

Symmetry of Carboxylate Ions. Infrared Spectra of ^{18}O Labelled Sodium Deuterioformate

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The band shifts in the i.r. spectra of solid 40–60% ^{18}O enriched sodium deuterioformate show unambiguously that the two C–O force constants are equal and the charge and bond delocalisation in the carboxylate group is complete. This is in contrast to Spinner's conclusion.

In textbooks the carboxylate ion is commonly formulated as a symmetric resonance hybrid A. The two i.r. C–O stretching frequencies are assigned to the anti-symmetric and symmetric vibrations. According to

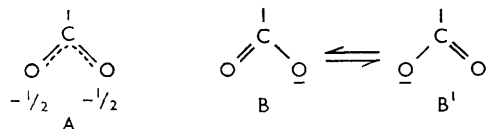
¹ W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1940, **62**, 1011.

² E. Spinner, *J. Chem. Soc.*, 1964, 4217; *J. Chem. Soc. (B)*, 1967, 874.

³ E. Spinner, *J. Chem. Soc. (B)*, 1967, 879.

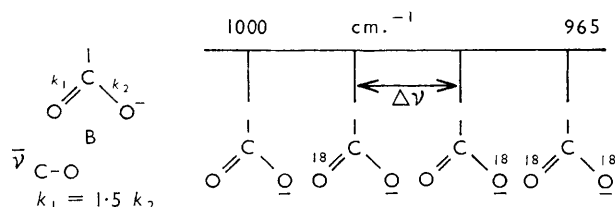
X-ray analysis, the structure of sodium formate is A, the two C–O bond lengths being equal (1.27 Å).¹ From the shifts of the C–O bands caused by numerous different substituents,² and from a detailed discussion of the sodium deuterioformate Raman and i.r. spectrum,³ Spinner deduced a classical formulation for the carboxylate group with a rapid equilibrium between asymmetric

structures $B \rightleftharpoons B'$. He assigned the higher frequency to the C=O and the lower to the C-O bond vibration.



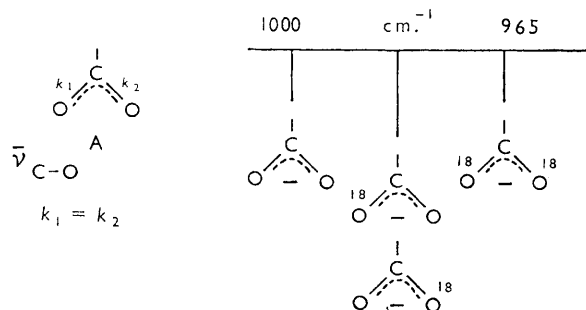
Therefore, we have tried to solve this problem in an unambiguous and independent way. The technique used in this study has been applied successfully to acetylacetones, acetylacetone, and copper acetoacetic ester,⁴ and has been shown to be able to distinguish easily between a symmetrical delocalisation A and even a very rapid equilibrium $B \rightleftharpoons B'$.⁵ †

If the doubly bonded oxygen in B is replaced by the heavy isotope ^{18}O , the C=O stretching frequency should be shifted strongly to higher wavelengths whereas the C-O stretching frequency should be shifted only slightly. Correspondingly, if the singly bonded oxygen is labelled, the C-O stretching frequency should be shifted strongly and the C=O stretching frequency only slightly. If both oxygens in B are replaced by ^{18}O , both frequencies are expected to be shifted very strongly. A mixture of unlabelled, singly ^{18}O and doubly $^{18}\text{O}_2$ labelled molecules should show a C=O and a C-O stretching frequency, both split into four bands.



If the two C-O force constants become more and more equal in magnitude, calculations show that the two centre

sense in discussing this problem if the frequency of the equilibrium $B \rightleftharpoons B'$ reaches the i.r. region. In this case B and B' are vibrational amplitudes of the symmetric structure A.



All carboxylate vibrations of the i.r. spectrum of sodium deuteroformate enriched in ^{18}O to about 60% show drastic frequency shifts to higher wavelengths (Table and Figure 1). The first C-O frequency at 1590 cm^{-1} is broad and shifted to 1577 cm^{-1} . The second C-O frequency at 1332.0 cm^{-1} , however, is split into a well resolved triplet at 1332.0, 1309.5, and 1289.0 cm^{-1} . The less intense component at 1332.0 cm^{-1} is assigned to the 16% unlabelled molecules present in the mixture obtained from sodium cyanide by hydrolysis with 60% ^{18}O enriched deuterium oxide; the second most intense frequency at 1309.5 cm^{-1} belongs to the singly labelled molecules $\text{DCO}^{18}\text{ONa}$ (48%), and the third component at 1289.0 cm^{-1} is assigned to the doubly ^{18}O substituted molecules (36%). This assignment is confirmed by the intensities of these bands in the spectrum of a sample obtained from sodium cyanide and deuterium oxide 40% in ^{18}O . The observed intensities agree well with the calculated ones (Found: 35, 50, and 15%. Calc.: 36, 48, and 16%, Figure 2a). The same situation is found for the C-D in-plane bending fre-

