

## 812. The Vibration Spectra of Some Substituted Acetate Ions.

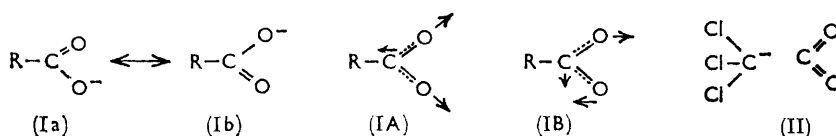
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The infrared and Raman spectra of the sodium salts  $\text{RCO}_2\text{Na}$ , where  $\text{R} = \text{Me}$ ,  $\text{Bu}^t$ ,  $\text{CF}_3$ ,  $\text{CCl}_3$ ,  $\text{CBr}_3$ ,  $\text{CHCl}_2$ ,  $\text{CHBr}_2$ ,  $\text{Et}$ ,  $\text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{F}$ ,  $\text{CH}_2\text{Cl}$ ,  $\text{CH}_2\text{Br}$ , and  $\text{CH}_2\text{I}$ , have been determined.

The frequency of the very intense infrared band near  $1600\text{ cm}^{-1}$ , which is normally attributed to antisymmetric OCO stretching, increases very markedly with the electron-withdrawing effect of R and shows no mass effect. The strongly infrared- and Raman-active frequency near  $1400\text{ cm}^{-1}$ , generally attributed to symmetric OCO stretching, by contrast, is not noticeably affected by polar effects but decreases markedly as the mass of R increases. The lack of correlation between these two supposedly related frequencies is discussed in relation to the structure of the carboxylate grouping, the unsymmetrical non-resonant structure  $\text{R}\cdot\text{C}\cdot\text{O}\cdot\text{O}^-$  being preferred.

Below  $1200\text{ cm}^{-1}$  the vibration spectrum of an acetate ion resembles that of the corresponding acetic acid. The values of the C-Hal stretching frequencies indicate that, in the preferred conformation, an oxygen atom eclipses a halogen atom in the mono- and di-chloro- and -bromo-acetate ions, but a hydrogen atom in monoiodoacetate.

IN  $\text{CXYZ}\cdot\text{CO}\cdot\text{R}'$  the carbonyl stretching frequency is well known to increase as the electron-withdrawing effects of X, Y, and Z increase, especially if the electron-withdrawing group is spacially close to the oxygen atom.<sup>1</sup> A similar dependence on the electron-withdrawing effects of X, Y, and Z is to be expected for the in-phase (IA) and out-of-phase (IB) stretching frequencies of the symmetrical carboxylate group in an ion  $\text{CXYZ}\cdot\text{CO}_2^-$  (I); on the basis of resonance theory this is readily visualized in terms of contributions from structures such as (II) for trichloroacetate which raise the CO bond order.



Given localization of both OCO stretching vibrations and constancy in both the OCO bond angle and the ratio CO-CO interaction/CO stretching force constant, the frequencies of vibrations (IA) and (IB) would be equally affected by the polar effects of substituents. However, in compounds  $\text{R}\cdot\text{SO}_2\cdot\text{R}'$ , which serve as a model, SO and OSO stretching frequencies being sensitive to polar effects,<sup>2</sup> the relative effect on the symmetric stretching frequency is only  $\sim 0.8$  times that on the antisymmetric one. For the shifts of the acetate ion frequencies at  $1583$  and  $1421\text{ cm}^{-1}$  produced by substituents, a similar parallelism is expected, but here the corresponding factor could be less than  $0.8$  (*e.g.*, CC and symmetric OCO stretching could mix more strongly than symmetric  $\text{RSR}'$  and OSO stretching).

The vibration spectra of the formate<sup>3,4</sup> and acetate<sup>4,5</sup> ions and of their deuterated derivatives<sup>4,6</sup> have been studied extensively. Isolated infrared or Raman spectra have

<sup>1</sup> Jones and Sandorfy, in Weissberger, "The Technique of Organic Chemistry," Vol. IX, Interscience, New York, 1956, pp. 474 *et seq.*

<sup>2</sup> Bellamy and R. L. Williams, *J.*, 1957, 863; Hesse, Reichold, and Majmudar, *Chem. Ber.*, 1957, 90, 2106.

<sup>3</sup> Edsall, *J. Chem. Phys.*, 1936, 4, 1; Newman, *ibid.*, 1952, 20, 1663.

<sup>4</sup> Ito and Bernstein, *Canad. J. Chem.*, 1956, 34, 170.

<sup>5</sup> Jones and McLaren, *J. Chem. Phys.*, 1954, 22, 1796.

<sup>6</sup> Fonteyne, *Naturwiss.*, 1943, 31, 441.

TABLE I.

Band maxima <sup>a</sup> in the vibration spectra of compounds CX<sub>3</sub>·CO<sub>2</sub><sup>-</sup>Na<sup>+</sup>.

