Assignment for the Infrared Spectrum of Solid Sodium Propionate from Low-Temperature Measurements in Combination with ^{13}C Isotopic Shifts

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The infrared spectra of CH_3CH_2COONa and its ^{13}C-labeled modifications (1-^{13}C, 2-^{13}C, and 3-^{13}C) suspended in KBr disks were measured in the region 4000 – 200 cm^{-1} at room temperature and liquid nitrogen temperature. Overlapping complex band contours appeared in some regions of the room temperature spectrum, most notably in the region 1500 – 1350 cm^{-1}, where 5 fundamentals having contributions from the methyl deformation, methylene bending, and carboxylate stretching modes should occur. In contrast to this, excellent resolution was reached at the low temperature, from which all 22 fundamentals expected in the whole spectral region investigated were detected. A complete assignment of the fundamentals is proposed mainly on the basis of the characteristic isotopic shifts of the three ^{13}C substituted sodium propionate species. A fair number of the fundamentals were found to feature coupled modes having contributions from several group vibrations.

Introduction

Propionate ion is important not only in organic chemistry but also in inorganic chemistry as one of the simplest ligands forming metal complexes. To our knowledge, however, no assignment for the infrared spectrum of the ionized form of propionic acid [1] has been reported so far. In recent papers [2 – 4] relating to the vibrational analyses of sodium acetate and pyruvate, we have shown that i) low-temperature infrared spectra make it possible to clarify regions of the spectra which are overlapped at room temperature, and thus to locate the fundamental frequencies without ambiguity, and that ii) the frequencies from heavy atom isotope (^{13}C, ^{18}O, etc.) labeled modifications rather than D-labeled species allow for more reliable assignments of the fundamentals.

In the present work, the infrared spectra of CH_3CH_2COONa (parent species), $CH_3CH_2{}^{13}COONa$ (1-^{13}C), $CH_3{}^{13}CH_2COONa$ (2-^{13}C), and $^{13}CH_3CH_2COONa$ (3-^{13}C) were measured at 80 and 290 K. Detailed profiles of the low-temperature spectra are given in order to demonstrate their great advantage in reaching excellent resolution. Vibrational assignments are presented for all the fundamentals observed in the spectral region 4000 – 200 cm^{-1} with the aid of the ^{13}C shifts of the fundamentals.

Experimental

Potassium bromide and CH_3CH_2COONa were obtained commercially (E. Merck Co. Ltd., Darmstadt). The ^{13}C-enriched modifications of sodium propionate were purchased from Merck Sharp and Dohme Canada Ltd. with 99% ^{13}C isotopic purity for 1-^{13}C and with 90% for 2 and 3-^{13}C. The handling of the samples and the preparation of KBr disks were as described in [2]. The infrared spectra were measured in the frequency regions of 4000 – 450 cm^{-1} and 450 – 200 cm^{-1} by using a Bruker IFS-113 v FT-IR spectrometer with a resolution of 0.5 cm^{-1} and a Jasco Model A-702 spectrometer with slit program N (spectral resolution 2.5 cm^{-1}), respectively. Liquid nitrogen cryostats with KRS-5 windows, Model CF-1104 (Oxford Instrument) and Model TM-1-511 (Cryogenic Research Laboratory), were used for the low-temperature measurements. The band frequencies lying in the region 450 – 200 cm^{-1} were calibrated against the standard absorption bands of gaseous H_2O [5].

Results and Discussion

The great advantage of measuring spectra at low temperature is demonstrated for the parent species in Figs. 1 and 2 covering the spectral regions 3040 – 2880 cm^{-1} and 1700 – 250 cm^{-1}, respectively. The ν_2 band in Fig. 1 and the ν_5, ν_6, and ν_{18} bands in