Observed frequencies and assignments for the fundamentals of ^{18}O enriched DCOONa

Mode	Assignment	DCOONa (ν)	$\text{DCO}^{18}\text{ONa}$ (ν')	$\text{DC}^{18}\text{O}^{18}\text{ONa}$ (ν'')	$\Delta\nu'$	$\Delta\nu''$	ν'/ν	ν''/ν
$\nu_1(A_1)$	$\nu(\text{C-D})$	2135.0		2132.0 *	-3.0 *		0.9986 *	
$\nu_2(A_1)$	$\nu_8(\text{O}=\text{C}=\text{O})$	1332.0	1309.5	1289.0	-22.5	-43.0	0.9831	0.9679
$\nu_3(A_1)$	$\delta(\text{O}=\text{C}=\text{O})$	766.5	750.0	732.0	-16.5	-34.5	0.9790	0.9550
$\nu_4(B_1)$	$\nu_{\text{as}}(\text{O}=\text{C}=\text{O})$	1590		1577 *	-13 *		0.9918 *	
$\nu_5(B_1)$	$\delta(\text{C-D})$	1013.0	1009.0	1005.0	-4.0	-8.0	0.9960	0.9921
$\nu_6(B_2)$	$\gamma(\text{C-D})$	914.0		911.0 *	-3.0 *		0.9967 *	

Observed frequencies are in cm^{-1} .

* The $\text{DCO}^{18}\text{ONa}$ and $\text{DC}^{18}\text{O}^{18}\text{ONa}$ fundamentals are not resolved.

bands move closer together and finally collapse to a single band in the middle of the triplet for the symmetric structure A. ‡ In this case it is impossible to distinguish whether the right- or left-hand oxygen in structure A is substituted by ^{18}O . On the other hand, there is no

† Very rapid is used for the frequency range from i.r. to n.m.r. or e.s.r. spectroscopy, e.g. the equilibration of the methyl groups in acetylacetone is so fast that they cannot be distinguished by n.m.r.

‡ Frequency differences $\Delta\nu$ of the centre bands of 6.5, 3.5, and 1.0 cm^{-1} correspond to force constant ratios k_1/k_2 of 1.2, 1.1, and 1.03.

quency (1013.0 cm^{-1}) and the O-C-O in-plane deformation mode (766.5 cm^{-1}) (Figure 2b and 2c).

The good agreement between the theoretical frequency product ratio for the A_1 modes (0.9269), calculated on the basis of the Teller-Redlich product rule⁶) and the

⁴ H. Musso and H. Junge, *Tetrahedron Letters*, 1966, 4003; *Spectrochim. Acta*, in the press.

⁵ H. Junge and H. Musso, *Tetrahedron Letters*, 1966, 4009; *Chem. Ber.*, in the press.

⁶ N. B. Colthup, L. H. Daly, and S. E. Wiberley, 'Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1964.

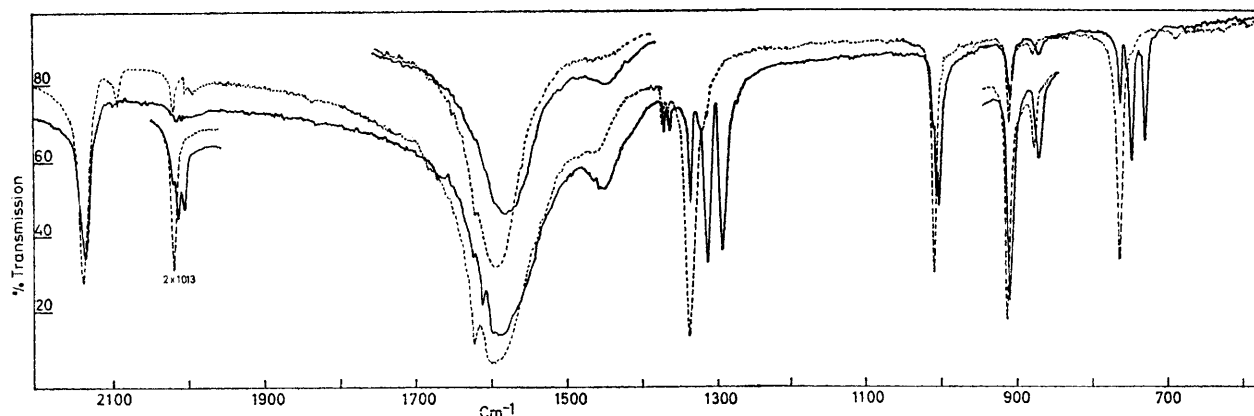


FIGURE 1 KBr Pellet spectra of ^{18}O labelled sodium deuterioformate; — labelled (60% ^{18}O); --- unlabelled; concentrations are 0.23 mg./200 mg. KBr, 0.54 mg./200 mg. KBr, and 2.41 mg./300 mg. KBr