CX <sub>3</sub> Assignment <sup>b</sup>	CH <sub>3</sub>		C(CH <sub>3</sub> ) <sub>3</sub>		CF <sub>3</sub>		CCl <sub>3</sub>		CBr <sub>3</sub>	
	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman
CO <sub>2</sub> st I	1583	1-6	1564 0-9 1551 2-5		1689 1-8	1676	1677 1-7	1684 3 1670 4	1664 1-4 1355 0-9 1338 0-4	1659 3 1331 3 1336 3
CO <sub>2</sub> st II	1421	0-5	1413 1-7 (806)	1414 7 (800)	1446 0-15 (850)	1441	1353 1-3	1343 12	914 0-2 819 0-05 <sup>t</sup>	911 2 819 1 510 3 398 1
"CC st"	924	0-05			726 0-6 <sup>j</sup>	(846) 728	940 0-04	937 3		
CCO <sub>2</sub> ip be I	650	0-2		592 5	?					
CCO <sub>2</sub> ip be II	?	1?		510 3	?					
CCO <sub>2</sub> op be	247	2		172 6	?	410 4				
tors	228	1?				224 2				
"CX <sub>3</sub> s st"	2955	0-02	806 0-15 <sup>e</sup>	800 9	850 0-35 <sup>e</sup>	846 8	685 1-0	685 6		602 3
"CX <sub>3</sub> as st"	3000	0-05	941 0-05	939 5	1213 1-6	1211 4 1239 4	849 0-5 833 1-3 746 0-9?	845 10 750 4	756 0-6	767 3
"CX <sub>3</sub> as st"			892 0-3	887 3	1140 1-0				720 0-4 709 0-4	718 2
CX <sub>3</sub> s be	1333	0-02		370 3						
CX <sub>3</sub> as be	1440	0-2				596 3 505 2 429 3 262 3		430 50 283 22 306 5 198 10		311 5 [137] <sup>m</sup> [220] <sup>m</sup> [182] <sup>m</sup>
CCX <sub>3</sub> ip rock	1043	0-1		242 2?						
CCX <sub>3</sub> op rock	1012	0-15								
X internal			2866 0-1 <sup>j</sup> 2958 0-5 <sup>g</sup> 1484 1-0 <sup>h</sup> 1461 0-3 1453 0-05 <sup>h</sup> 1362 0-9 <sup>i</sup> 1251 0-5 <sup>i</sup>							
Overtone	506	2?	1208 0-1 <sup>i</sup>	{ 1225 8 1213 8	1189 0-2	1188 3 952 2	1384 0-5 <sup>k</sup>	1372 5	1431 0-05	
?			721 0-15	1652 2	807 0-4					
?										
CH <sub>2</sub> X										
Assignment										
CO <sub>2</sub> st I	1573 1565 1553	1-9 0-7	1619 1-0 1602 1-9					1624	1-8	1608 6
CO <sub>2</sub> st II	1429	0-7	1384 0-9	1370 10				1448	0-7	1442 25
CCX pas st	1076	0-15	957 0-05?	968 1				1011	0-5	
CCX ps st	880	0-3	905 0-35	906 8				923	0-35	929 24
CCO <sub>2</sub> ip be I			713 0-1?	713 1				700	0-25	688 4
CCO <sub>2</sub> ip be II				591 ?						
CH <sub>2</sub> CH <sub>3</sub>										
Assignment										
CH <sub>2</sub> F										
CH <sub>2</sub> CN										

Compounds CH<sub>2</sub>X·CO<sub>2</sub><sup>-</sup>Na<sup>+</sup>, where X is a first-row element.

TABLE I. (Continued.)

Assignment	CH <sub>2</sub> X		CH <sub>2</sub> CH <sub>3</sub>		CH <sub>3</sub> CN		CH <sub>2</sub> F	
	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman
CCO <sub>2</sub> op be tors	499	2	499	2	508 171 159	4 5 4	499 251 225	9 2? 2?
CH <sub>2</sub> s st	2915	0.1	2945 2965	0.1	2945 2965	0.1	2992	0.03
CH <sub>2</sub> as st			1426 1407	0.5 0.3	1426 1407	0.5 0.3		
CH <sub>2</sub> sciss	1418	0.2	1407	0.3	1404	4	1414	13
CH <sub>2</sub> twist	1370	0.4	1267	0.3	1404 1267	4 5	1340	17
CH <sub>2</sub> wag	1298	0.3	1197	0.03	1208	4	1245	9
CH <sub>2</sub> rock	815	0.25	935	0.25	1208	4	1258	9
XCC sciss					403	2	1037	6
X internal	2870	0.05 <sup>f</sup>	2255	0.1 <sup>e</sup>	2261	29	448	4
	2965	0.2 <sup>v</sup>			367	4		
	1463	0.3 <sup>h</sup>						
	1443	0.1	1458	p				
	1377	0.1 <sup>i</sup>	1374					
	1003	0.1 <sup>n</sup>	1009					
	1249	0.03	1254					
?								
Compounds CH <sub>2</sub> X·CO <sub>2</sub> <sup>-</sup> Na, where X is not a first-row element.								
Assignment	CH <sub>2</sub> Cl		CH <sub>2</sub> Br		CH <sub>2</sub> I			
	Infrared	Raman	Infrared	Raman	Infrared	Raman		
CO <sub>2</sub> st I	1603	1.8	1596	1.6	1583	1.6		
CO <sub>2</sub> st II	1418	1.6	1415	0.9 <sup>a</sup>	1394	0.8		
"CC st"	932	0.3	927	0.1	924	0.3		
CCO <sub>2</sub> ip be I	682	0.4	669	0.2	671	0.7		
CCO <sub>2</sub> ip be II				?				
CCO <sub>2</sub> op be tors	769	0.8	698	0.4	177	440		
"CX st" tra <sup>g</sup>					710	166		
"CX st" gau <sup>r</sup>					548	598		
CH <sub>2</sub> s st	2975	0.05	2980	0.05	2960	0.04		
CH <sub>2</sub> as st	3005	0.05	3005	0.05	3000	0.06		
CH <sub>2</sub> sciss	1399	0.2	1388	0.3 <sup>a</sup>	1426	0.3		
CH <sub>2</sub> twist	1260	0.2	1225	0.3				
CH <sub>2</sub> wag	1251	1.0	1218	0.8	1177	1.1		
CH <sub>2</sub> rock	1166	0.05	1172	0.1	1099	0.03		
XCC sciss	926	0.1	901	0.25	853	0.35		
			386					
			1420					
			927					
			672					
			500					
			177					
			710					
			548					
			1388					
			1218					
			893					
			380					

TABLE I. (Continued.)  
 Compounds  $\text{CHX}_2 \cdot \text{CO}_2^- \text{Na}^+$ .