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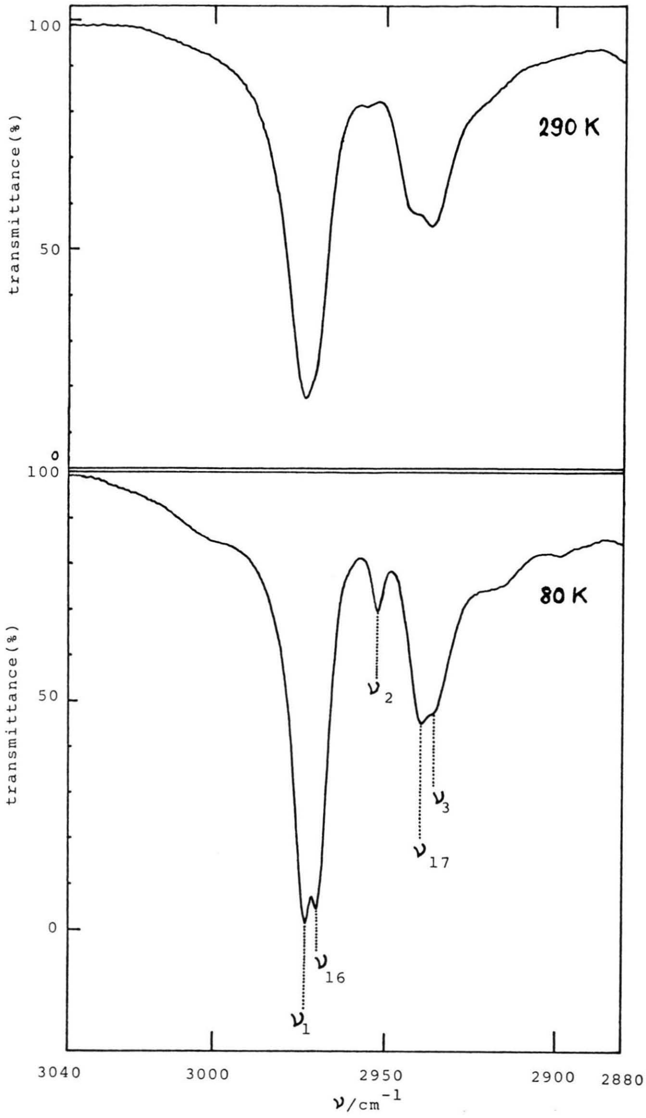

Fig. 1. Characteristic absorption bands due to CH_3- and CH_2-stretching modes of CH_3CH_2COONa at 80 (below) and 290 (above) K; 0.35 mg of sample suspended in 150 mg of KBr. The symbols ν_i ($i = 1-3$, 16, 17) correspond to those given in Table 1.

Fig. 2, which were hardly discernible in the room temperature spectra, clearly showed up in the low temperature spectra. Such a sharpening effect is also seen for the ν_{19}, ν_{22} and ν_{15} bands in Figure 2. Some of the lines at 80 K consist of two or more individual absorption lines. These lines presumably result from different crystal sites of sodium propionate. This interpretation is supported by an often similar structure of the corresponding absorption lines in ^{13}C-labeled modifications of sodium propionate. Low temperature spectra are used throughout in this paper for the identification of the absorption lines.

In the present vibrational assignments, all the isotopic species concerned are assumed to belong a symmetry point group C_s in which the vibrational representation has the form $15A' + 9A''$. Since the methyl and CO_2 torsional A'' modes are expected to be observed in a low frequency region (less than 200 cm^{-1}), they were not investigated in this paper. The fundamental frequencies observed at 80 K, along with their proposed assignments, are listed in Table 1. The initial assignments of the fundamentals were carried out on the basis of the qualitative empirical rules available [6] and of comparisons with the vibrational assignments on related molecules such as sodium acetate [3], pyruvate [4], and propane [7]. The present ^{13}C isotopic shifts of the fundamentals are quite useful to assess the proposed assignments as indicated below.

(1) CH-stretching region

In the region of 3000 cm^{-1}, a total of 5 fundamentals are expected to be observed; three of them are classified as CH_3 stretching modes, the others as CH_2 stretching vibrations. An expanded section of the low temperature spectrum for the parent species is shown in Fig. 3, together with the corresponding spectra for the ^{13}C-labeled modifications. Going from the high frequency side to the lower frequency side, one finds a strong intensity band with a doublet structure (ν_1 and ν_{16}), a weak intensity band (ν_2), and a medium intensity band (ν_{17}) with a shoulder (ν_3) at lower frequency (see Figure 3a). The doublet could be assigned to the near degenerate antisymmetric CH_3 stretching modes, since the ^{13}C-substitution at the methyl carbon caused a significant lower frequency shift (ca. 8 cm^{-1}) of the band in question (see Figure 3d). The ν_2 and ν_{17} bands observed at 2952.5 and 2940.0 cm^{-1} for the parent species could be due to the symmetric and antisymmetric stretching motions of the CH_2 group. The corresponding fundamentals for the 2-^{13}C labeled modification were found at 2943.5 and 2933.3 cm^{-1} with lower frequency shifts (see Figure 3c). The remaining symmetric CH_3 stretching fundamental for the parent species is submerged under the ν_{17} band assigned to the CH_2 antisymmetric stretching mode, and it was observed only as

