

Internal Modes of $HCOO^-$

The internal modes $\nu_1(A_1)$, $\nu_2(A_1)$, $\nu_3(A_1)$, $\nu_4(B_1)$, $\nu_5(B_1)$, and $\nu_6(B_2)$ of $HCOO^-$ with C_{2v} symmetry usually occur around 2940, 1375, 820, 1550, 1350, and 1070 cm^{-1}, respectively (*2, 9–11*). In all polarization geometries there is a band around 2990 cm^{-1} in Raman. This band is also observed in the spectrum of CFT. The C–H symmetric stretching mode (ν_1) is found to be strong in CFT. However, in CFUH this polarized band appears only as medium intense around 2890 cm^{-1}. The band around 2990 cm^{-1} is assigned to a combination mode. The enhancement in intensity of this band and lowering of the intensity of the ν_1 mode are probably due to Fermi resonance between $\nu_2 + \nu_4$ and ν_1 modes. A similar result is reported by McQuaker and Harvey (*9*) in their study of the vibrational spectra of $Sr(HCOO)_2$. The band due to CO asymmetric stretching mode (ν_4) overlaps with the bending modes of NH_2 and H_2O (Table III). The polarized spectra suggest that this mode can be associated to the reflectance maximum appearing near 1590 cm^{-1} in the polarization parallel to the b axis, which corresponds to the absorption at 1589 cm^{-1}. This mode is intense in the Raman spectrum of CFT. The lowering of its intensity may be due to vibrational interaction between urea molecules and formate ions. The strong band at 1568 cm^{-1} in turn corresponds to the reflectance maximum observed at 1574 cm^{-1} with light polarized along the c axis: the polarization is consistent with the assignment of this band to the symmetric NH_2 bending which falls in the A_1 species under C_{2v} symmetry.

Keeping in mind the spectra of other formates (*12*), the OCO symmetric stretching mode (ν_2) is expected to be strong and polarized in Raman and therefore the very strong band around 1387 cm^{-1} can be safely assigned to it. There are two possible candidates for this mode in IR, namely the strong bands at 1357 and 1376 cm^{-1}. In the measurements with polarized light we observed a reflectance maximum around 1351 cm^{-1} only for the polarization parallel c axis, and a maximum near 1365 cm^{-1} only for the polarization parallel to the b axis. These findings indicate that the absorption band at 1357 cm^{-1} arises from ν_2, whereas the band at 1376 cm^{-1} corresponds to the in-plane CH bend (ν_5). For the latter mode, the Raman active components can be tentatively identified with the weak bands at 1350/1365 cm^{-1}. The above assignments entail somewhat large factor group splittings: however, comparable splittings were previously observed in the spectra of formates (*12, 13*).

The out-of-plane CH bend (ν_6) appears

TABLE III

VIBRATIONAL SPECTRAL DATA (cm^{-1}) AND ASSIGNMENTS

IR (cm^{-1})		Raman (cm^{-1})				
Absorption	Reflection	*c*(*bb*)*a*	*c*(*bc*)*a*	*c*(*ab*)*a*	*c*(*ac*)*a*	Assignment
3430(s)	$3430 \parallel b$	3432(s)	3432(m)	3430(s)	3434(m)	
	$3410 \parallel c$					N–H stretch
3337(m)	$3330 \parallel c$	3350(s,br)		3320(m,br)		
		3308(sh)				
3275(m)	. . . .					
		3243(s,br)	3248(m,br)	3246(s,br)	3256(m,br)	O–H stretch
3233(m)	. . . .					
2980(m)		2990(m,br)	2984(w)	2986(m)	2992(w)	$\nu_2 + \nu_4$ (F)
2920(m)	$2910 \parallel b,c$		2954(w)	2954(w)	2952(w)	Split component of ν_1 (F)
						δ
2888(m)		2888(m)	2892(w)	2891(m)	2892(w)	ν_1 (F)
			2328(vw)			
		2116(w)	2116(vw)	2118(w)		Combination
1672(vs)	$1669 \parallel c$			1661(w)	1664(vw)	
		1660(w)	1660(vw)			C═O stretch of urea
1660(sh)				1643(w)	1645(vw)	O–H bend?
1610(sh)						
	$1590 \parallel b$					
1589(sh)				1584(m)		
		1578(w)			1550(vw)	δNH_2, ν_4 (F),
1568(s,br)	$1572 \parallel c$					OH bend?
				1543(m)		
1482(sh)	$1485 \parallel b$	1481(w)		1483(w)	1483(vw)	Antisymmetric C–N
						stretch of urea
	. . . .					
	. . . .					
1376(vs)	$1366 \parallel b$	1377(vs)	1378(s)	1378(vs)	1377(s)	
						ν_2 (F), ν_5 (F)
1357(vs)	$1350 \parallel c$	1349(w)	1363(vw)	1351(w)	1365(vw)	
					1351(vw)	
	. . . .					
	. . . .					
1158(vs)	$1162 \parallel b$	1161(vw)		1168(vw)	1166(vw)	NH_2 rocking
1981(vw)	$1060 \parallel c$					Symmetric C–N
	$1055 \parallel b$	1042(vw)	1056(vw)		1059(vw)	stretch of urea
1019(vw)	$1015 \parallel b,c$	1022(s)	1022(m)	1022(s)	1022(m)	ν_6 (F)
. . .	$960 \parallel b$					
	$950 \parallel c$					
833(s)	$820 \parallel c$	830(m)	828(m)	829(m)	830(w)	ν_3 (F)
					824(w)	
786(m)	$795 \parallel c$					Out-of-plane skel.
	$793 \parallel b$					deformation of urea
758(m,br)	. . .					NH_2 wagging and
735(sh)	. . .					H_2O libration
	$621 \parallel b$			611(w)	599(w)	
595(m)	$616 \parallel c$			611(w)	599(w)	In-plane CO bend
550(ms)	$559 \parallel c$	548(m)	55(w)	559(m)	548(w)	NCN scissoring
	$538 \parallel b$					H_2O libration