CHX <sub>2</sub> Assignment	CHCl <sub>2</sub> <sup>i</sup>		CHBr <sub>2</sub>							
	Infrared- $\alpha$	Infrared- $\beta$	Raman	Infrared	Raman					
	1660	0.5								
CO <sub>2</sub> st I.....	1640	1.8	1631	1.8	1646	2	1616	1.9	1621	4
CO <sub>2</sub> st II.....	1399	0.9	1376	0.6	1388	10	1378	0.7	1369	10
"CC st".....	934	0.05	922	0.03	933	3	931	0.1	928	3
CCO <sub>2</sub> ip be I.....	738	0.6	725	0.1	724	3	814	0.1 <sup>l</sup>	810	3
	710	0.1	710	0.1						
CCO <sub>2</sub> ip be II.....					593	2			577	4
CCO <sub>2</sub> op be.....							?		498	1 <sup>o</sup>
"CX <sub>2</sub> s st".....			777	0.1	779	6	698	0.7	703	9
"CX <sub>2</sub> as st".....	818	0.2	821	0.2	829	4			725	5
	807	0.6	800	0.3						
CH st.....	2985	0.05	2985	0.05			3015	0.1		
CH be.....	1228	0.05	1236	0.1	1213	3	1191	0.35	1184	5
	1218	0.05	1216	0.1						
CH be.....	1203	0.2	1199	0.05			1148	0.2	1151	3
CX <sub>2</sub> C ps be.....					429	9			365	7
X <sub>2</sub> CC pas be.....					297	2			241	2
XCX sciss.....					260	2				
Overtone.....							1412	0.5 <sup>k</sup>	1394	4
	? 656	0.1	656	0.1						

<sup>a</sup> Frequencies are in  $\text{cm}^{-1}$ . The relative peak intensities of the bands within each spectrum, over and above any background absorption or scatter, are in optical density units in the infrared and in arbitrary units in the Raman spectra. *Note:* These intensities possess no absolute significance and must not be compared as between different compounds. Very weak bands are generally not listed. <sup>b</sup> See text. Inverted commas indicate that some mixing of vibrations is likely to be involved. " ? " after (low) intensity value indicates doubtful band; " ? " between " Infrared " and " Raman " columns indicates doubtful band assignment. <sup>d</sup> Observed band excited by Hg line at 4047 Å. <sup>e</sup> Symmetrical stretching of all four CC (or CC and CX) bonds. <sup>f</sup> Symmetric CH stretching band. <sup>g</sup> Antisymmetric CH stretching band. <sup>h</sup> Asymmetric CH<sub>3</sub> bending band. <sup>i</sup> Symmetric CH<sub>3</sub> bending band. <sup>j</sup> Mixed CCO<sub>2</sub> in-plane bending/CF<sub>3</sub> symmetric bending bands. <sup>k</sup> Intensified by interaction with CO<sub>2</sub> st II. <sup>l</sup> Mixed CCO<sub>2</sub> ip be I/CBr<sub>2</sub> asst bands. <sup>m</sup> Quoted from Fonteyne.<sup>5</sup> <sup>n</sup> CH<sub>2</sub> rocking band. <sup>o</sup> C≡N stretching band. <sup>p</sup> CCN bending band. <sup>q</sup> tra = *trans*-conformation. <sup>r</sup> Gau = *gauche*-conformation. <sup>s</sup> Mixed CO<sub>2</sub> st II/CH<sub>2</sub> sciss. bands. <sup>t</sup> Two modifications of solid sodium dichloroacetate are obtainable in potassium bromide.

been determined for several substituted acetate ions,<sup>7-9,10a,11-14</sup> but no systematic study of the effect of substituents on the vibration spectra has been reported, other than Fonteyne's Raman-spectral study of three trihalogenoacetate ions.<sup>7</sup>

*Experimental.—Materials.* A few of the sodium salts were recrystallized commercial specimens, but the majority were obtained by quantitative neutralization of the pure carboxylic acid with sodium carbonate. Sodium acetate was freshly fused before use, the other salts were dried at 0.05 mm. at elevated temperatures. All the salts used for infrared investigation were anhydrous, except for sodium trimethylacetate dihydrate, which did not lose its water of crystallization even at 110°/0.05 mm. Hygroscopic salts were handled in the dry-box.

*Spectra.*—Infrared spectra (from 4000 to 650  $\text{cm}^{-1}$ ) of the solid sodium salts dispersed in potassium bromide discs and Raman spectra (2600—200  $\text{cm}^{-1}$ ) of the salts in concentrated aqueous solution were determined as before.<sup>15</sup> The anion concentrations ranged from 30 to

<sup>7</sup> Fonteyne, *Natuurwetensch. Tijdschr.*, 1942, **24**, 161.

<sup>8</sup> Klemperer and Pimentel, *J. Chem. Phys.*, 1954, **22**, 1399.

<sup>9</sup> Robinson and Taylor, *Spectrochim. Acta*, 1962, **18**, 1093.

<sup>10</sup> Kohlrausch, "Ramanspektren," Becker and Erler, Leipzig, 1943, (a) p. 264; (b) p. 190; (c) pp. 234, 239; (d) p. 246; (e) pp. 173—179; (f) p. 139; (g) p. 142.

<sup>11</sup> Duval, Lecompte, and Douville, *Bull. Soc. chim. France*, 1942, **8**, 263; *Ann. Physique*, 1942, **17**, 68.

<sup>12</sup> Wittek, *Z. phys. Chem.*, 1942, **B**, **51**, 103.

<sup>13</sup> Tsuboi, Onishi, Nakagawa, Shimanouchi, and Mizushima, *Spectrochim. Acta*, 1958, **12**, 253; Suzuki, Shimanouchi, and Tsuboi, *ibid.*, 1963, **19**, 1195.

<sup>14</sup> Nakamura, *J. Chem. Soc. Japan*, 1958, **79**, 1420.

<sup>15</sup> Spinner and White, *J.*, 1962, 3115.

60% but the Raman spectra were nevertheless often of remarkably low intensity. The determinations of the Raman spectra of the mono- and di-halogenoacetate ions, which undergo self-condensation with halide ion elimination in aqueous solution, were completed sufficiently speedily to ensure that no appreciable reaction had taken place.