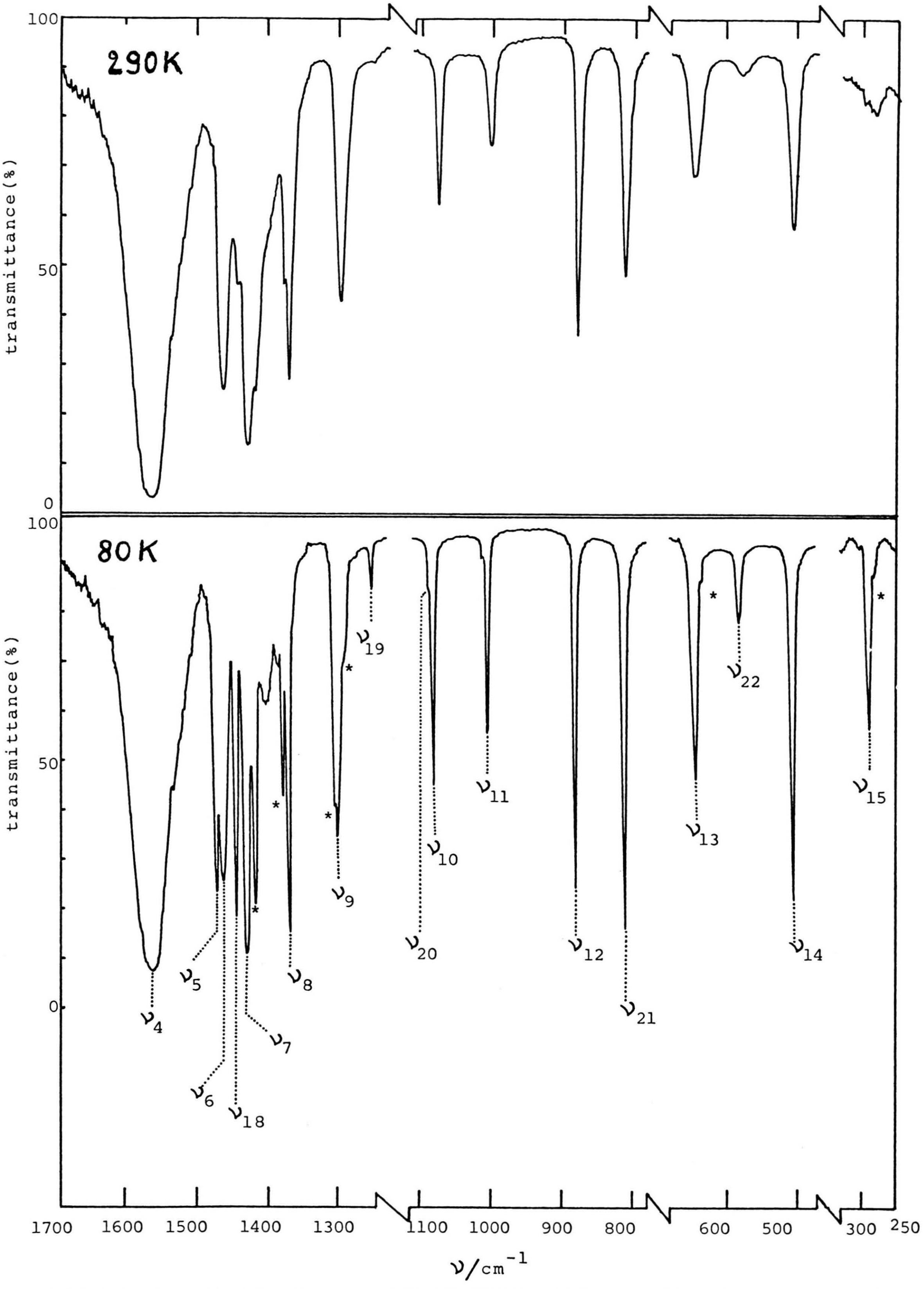

Fig. 2. Selected regions of the infrared spectrum of CH_3CH_2COONa at 80 (below) and 290 (above) K; 0.35 mg of sample suspended in 150 mg of KBr. For the symbols ν_i ($i = 4-22$) see the notations in Table 1. Bands in the spectrum at 80 K marked by an asterisk represent factor group splittings.