TABLE III—*Continued*

IR (cm^{-1})		Raman (cm^{-1})				
Absorption	Reflection	*c*(*bb*)*a*	*c*(*bc*)*a*	*c*(*ab*)*a*	*c*(*ac*)*a*	Assignment
511(s,br)						NH_2 twisting
480(sh)	$473\|b$					
	$411\|b$					
387(ms)	$393\|c$					Cu–O vibrational modes
300(ms)						
				247(vw)	228(vw)	
199(s)		203(w)	221(vw)			T (F), T (W)
				215(vw)	208(vw)	
				172(w)		
		168(w)	168(w)	160(vw)	167(w)	ω (F)
		137(w)				
			135(m)	136(m)	134(m)	τ (F)
			106(w)		104(w)	
		95(w)		97(m)		T (F), T (W)
			97(w)		96(w)	
		81(s)	81(s)	81(s)	80(s)	ρ (F)

Note. vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad, sh, shoulder; ν (F), vibrational frequency of formate ion; T(F), translation of formate; T(W), translation of water; ω (F), wagging mode of formate; τ(F), twisting mode of formate; ρ(F), rocking mode of formate; δ, bending mode.

with considerable intensity at a wavenumber lower than that of CFT in Raman. This lowering of the bending wavenumber may be due to the presence of large urea molecules between the layers. The behavior of the IR counterpart agrees with the predictions of the oriented-gas: in fact, two rather weak reflectance peaks of comparable strength are observed both in the *b*- and *c*-polarized spectra. The polarized band around 830 cm^{-1} in Raman (833 cm^{-1} in IR) is assigned to the symmetric OCO bending mode (ν_3): the analysis of the reflectance data shows that it develops its strength in the polarization along the *c* axis (S_k = 0.005). As multiplicity is not observed in most of its vibrational modes, it may be inferred that the formate ions are identical in the crystal.

High Wavenumber Bands of $(NH_2)_2CO$ and H_2O

The IR bands at 3337 and 3430 cm^{-1} and the Raman bands between 3300 and 3450 cm^{-1} could be easily assigned to the N–H stretching modes. The polarized reflection spectra reveal that the band at 3430 cm^{-1} develops its intensity along the *b* axis and, therefore, according to the oriented-gas model, it could be assigned to one of the antisymmetric N–H stretching fundamentals. On the other hand, the band at 3337 cm^{-1}, which is associated to a reflectance maximum in polarization parallel to the *c* axis, is assigned to one of the totally symmetric N–H stretching modes. The observation of another reflectance maximum, in the same polarization, near 3410 cm^{-1}, suggests that, as found by Kutzelnigg *et al.* (*14*) in urea crystals, another totally symmetric N–H stretching fundamental is present in this range. The O–H stretching modes of water appear as a single broad band around 3245 cm^{-1} in Raman. They give rise to a very strong, broad band in IR with well-defined absorption maxima at 3233 and 3275 cm^{-1}: the intensity is reduced in partially dehydrated materials. Keeping in mind the oriented gas model predictions, the analysis of the reflection spectra suggests that one of the antisymmetric stretching modes can be related to the maximum appearing at 3250 cm^{-1} in the polarization parallel to the c axis, but the presently available data don't allow a definite attribution of the symmetric stretching modes. Although the spectra of the partly dehydrated samples clearly show that water contributes to the absorption intensity in the range 1700–1500 cm^{-1}, the OH bending fundamental cannot be definitely located: a similar situation occurs for other hydrated formates (*15*).