## DISCUSSION

*Band Assignments.—Nomenclature used.* CO<sub>2</sub> stretching motions, "CO st I" and "CO st II"; CCO<sub>2</sub> in- and out-of-plane bending, "CCO<sub>2</sub> ip be I," "CCO<sub>2</sub> ip be II," "CCO<sub>2</sub> op be"; torsion about CC bond, "tors." Bending in ions CH<sub>2</sub>X·CO<sub>2</sub><sup>-</sup>: HCH and XCC scissoring, "CH<sub>2</sub> sciss" and "XCC sciss," CH<sub>2</sub>/CCX twisting "CH<sub>2</sub> twist"; CH<sub>2</sub> wagging/CCX rocking, "CH<sub>2</sub> wag"; CH<sub>2</sub> rocking/CCX wagging, "CH<sub>2</sub> rock." Bending in CHX<sub>2</sub>·CO<sub>2</sub><sup>-</sup>: CH/CX<sub>2</sub>C rocking (2 vibrations), "CH be"; CX<sub>2</sub>C *pseudo*-symmetric and X<sub>2</sub>CC *pseudo*-antisymmetric bending, "CX<sub>2</sub>C ps be" and "X<sub>2</sub>CC pas be."

*The acetate ion.* In disagreement with previous<sup>4,5,16</sup> assignments, the lowest CCO<sub>2</sub> bending frequency is now assigned to the out-of-plane motion (*cf.* the bending frequencies of acetone<sup>17,18</sup>). The two doubtful Raman bands at 247 and 228 cm.<sup>-1</sup> (which have not been reported previously) are tentatively assigned to the torsional movement, the second one being a "hot" band.

*The trimethylacetate ion.* All CC bonds may be expected to vibrate in unison, and the intense Raman band at 800 cm.<sup>-1</sup> is attributed to the corresponding all-in-phase CC stretching. The non-equivalence of the three methyl groups seems marked, both neopentane-like CH<sub>3</sub> bending frequencies<sup>10b</sup> (1450 and 1250 cm.<sup>-1</sup>) and normal ones (1480 and 1365 cm.<sup>-1</sup>) being observed.

*The trifluoroacetate ion.* Fluorine being a first-row element like carbon, first-order mixing between CC and CF stretching is expected. The vibration of frequency 850 cm.<sup>-1</sup> is presumably a *pseudo*-symmetric stretching motion of all four CF and CC bonds (analogous to the carbon tetrafluoride vibration at 904 cm.<sup>-1</sup>).<sup>19</sup>

*The trichloroacetate and tribromoacetate ions.* Substantial second-order mixing between CC, CO, and CHal stretching must be invoked to explain the unexpectedly high Raman intensities of the antisymmetric CHal<sub>3</sub> stretching bands (at 845 and 767 cm.<sup>-1</sup>, respectively) which cause the band assignments here to be less than straightforward.

*Ions CH<sub>2</sub>X·CO<sub>2</sub><sup>-</sup>.* For X = Me, CN, and F first-order mixing of stretching vibrations is expected to give rise to a *pseudo*-symmetric ("CCX ps st") and a *pseudo*-antisymmetric ("CCX pas st") stretching motion. On the basis of Nakamura's work on deuterated sodium chloroacetate<sup>14</sup> the CH<sub>2</sub> bending frequencies can be identified with certainty. In the bromoacetate ion the frequencies of CH<sub>2</sub> scissoring and CO<sub>2</sub> stretching II seem to coincide; one of the resultant mixed motions is strongly infrared-active, the other strongly Raman-active.

*Evidence Concerning the Preferred Conformation.*—In  $\alpha$ -halogenated carbonyl compounds the molecular conformation can, in general, be deduced from the value of the carbonyl stretching frequency, but the applicability of this approach to halogenoacetate ions is not certain *a priori*. A far safer approach, usable for the mono- and di-chloro-, bromo-, and iodo-acetate ions, is *via* the carbon-halogen stretching frequencies, which are readily identified by their high intensities in the Raman spectra, and for which the necessary reference data are available.

Each C<sub>primary</sub>-Hal stretching frequency may occur within two ranges, depending on the molecular environment of the C-Hal bond, and halogenated paraffins which can exist in two rotationally isomeric forms normally show both the low and the high frequency.<sup>10c,20</sup> The data for 1-halogeno-ethanes and -propanes and for 1,2-dihalogenoethanes are collected

<sup>16</sup> Nakamura, *J. Chem. Soc. Japan*, 1958, **79**, 1411.

<sup>17</sup> Hadni, *Ann. Physique*, 1955, **10**, 874.

<sup>18</sup> Katon and Bentley, *Spectrochim. Acta*, 1963, **19**, 639.

<sup>19</sup> Yost, Lassetre, and Gross, *J. Chem. Phys.*, 1936, **4**, 325.

<sup>20</sup> Shipman, Folt, and Krimm, *Spectrochim. Acta*, 1962, **18**, 1603.

in Table 2, and may be summarized thus: The high C-Hal stretching frequencies are associated with the planar Z-C-C-Hal system with ZC and CHal *trans* to one another where Z is a first-row or heavier element, and the low ones are due to molecules in which Z is light (e.g., H or D), as in monohalogenoethanes and *gauche*-conformations. The interaction between C-Hal and other stretching vibrations is thus strongly affected by the arrangement of the bonds present.

TABLE 2.

Carbon-halogen stretching frequencies <sup>a</sup> in mono- and di-halogeno-ethanes, -propanes, -acetic acids, and -acetate ions.