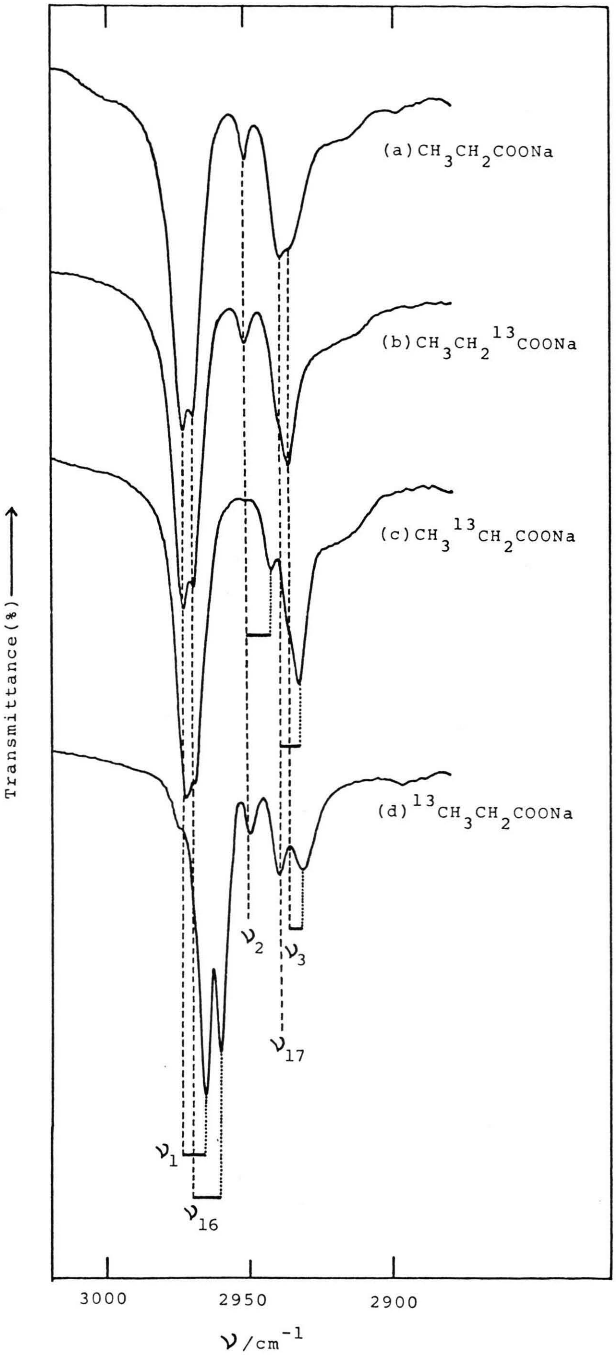

Fig. 3. CH_3- and CH_2-stretching region of the spectra of CH_3CH_2COONa (a) $CH_3CH_2{}^{13}COONa$ (b), $CH_3{}^{13}CH_2COONa$ (c), and $^{13}CH_3CH_2COONa$ (d) at 80 K; 0.35 mg of sample suspended in 150 mg of KBr. Broken and dotted lines indicate positions of fundamentals for the parent and ^{13}C-labeled species, respectively. Horizontal lines connecting broken and dotted lines represent magnitudes of ^{13}C-shifts of fundamentals. For symbols ν_i, see the notations given in Table 1.

a shoulder (ν_3) at about 2937 cm^{-1}. The ^{13}C-substitution at the methyl carbon caused a lower frequency shift (ca. 8 cm^{-1}) of the ν_3 band, so that the fundamental due to the CH_3 symmetric stretching mode for the 3-^{13}C labeled modification was separately observed from the ν_{17} band as shown in Figure 3d.