Besides the modes already discussed some of the remaining fundamentals of urea could be identified both using correlative criteria (*14, 16*) and keeping in mind the behavior in polarized light. In particular, the strong IR band at 1672 cm^{-1} is assigned to the C = 0 stretching fundamental: it is associated to a strong reflectance maximum near 1669 cm^{-1} which develops its strength prevailingly in the polarization parallel to the c axis. Likewise, the reflectance spectra in the b polarization support the location of an asymmetric C–N stretching mode near 1480 cm^{-1}.

Low Wavenumber Bands

The assignment of the libration modes of water and wagging and twisting modes of NH_2 is complicated because, on correlative grounds, they are expected to overlap to some extent. The consideration of the spectra of partly dehydrated compounds was of some help in these assignments. So, at least one of the water librations can be located in the range 800–650 cm^{-1}: in fact, as an effect of the dehydration, there is a marked reduction of the intensity of the broad absorption with center of gravity near 750 cm^{-1}. On the other hand, the bands around 740 and 780 cm^{-1}, which persist after dehydration, can be assigned to internal fundamentals of urea, likely a skeletal mode and a NH_2 wagging mode. A comparison between the spectra of the hydrated and partly dehydrated compounds reveals also that the absorption bands at 550 and 511 cm^{-1} are little affected by the dehydration process: this observation supports their assignment to internal fundamentals of urea. The analysis of the reflection spectra shows that two modes with noticeable strength have their TO wavenumbers at 513 and 542 cm^{-1} in the c polarization (S_k = 0.1429 and S_k = 0.2552, respectively). This behavior is consistent with an assignment both to the A_1 and B_1 species of urea: the choice of the high-wavenumber mode as a symmetric skeletal scissoring has been suggested by correlative arguments (*14, 16*). A decrease of the intensity of the diffuse absorption between 650 and 500 cm^{-1} is also clearly observed upon dehydration and so another librational mode of water can be located in this range. This mode should be approximately described as a wagging motion, which conforms to the B_1 symmetry for the water molecule and hence is expected to develop its intensity prevailingly in the polarization parallel to the b axis. The analysis of the reflectance data in the b polarization suggests that this libration could be identified with the mode whose TO wavenumber falls at 528 cm^{-1} (S_k = 0.1771). The analysis shows also that a component of medium intensity (S_k = 0.088), polarized along the b axis, is associated to the absorption band near 590 cm^{-1}, supporting its assignment to the in-plane CO deformation mode of urea which belongs to the B_2 species in the local symmetry C_{2v} of urea.

Heyns (*17*) observed Cu–O vibrational

bands of CFT in the region 316–414 cm^{-1}. Therefore, the strong absorption bands at 387 and 300 cm^{-1} may be due to Cu–O vibrational modes. In particular, the former band, which is strongly affected by the dehydration process, is likely associated to a Cu–O stretching mode. In the vibrational spectra of CFT (*12*) and lithium formate monohydrate (*18*) it is observed that $\nu_{\text{wagging}} > \nu_{\text{twisting}} > \nu_{\text{rocking}}$ for the formate ion. Based on this fact the librational modes of the formate ion are identified. Some of the translational modes of formate ion and water molecules are also identified (*18*).

A satisfactory fitting to experimental reflection spectra required the introduction of some resonances not obvious from the absorption spectra, particularly in the ranges 3100–3000 cm^{-1}, 1200–900 cm^{-1}, and 650–500 cm^{-1}. This fact can be interpreted as an indication that multiphonon processes (*19*) contribute to the absorption intensity in these regions. The vibrational assignments are collected in Table III.

Conclusion

The presence of large interlayer urea molecules between copper formate layers is responsible for the lowering of the wavenumber of out-of-plane CH bend and reduction in intensity of the CO asymmetric stretch of $HCOO^-$. All the formate ions are identical in the crystal. Fermi resonance between symmetric C–H stretch of $HCOO^-$ and combination bands in the region between 2800 and 3000 cm^{-1} is observed. The low wavenumber bands are also assigned. As expected, all the internal modes of $HCOO^-$ are observed in A_g and B_g spectra.

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