	C-Cl		C-Br		C-I
CH <sub>3</sub> ·CH <sub>2</sub> Hal <sup>b</sup> .....		656		560	500
CH <sub>3</sub> ·CH <sub>2</sub> ·CH <sub>2</sub> Hal <sup>b,c</sup> .....	726	648	647	563	593
CH <sub>3</sub> ·CHHal <sub>2</sub> <sup>d,e</sup> .....		689 <sup>j</sup>		606 <sup>j</sup>	
		641 <sup>k</sup>		546 <sup>k</sup>	
CH <sub>3</sub> ·CH <sub>2</sub> ·CHHal <sub>2</sub> <sup>d,e</sup> .....	810 <sup>j</sup>	689 <sup>j</sup>			
	740 <sup>k</sup>	648 <sup>k</sup>			
(CH <sub>2</sub> Hal) <sub>2</sub> <sup>f,g</sup> .....		730 <sup>l</sup>	655 <sup>l</sup>	567 <sup>m</sup>	611
CH <sub>2</sub> Hal·CO <sub>2</sub> H <sup>h</sup> .....	790		722	540	496 <sup>m,n</sup>
CH <sub>2</sub> Hal·CO <sub>2</sub> <sup>-i</sup> .....	780		710	548	491 <sup>i</sup>
CHHal <sub>2</sub> ·CO <sub>2</sub> H <sup>h,e</sup> .....		823 <sup>j</sup>		793 <sup>j,i</sup>	491
		776 <sup>k</sup>		700 <sup>k,i</sup>	
CHHal <sub>2</sub> ·CO <sub>2</sub> <sup>-i,e</sup> .....		829 <sup>j</sup>		~767 <sup>j</sup>	
		779 <sup>k</sup>		703 <sup>k</sup>	

<sup>a</sup> In cm.<sup>-1</sup>. <sup>b</sup> Data from ref. 10c. <sup>c</sup> The intensity of the high-frequency band relative to that of the low-frequency one increases from the chloride to the iodide. <sup>d</sup> Data from ref. 10d. <sup>e</sup> The same halogen is present twice. <sup>f</sup> Data from refs. 10e and 28b. <sup>g</sup> Mean of symmetric and antisymmetric stretching frequency. <sup>h</sup> Data from refs. 10a and 21. <sup>i</sup> Present work. <sup>j</sup> Antisymmetric stretching frequency. <sup>k</sup> Symmetric stretching frequency. <sup>l</sup> *trans*-Conformation. <sup>m</sup> *gauche*-Conformation. <sup>n</sup> Weak band, attributed to the presence of a small amount of the less-stable rotational isomer.

Below 1200 cm.<sup>-1</sup> the vibration spectrum of a substituted acetate ion resembles that of the un-ionized acid. Data <sup>10a,21,22</sup> for the acids have therefore been included in Table 2. Mono- and di-chloroacetic acid and dibromoacetic acid, and their anions, show only high carbon-halogen stretching frequencies. In the predominant conformations therefore a C-Hal bond is *trans* to one oxygen atom (in the acids, O<sub>OH</sub>) and eclipses the other (in the acids, O<sub>CO</sub>). Bromoacetic acid and its anion, in the liquid phase, show both the high- and the low-frequency C-Br stretching bands, with roughly equal intensity; the two conformations seem to coexist, in roughly equal amounts. In solid sodium bromoacetate the anion is presumably wholly in the *trans* [*≡cis*] form. Iodoacetic acid and its anion, by contrast, show prominent C-I stretching bands of the *low* frequency, *i.e.*, the *gauche*-form must predominate.

There is a parallelism between halogenoacetic acids and halogenoacetate ions on the one hand, and methyl-substituted acetophenones <sup>23</sup> on the other: in all three series the form in which the C-Hal bond eclipses a CO bond is least favoured for the iodo-derivative, more favoured for the bromo-derivative, and even more so for the monochloro-, dichloro-, and dibromo-derivatives.

The preferred conformations for the propionate, cyanoacetate, and fluoroacetate ions cannot be ascertained in this manner because no suitable frequencies characteristic of the two conformations in appropriate reference compounds are known.

<sup>21</sup> Kohlrausch, Koeppl, and Pongratz, *Z. phys. Chem. (Leipzig)*, 1933, **21**, B, 242; Zeil, Buchert, Heel, and Pfoertner, *Z. Elektrochem.*, 1960, **64**, 769; Kagarise, *J. Chem. Phys.*, 1957, **27**, 519; Tschernitzkaya, *Zhur. fiz. Khim.*, 1949, **23**, 251; Canals and Gastaud, *Bull. Soc. chim. France*, 1937, **4**, 2042; Jorge and Barcelo, *Anales real Soc. españ. Fis. Quim.* 1957, **53**, B, 339; 1958, **54**, 5; Barcelo and Otero, *Spectrochim. Acta*, 1962, **18**, 1231; Cheng, *Z. phys. Chem. (Leipzig)*, 1934, **24**, B, 293; Kahovec and Kohlrausch, *Monatsh.*, 1936, **68**, 359; Saksena, *Proc. Ind. Acad. Sci.*, 1940, **12**, A, 312.

<sup>22</sup> (a) Hadzi and Sheppard, *Proc. Roy. Soc.*, 1953, **A**, 216, 247. (b) Fuson, Josien, Jones, and Lawson, *J. Chem. Phys.*, 1952, **20**, 1627; (c) Barcelo, Jorge, and Otero, *ibid.*, 1958, **28**, 1230; Otero, Barcelo, and Herrera, *Anales real Soc. españ. Fis. Quim.* 1959, **55**, B, 205.

<sup>23</sup> Jones and Spinner, *Canad. J. Chem.*, 1958, **36**, 1020.

*Substituent Effects on The Vibration Frequencies.*

$\text{CH}_2$  bending frequencies in ions  $\text{CH}_2\text{X}\cdot\text{CO}_2^-$ . The  $\text{CH}_2$  scissoring frequency is somewhat and the others are strongly mass-sensitive (*cf.* molecules<sup>10f</sup>  $\text{CH}_2\text{X}_2$ ).

$\text{CO}_2^-$  stretching bands. The most important topic examined in this work is the effect of substituents on the  $\text{CO}_2^-$  stretching frequencies in ions  $\text{R}\cdot\text{CO}_2^-$ .