(2) CO_2-stretching and (HCH)-bending region

The band observed at 1563.2 cm^{-1} (ν_4) for the parent species is very intense as shown in Figure 2. The ν_4 band shifts by ca. 40 cm^{-1} upon ^{13}C-substitution of the carboxylate group, whereas the same band has a high degree of the antisymmetric CO_2 of the methylene and methyl groups (see ν_4 in Table 1). The intensity of the band and the result of the ^{13}C isotopic shift strongly suggest that the ν_4 band has a high degree of the antisymmetric CO_2 stretching character. In the low temperature spectrum for the parent species all 7 fundamentals $(5A' + 2A'')$ expected in the spectral region 1500 to 1200 cm^{-1} may be localized as shown in Figure 4. Of these, the assignment of the fundamental due to a symmetric CO_2 stretching motion is straightforward; the ν_7 band at 1428.6 cm^{-1} for the parent species undergoes a large frequency shift (ca. 18 cm^{-1}) only in the IR spectrum of the 1-^{13}C labeled modification, and therefore the ν_7 band is assignable to the symmetric CO_2 stretching mode.

The three distinct bands observed at 1471.2 (ν_5), 1461.4 (ν_6), and 1442.4 (ν_{18}) cm^{-1} for the parent molecule may be assigned to two antisymmetric CH_3 deformation modes and one CH_2 bending mode. However, the results of the ^{13}C-isotopic shifts suggest that the three normal modes are strongly intermixed or coupled with several group modes. Since the ν_5 and ν_6 bands are significantly shifted by the ^{13}C-substitution of the CO_2 and CH_2 carbon atoms, they may be assigned to coupling modes of the antisymmetric CH_3 deformation (A'), CH_2 bending, and CO_2 symmetric stretching vibrations. The remaining ν_{18} band slightly shifts upon ^{13}C-substitution of the CO_2 and CH_2 groups and is tentatively assigned to the antisymmetric CH_3 deformation mode (A''). It is noteworthy that the three bands shift only by ca. 1 cm^{-1} upon ^{13}C-substitution of the CH_3 group. Such a feature has been found in the spectra of methylnitrite [8], thioacetamide [9], and pyruvic acid [10], where the bands assigned to

Table 1. Observed frequencies and tentative assignments for the fundamentals of four isotopic species of sodium propionate at 80 K.

Representation C_s	Notation	Approximate description	CH_3CH_2COONa	((1-): COO.	(2-): CH_2.	(3-): CH_3.)
			parent	1-^{13}C	2-^{13}C	3-^{13}C
A'	ν_1	asym CH_3 str.	2973.5	2973.1	2972.4	2966.3
	ν_2	sym CH_2 str.	2952.5	2952.6	2943.5	2950.1
	ν_3	sym CH_3 str.	2937[a]	2937.4	2937[a]	2932.4
	ν_4	asym CO_2 str.	1563.2	1523.7	1563.7	1563.7
	ν_5	asym CH_3 deform. +	1471.2	1465.6	1468.5	1470.2
	ν_6	CH_2 sciss. + sym CO_2 str.	1461.4	1454.0	1453.5	1460.8
	ν_7	sym CO_2 str.	1428.6	1410.4	1428.7	1429.1
			1417[b]	1421, 1402[b]	1414[b]	1416[b]
	ν_8	sym CH_3 deform.	1369.1	1367.7[c]	1368.4	1360.2
			1376[b]		1375[b]	1367[b]
	ν_9	CH_2 wag.	1301.4[c]	1298.4[c]	1286.5	1299.6[c]
	ν_{10}	in-plane CH_3 rock + CH_3-C str.	1077.7	1077.7	1061.8	1067.3
	ν_{11}	CH_3-C str. (asym CCC str.)	1009.9	1000.0	994.5	995.6
	ν_{12}	CO_2-C str. (sym CCC str.)	881.4	874.9	879.5	879.3
	ν_{13}	CO_2 bend + asym CCC str.	646.7	646.8	637.2	646.8
	ν_{14}	in-plane CO_2 rock + sym CCC str.	507.4	505.1	505.8	502.7
	ν_{15}	CCC bend	291.5	290.8	291.2	289.8
A''	ν_{16}	asym CH_3 str.	2970.2	2970.2	2970.0	2960.7
	ν_{17}	asym CH_2 str.	2940.0	2940[a]	2933.3	2940.0
	ν_{18}	asym CH_3 deform.	1442.4	1438.6	1438.8	1441.5
	ν_{19}	CH_2 twist + out-of-plane CH_3 rock	1250.4	1248.4	1249.8	1245.4
	ν_{20}	out-of-plane CH_3 rock + CH_2 twist or rock	1080[a]	1080[a]	1071.4	1075.9
	ν_{21}	CH_2 rock	812.9	805.0	810.5	811.7
	ν_{22}	out-of-plane CO_2 rock	584.9	576.4	583.9	584.8