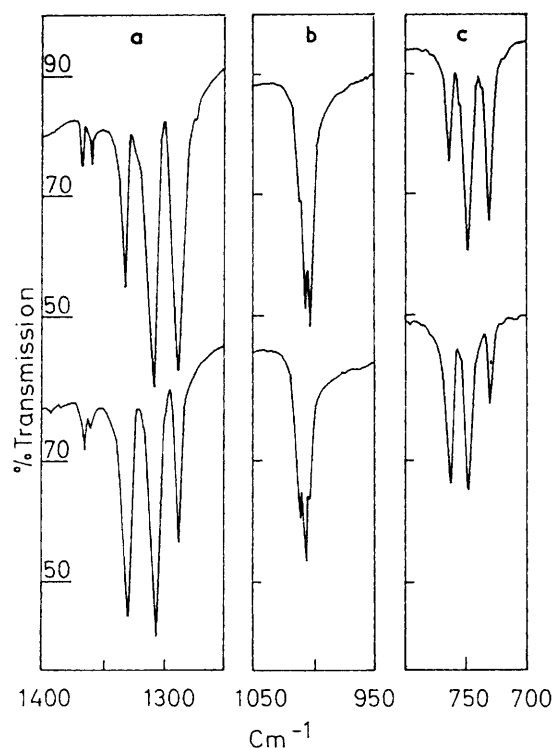


FIGURE 2 KBr Pellet spectra of ^{18}O labelled sodium deuterioformate (0.54 mg./200 mg. KBr): the upper spectra are for the 60% ^{18}O sample while the lower spectra are for the 40% ^{18}O sample. In D_2O solution (0.8m) the same spectrum is observed as shown in (a) shifted to longer wavelengths by 5 cm^{-1}

observed product ratio (0.9230) confirms the given assignments. (Failure to resolve the isotope ^{18}O and $^{18}\text{O}_2$ splittings (ν' and ν'') of ν_4 and ν_6 renders the calcul-

§ C(1)—O(1) 1.33 Å, C(1)—O(2) 1.22 Å.^{7a} Copper formate dihydrate; C(1)—O(1) 1.19 Å, C(1)—O(2) 1.29 Å, C(2)—O(3) 1.21 Å, C(2)—O(4) 1.27, but in the tetrahydrate equal distances are observed: C(1)—O(1) 1.26 Å, C(1)—O(2) 1.25 Å.^{7b}

ation of the $\nu_4 \times \nu_5$ and ν_6 frequency product ratios impossible for the observed data).

Since the two most intense components of the triplets in Figures 2a and 2c are equal in their half-band width within $\pm 1\text{ cm}^{-1}$, the second frequency at 1309.5 cm^{-1} is a single vibration or a mixture of two, different in $\Delta\nu$ not more than 1 cm^{-1} . Therefore the two C—O force constants of the carboxylate group must be equal within $\pm 3\%$. This result provides strong evidence for complete bond and charge delocalisation. Hence the carboxylate group in carboxylic acids is still best formulated as a symmetric resonance hybrid A.

In principle it is of course possible that in a crystal—especially if it contains water—the two oxygen atoms of the carboxylate group are in different orientations in the crystal lattice or water association and thus two different C—O distances can be formed, as in lithium acetate dihydrate.[§] This situation, however, is very unlikely to be the most stable one of the free ion.

EXPERIMENTAL

^{18}O -Labelled sodium deuterioformate with 60 atom % of ^{18}O was prepared by heating dry sodium cyanide (23.2 mg.), D_2^{18}O (31.3 mg.) (Yeda, Rehovoth, 98.8 atom % of ^{18}O), D_2O (19.8 mg.), and sodium methoxide (0.2 mg.) for 7 hr. at 175° in a pressure tube. After removal of excess of water *in vacuo* the residue was dried at $100^\circ/0.03\text{ mm.}$ (32.2 mg.) and used without further purification.

The i.r. spectra were recorded on a Perkin-Elmer model 421 spectrophotometer and were calibrated with polystyrene. The frequencies are believed to be accurate to $\pm 1\text{ cm}^{-1}$, reproducibility to $\pm 0.5\text{ cm}^{-1}$.

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⁷ (a) V. Amirthalingam and V. M. Padmanashan, *Acta Cryst.*, 1958, **11**, 896; (b) M. Bukowska-Strzyzewska, *Acta Cryst.*, 1965, **19**, 357.