For the high-frequency band ("CO<sub>2</sub> st I"), which is the most intense one in the infrared spectrum, the frequency increases very markedly with the electron-withdrawing effect of R, the sequence being  $\text{Bu}^t$  (1551  $\text{cm}^{-1}$ ) < Et < Me (1583  $\text{cm}^{-1}$ ) =  $\text{CH}_2\text{I}$  <  $\text{CH}_2\text{Br}$  <  $\text{CH}_2\text{CN}$  =  $\text{CH}_2\text{Cl}$  <  $\text{CHBr}_2$  <  $\text{CH}_2\text{F}$  <  $\text{CHCl}_2$  <  $\text{CBr}_3$  (1659  $\text{cm}^{-1}$ ) <  $\text{CCl}_3$  <  $\text{CF}_3$  (1689  $\text{cm}^{-1}$ ). This sequence is the same as for the carbonyl stretching frequency of the corresponding acids  $\text{R}\cdot\text{CO}_2\text{H}$ ,<sup>24</sup> where, however, the effect is not nearly so marked (difference in  $\nu_{\text{C=O st}}$  between  $\text{Me}_3\text{C}\cdot\text{CO}_2\text{H}$  and  $\text{CCl}_3\cdot\text{CO}_2\text{H}$ , 60  $\text{cm}^{-1}$ , as compared with 126  $\text{cm}^{-1}$  in the ions). Although iodine is electron-withdrawing it produces no frequency shift in either iodacetic acid or the anion, but this is not surprising since the C-I bond does not eclipse a C=O (or C<sup>+</sup>O) bond (in either species).

The effect of substituents on the second  $\text{CO}_2^-$  stretching frequency is quite different; this increases in the order  $\text{CBr}_3$  (i.r. 1338 + 1355  $\text{cm}^{-1}$ ) <  $\text{CCl}_3$  <  $\text{CHBr}_2$  <  $\text{CH}_2\text{CN}$  <  $\text{CH}_2\text{I}$  <  $\text{CHCl}_2$  <  $\text{CH}_2\text{Br}$  <  $\text{CH}_2\text{Cl} \approx \text{Bu}^t$  (i.r., 1413  $\text{cm}^{-1}$ ) < Me (i.r., 1421  $\text{cm}^{-1}$ ) < Et <  $\text{CF}_3 \approx \text{CH}_2\text{F}$  (i.r., 1448  $\text{cm}^{-1}$ ). There is no correlation between this sequence and the polar effect of R. For the ions in which X is a first-row element (and in which there is first-order mixing between C-C and C-X stretching), *i.e.*, for R = Et,  $\text{CH}_2\text{CN}$ ,  $\text{CH}_2\text{F}$ ,  $\text{Bu}^t$ , and  $\text{CF}_3$ , this frequency varies irregularly. For all the remaining ions it decreases as the masses of the substituents in R increase. The comparison between two pairs of groups of roughly equal weight,  $\text{CHCl}_2$  (i.r., 1399  $\text{cm}^{-1}$ ) and  $\text{CH}_2\text{Br}$  (~1403  $\text{cm}^{-1}$ ), and  $\text{CCl}_3$  (1353  $\text{cm}^{-1}$ ) and  $\text{CH}_2\text{I}$  (1394  $\text{cm}^{-1}$ ) shows that (a) two or three small masses seem to be more effective in lowering the frequency than one equivalent large mass attached to the  $\alpha$ -carbon atom; (b) the electron-withdrawing effect of R does not even make a minor contribution towards raising the frequency;  $\text{CHCl}_2$  is more electron-withdrawing than  $\text{CH}_2\text{Br}$ , and  $\text{CCl}_3$  much more electron-withdrawing than  $\text{CH}_2\text{I}$ .

*Mixing between the CC and the lower-frequency  $\text{CO}_2^-$  stretching vibrations.* Previous investigators have attributed the acetate-ion frequencies of 930 and 1420  $\text{cm}^{-1}$  to CC stretching and symmetric OCO stretching, respectively.<sup>4,5</sup> However, there are four pieces of evidence for regarding both the observed frequencies as arising from appreciably mixed vibrations. (1) The "CO<sub>2</sub> st II" frequency in the acetate ion is considerably higher than that in the formate ion<sup>4</sup> (1366  $\text{cm}^{-1}$ ). (2) The polarizability change accompanying  $\text{CO}_2^-$  symmetric stretching is considerably greater than that accompanying CC stretching. The former vibration should therefore give rise to a rather more intense Raman band; actually the Raman bands at 1416 and 931  $\text{cm}^{-1}$  are about equally intense. (3) The dependence on the mass of R expected for the CC stretching frequency is not observed for the band near 930  $\text{cm}^{-1}$  (the position of which remains practically constant); it is observed for the "CO<sub>2</sub> st II" frequency instead. (4) The latter frequency is anomalous whenever there is first-order mixing between CC and CX stretching.

Extensive mixing of stretching vibrations in the trifluoroacetate ion is strikingly demonstrated by the low intensity of the "CO<sub>2</sub> st II" band in the infrared spectrum (where normally this band is intense).

*The nature of the  $\text{CO}_2^-$  stretching vibrations and of the  $\text{CO}_2^-$  grouping.* Where the stretching frequencies of a symmetrical grouping are sensitive to the polar effects of substituents, the effects on the symmetric and the antisymmetric stretching frequencies are normally of the same order of magnitude (*cf.* the OSO stretching frequencies in compounds  $\text{R}\cdot\text{SO}_2\cdot\text{R}^2$  and HNH stretching frequencies in aromatic amines<sup>25</sup>). Conversely, where the

<sup>24</sup> Gillette, *J. Amer. Chem. Soc.*, 1936, **58**, 1143.

<sup>25</sup> Bellamy and R. L. Williams, *Spectrochim. Acta*, 1957, **9**, 341; Hambly and O'Grady, *Austral. J. Chem.*, 1962, **15**, 626.

stretching frequencies of a symmetrical grouping are mass-sensitive, the mass effects on the two frequencies are of the same order of magnitude (cf. the  $\text{CHal}_3$  stretching frequencies in compounds  $\text{HCHal}_3$  and  $\text{DCHal}_3$ , where  $\text{Hal} = \text{Cl}$  or  $\text{Br}$ ; <sup>26,107</sup> the  $\text{CICl}$  stretching frequencies in carbonyl chloride and thiocarbonyl chloride; <sup>27</sup> \* the skeletal stretching frequencies in  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{D}_6$  <sup>28a</sup>).