[a] Shoulders.
[b] Minor components resulting from factor-group splittings.
[c] Averaged values of factor-group doublets of similar intensity.

the methyl antisymmetric deformation modes experience downward shifts of only about 2 cm^{-1} upon ^{13}C-substitution of the methyl groups.

In contrast to the ν_5, ν_6, and ν_{18} bands, the ν_8 band observed at 1369.1 cm^{-1} for the parent species undergoes a significant shift to 1360.2 cm^{-1} upon ^{13}C-substitution of the CH_3 group. Thus, by analogy with the CH_3 deformational property of sodium acetate [3] and pyruvate [4], the ν_8 band can be reasonably assigned to the symmetric CH_3 deformation mode.

The ν_9 band observed at 1301.4 cm^{-1} for the parent species, which shifts to 1286.5 cm^{-1} upon ^{13}C-substitution of the CH_2 group, may be due to a CH_2 wagging motion. The weak ν_{19} band centered at 1250.4 cm^{-1} is tentatively assigned to a CH_2 twisting mode, however a significant methyl ^{13}C-shift (5 cm^{-1}) of the ν_{19} band suggests considerable coupling of this vibration to an out-of-plane rocking mode of the CH_3 group (ν_{20}, discussed later).

(3) Fingerprint region, 1200 – 200 cm^{-1}

The main problem of the assignment in this region, in which $6A' + 3A''$ fundamentals are to be expected, focuses on two methyl rocking and two skeletal CC stretching modes. An expanded section of the low-temperature spectra for the parent and its three ^{13}C-isotopic species is shown in Fig. 5 in the frequency region 1100 – 860 cm^{-1}. One strong band

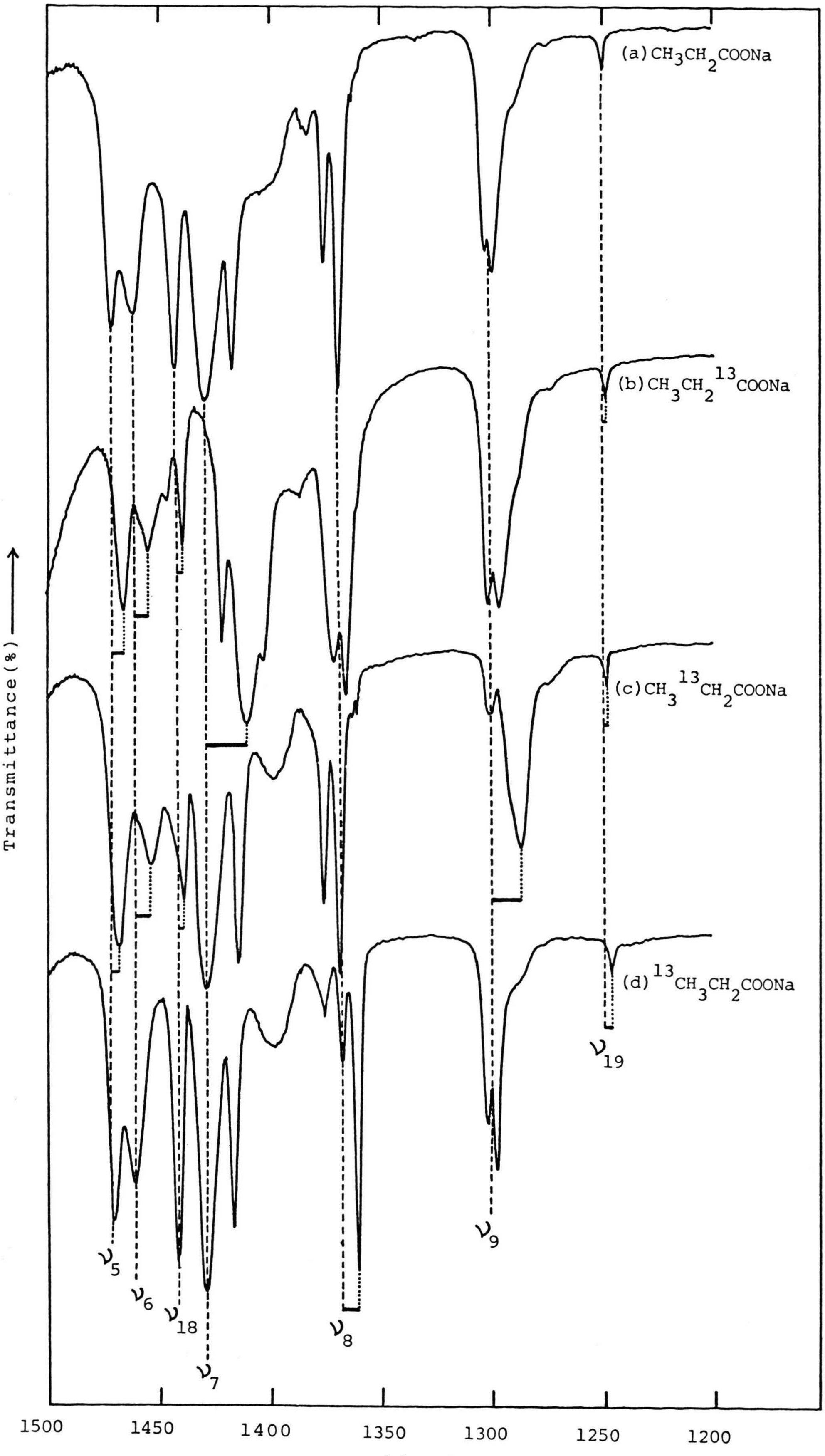

Fig. 4. CO_2-stretching, CH_3- and CH_2-bending region of the spectra of CH_3CH_2COONa (a), $CH_3CH_2{}^{13}COONa$ (b), $CH_3{}^{13}CH_2COONa$ (c), and $^{13}CH_3CH_2COONa$ (d) at 80 K; 0.35 mg of sample suspended in 150 mg of KBr. For broken, dotted, and horizontal lines, see Figure 3. For symbols ν_i, see the notations given in Table 1.