The two vibrations here labelled "CO<sub>2</sub> st I" and "CO st II" are normally regarded as the symmetric and antisymmetric stretching vibrations of a symmetrical  $\frac{1}{2}\text{-O}^{\ominus}\text{-C}^{\ominus}\text{-O}^{\ominus}$  grouping. However, on this basis it seems impossible to explain, in terms of changes in the CO stretching force constant, why the lower frequency is not raised in accordance with the electron-withdrawing effects of substituents while the higher one is raised so strongly; or why the lower frequency is appreciably affected by the masses of (not directly attached) substituents and the higher one is not. Other factors, which could cause the ratio of antisymmetric to symmetric stretching frequency to be anomalously high and (perhaps to vary irregularly), remain to be considered.

$$4\pi^2\nu_s^2 = k_s\left(\frac{1}{m_Y} + \frac{2}{m_X} \cos^2\theta\right) \quad 4\pi^2\nu_a^2 = k_a\left(\frac{1}{m_Y} + \frac{2}{m_X} \sin^2\theta\right)$$

From the valence force field equations for the frequencies ( $\nu$ ) of the pure XY stretching motions in an  $\text{XY}_2$  system <sup>29</sup> (where  $k_s$  and  $k_a$  are the force constants for the symmetric and antisymmetric vibration, respectively,  $m$  the atomic masses, and  $2\theta$  the YXY bond angle), it follows that the ratio  $\nu_a/\nu_s$  is raised by (a) an increase in  $\theta$ , (b) a decrease in the ratio  $\text{XY}-\text{XY}$  interaction force constant,  $\frac{1}{2}(k_s - k_a)$ , to mean force constant,  $\frac{1}{2}(k_s + k_a)$ .

For the trichloro- and tribromo-acetate ions, however, for which the ratio  $\nu_a/\nu_s$  is highest (1.239 and 1.233), steric factors prevent a widening of the OCO bond angle (in fact, they probably reduce it). Data on the effect of indirectly attached substituents on interaction constants are lacking; in Mason's <sup>30</sup> treatment of  $\text{NH}_2$  stretching frequencies in amines the ratio  $(k_s - k_a)/(k_s + k_a)$  was assumed to be independent of substituents.

Application of the above equations to the CO stretching vibrations in the formate ion ( $\nu_a = 1606$ ,  $\nu_s = 1366$   $\text{cm}^{-1}$  [in potassium bromide; this work];  $2\theta = 124^\circ$ ), treated as an  $\text{XY}_2$  system,† yields  $k_{\text{int}} = +1.6$   $\text{mdyne}/\text{\AA}$ ; this is only slightly greater than the  $k_{\text{int}} = +1.3$   $\text{mdyne}/\text{\AA}$  observed for carbon dioxide,<sup>28c</sup> which represents the extreme case approached in structure (II). The  $k_{\text{mean}}$  obtained for the formate ion is 9.5  $\text{mdyne}/\text{\AA}$ , as against 15.3  $\text{mdyne}/\text{\AA}$  in carbon dioxide.<sup>28c</sup> Thus the absolute CO-CO interaction constant should hardly be affected by substituents in the acetate ion, and be no less than 1.5  $\text{mdyne}/\text{\AA}$  in the trihalogenated ions.

Applying the equations to the trichloroacetate ion and taking  $\nu_a = 1677$ ,  $\nu_s = 1353$   $\text{cm}^{-1}$ ,  $2\theta = 124^\circ$ , one obtains  $k_{\text{int}} = 1.1$   $\text{mdyne}/\text{\AA}$ , which is even lower than that in carbon dioxide, even though  $k_{\text{mean}}$  (9.75) is only 0.25  $\text{mdyne}/\text{\AA}$  higher than it is in  $\text{HCO}_2^-$ .  $\nu_s$  in the trichloroacetate ion would have to be at least 1395  $\text{cm}^{-1}$  to give an acceptable value for  $k_{\text{int}}$ ; in the other ions a rise in  $\nu_a$  should similarly be accompanied by a rise in  $\nu_s$ .

Extremely generous assumptions regarding the effect of vibrational coupling were made above, namely that the coupling between CC and symmetric OCO stretching, which raises  $\nu_s$  in  $\text{CH}_3\cdot\text{CO}_2^-$  by 55  $\text{cm}^{-1}$  relative to  $\nu_s$  in  $\text{HCO}_2^-$ , is completely nullified in  $\text{CCl}_3\cdot\text{CO}_2^-$  by  $\text{CCl}_3/\text{CO}_2$  coupling, but that the latter coupling does not also reduce  $\nu_a$ . If the intrinsic

\* A polar effect probably operates here in addition to the mass effect.

† In view of the known small effect of deuteration <sup>6</sup> on the CO stretching frequencies in the formate ion this is permissible.

<sup>26</sup> Wood and Rank, *Phys. Rev.*, 1935, **48**, 63.

<sup>27</sup> Thompson, *Trans. Faraday Soc.*, 1941, **37**, 251.

<sup>28</sup> Herzberg, "Molecular Spectra and Molecular Structure. Vol. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, (a) pp. 364 and 365; (b) p. 348; (c) p. 187.

<sup>29</sup> Linnett, *Trans. Faraday Soc.*, 1945, **41**, 223.

<sup>30</sup> Mason, *J.*, 1958, 3619; Elliott and Mason, *J.*, 1959, 1275.