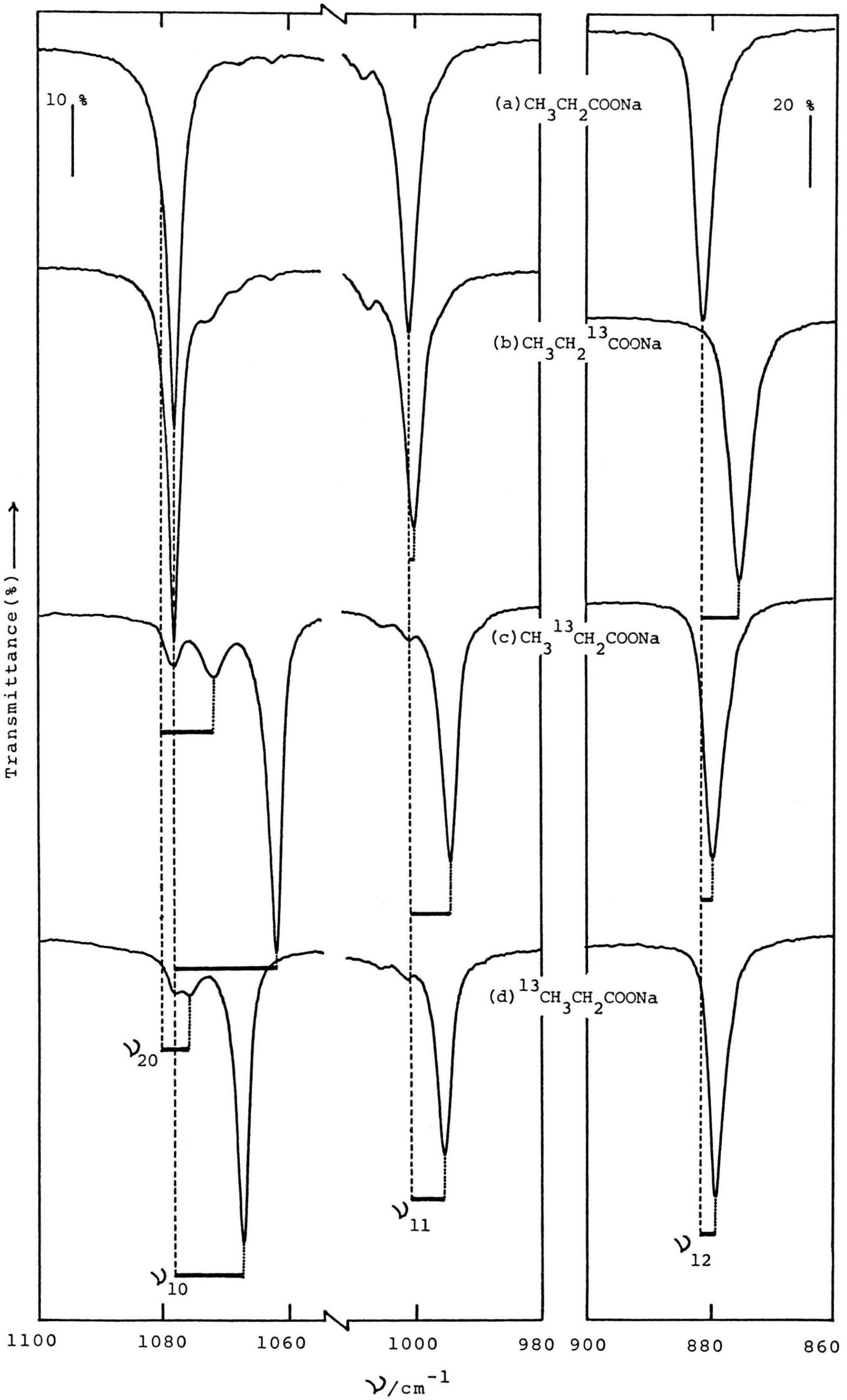

Fig. 5. Fingerprint region of the spectra of CH_3CH_2COONa (a), $CH_3CH_2{}^{13}COONa$ (b), $CH_3{}^{13}CH_2COONa$ (c), and $^{13}CH_3CH_2COONa$ (d) at 80 K; 0.35 mg of sample suspended in 150 mg of KBr. For broken, dotted, and horizontal lines, see Figure 3. For symbols ν_i, see the notations given in Table 1. Weak bands appearing in a higher frequency side of the spectra (c) and (d) are due to coexisting parent species.

(ν_{10}) with a shoulder (ν_{20}) was observed at 1077.7 cm^{-1} for the parent species, which undergoes large shifts by 15.9 cm^{-1} and 10.4 cm^{-1} upon ^{13}C-substitution of the CH_2 and CH_3 groups, respectively. Based on this observation of the ^{13}C-shifts, the ν_{10} band can be assigned to a coupled mode having contributions from the in-plane CH_3 rocking and CH_3-C stretching vibrations. The large isotopic shifts of the ν_{10} band enable us to locate the ν_{20} bands at 1071.4 and 1075.9 cm^{-1} in the spectra of 2- and 3-^{13}C labeled modifications, respectively (see Fig. 5c and 5d). The ν_{20} band could be assigned to a coupled mode of the out-of-plane CH_3 rocking and CH_2 twist or rocking vibrations.

The ν_{11} and ν_{12} bands centered at 1000.9 and 881.4 cm^{-1} for the parent species were tentatively assigned to the CH_3-C and $C-CO_2$ stretching modes, respectively, by taking into account the characteristic ^{13}C-shifts of the fundamentals (see Fig. 5 and Table 1). The assignments of the remaining 5 fundamental bands to the descriptions given in Table 1 were made by comparison with the vibrational assignments of sodium acetate [3] and propane [7], and with the result of a microwave study for propionic acid reported by Stiefvater [11]. It should finally be noted that the vibrational descriptions given for the 5 fundamental bands are only qualitative in the sense that many of the normal modes may be strongly intermixed or coupled with several group modes.

Conclusion

In this paper, we have presented IR fundamental frequeny data for sodium propionate including its three ^{13}C-substituted species. The fine structures of complex overlapping regions were revealed by measuring the spectra at liquid N_2 temperature. The low temperature measurements combined with ^{13}C-isotopic shifts have been demonstrated to be effective in elucidating vibrational assignments for some fundamentals of sodium propionate. The degree of coupling between several group modes has been clarified by taking into consideration the ^{13}C-shifts of the fundamentals.

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