$\nu_s$ , corresponding to the pure vibration, is less than  $1353 \text{ cm}^{-1}$ , or the intrinsic  $\nu_a$  greater than  $1677 \text{ cm}^{-1}$ , a  $k_{\text{int}}$  of even less than  $1.1 \text{ mdyne/\AA}$  is obtained. Actually the anti-symmetric  $\text{CCl}_3$  and  $\text{OCO}$  stretching motions could interact nearly as strongly as the symmetric ones. Certainly in ions  $\text{CH}_2\text{X}\cdot\text{CO}_2^-$  and  $\text{CHX}_2\cdot\text{CO}_2^-$  the interactions of anti-symmetric and symmetric  $\text{OCO}$  stretching with  $\text{CX}$  stretching, and hence the effect of the mass of  $\text{X}$  on  $\nu_a$  and  $\nu_s$ , should be of the same order of magnitude.

Thus, even when substituent effects on bond angles,  $\text{CO-CO}$  interaction constants, and on distant vibrational couplings are taken into account, there appears to be no satisfactory explanation in terms of symmetric and anti-symmetric  $\text{OCO}$  stretching for the gross difference in behaviour upon substitution found for the acetate ion frequencies of  $1583$  and  $1421 \text{ cm}^{-1}$ .

This difference is far less surprising if the two vibrations arise in different bonds, and, in the author's view, the  $\text{CO}_2^-$  grouping is not a symmetrical one but consists of a  $\text{C=O}$  and a  $\text{C-O}^-$  bond, as in (Ia). To convert the  $\text{O=C-O}^-$  system into the  $\frac{1}{2}\text{O}^-\text{C}^-\text{O}^{\frac{1}{2}}$  system, the  $\text{C=O}$  bond has to be stretched and the  $\text{C-O}^-$  bond compressed, which, in the absence of changes in electron delocalization, requires a distortion energy  $E_D$ . When the two bonds are equal in length the resonance energy is at a maximum, *i.e.*, a resonance energy  $\Delta E_R$  has been gained. If  $\Delta E_R \geq E_D$ , the resonance hybrid will be more stable; if  $E_D > \Delta E_R$ , the pure canonical form will be more stable. One cannot predict *a priori* whether  $\Delta E_R$  or  $E_D$  will be the greater, in this or any similar system.

It is known empirically, from the vibration spectrum, that the carbonate ion has trigonal symmetry and must be a resonance hybrid. However, there is no evidence which requires that the carboxylate grouping be symmetrical in its equilibrium configuration, and the results now obtained are strong evidence for the unsymmetrical structure. Like ammonia, the unsymmetrical  $\text{CO}_2^-$  grouping has two equilibrium configurations of equal energy, *i.e.*, (Ia) and (Ib), and will undergo inversion from one to the other; the inversion frequency cannot be predicted *a priori*.\*

On this basis, vibration "CO st I," which behaves like  $\text{C=O}$  stretching, is, in fact an (essentially localized)  $\text{C=O}$  stretching vibration, its low frequency being due to the strong electron-donating effect of  $\text{O}^-$  attached to  $\text{C=O}$ . The "CO st II" vibration is regarded as pure  $\text{C-O}^-$  stretching in the formate ion only.<sup>34</sup> In the acetate ion substantial mixing between  $\text{C-O}^-$  and  $\text{C-C}$  stretching is expected since both bonds are single bonds joining atoms of almost identical masses; the vibrations of frequencies  $930$  and  $1420 \text{ cm}^{-1}$  thus have some of the character of symmetric and anti-symmetric  $\text{C-C-O}^-$  stretching vibrations, respectively. The four above-mentioned manifestations of the involvement of vibration "CO<sub>2</sub> st II" in mixing are thus readily understood, as is the similarity between carboxylic acid and anion with regard to both preferred conformation and vibration spectrum in regions free from  $\text{OH}$  bands.

*Comparison with Nitro-compounds.*—The  $\text{CO}_2^-$  and  $\text{NO}_2$  groups being isoelectronic, the structural and vibrational possibilities are the same for substituted acetate ions and nitromethanes. The rather limited vibration-spectral data available for the latter (summarized by Mason and Dunderdale<sup>35</sup> and by Lunn<sup>36</sup>) suggest that the structural and vibrational situation may be similar in the two series, but they are not extensive enough to prove this (no data for monohalogenonitromethanes exist). The "NO<sub>2</sub> st II" vibration

\* Owing to this inversion, the dissymmetry is not at all likely to be detectable by *X*-ray crystallography. By this method equal  $\text{CO}$  bonds were found for sodium formate<sup>31</sup> and sodium oxalate,<sup>32</sup> but unequal ones, of lengths  $1.27$  and  $1.33 \text{ \AA}$ , for both gadolinium formate<sup>33</sup> and dipotassium nitroacetate, for both of which "incomplete resonance" was suggested.

<sup>31</sup> Zachariasen, *J. Amer. Chem. Soc.*, 1940, **62**, 1011.

<sup>32</sup> Jeffrey and Parry, *J. Amer. Chem. Soc.*, 1954, **76**, 5283.

<sup>33</sup> Pabst, *J. Chem. Phys.*, 1943, **11**, 145.

<sup>34</sup> Sutor, Llewellyn, and Maslen, *Acta Cryst.*, 1954, **7**, 145.

<sup>35</sup> Mason and Dunderdale, *J.*, 1956, 759.

<sup>36</sup> Lunn, *Spectrochim. Acta*, 1960, **16**, 1088.

and CN stretching undoubtedly interact,<sup>37</sup> and substituents capable of first-order mixing with the latter may be expected to affect also the former.

The (rather remarkable) correlation suggested by Lunn<sup>36</sup> between the *increase* in  $\nu(\text{NO}_2 \text{ st I})$  and the *decrease* in  $\nu(\text{NO}_2 \text{ st II})$  would probably not be observed for a sufficiently extended range of substituted nitromethanes free from this last-mentioned complication. No such correlation exists for substituted acetate ions, or for nitrobenzenes, for some of which the two  $\text{NO}_2$  stretching frequencies increase in parallel.<sup>38</sup>

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<sup>37</sup> Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

<sup>38</sup> Kross and Fassel, *J. Amer. Chem. Soc.*, 1956, **78**, 4225; van Veen, Verkade, and Wepster, *Rec. Trav. chim.*, 1957, **76**, 801; Bocek, Mangini, and Zahradnik, *J.*, 1963, 255.

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