Vibrational Spectroscopic Studies of Aqueous Alkali Metal Bicarbonate and Carbonate Solutions[1]

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The laser Raman and infrared spectra of Li, Na, K, Rb, Cs bicarbonates and carbonates in H_2O and D_2O have been determined at 25 °C. The relative integrated intensities of the Raman bands have been measured for each salt from 0.01 *M* up to saturation. Changes observed in the carbonate spectrum with concentration have been interpreted in terms of solvation and ion-pairing of the carbonate ion. Based on the vibrational spectrum, there was no evidence for ionic interactions in the bicarbonate solutions. The hydrogen–deuterium exchange on the bicarbonate ion in H_2O–D_2O mixtures has been followed using Raman spectroscopy and the concentration quotients for the pertinent reactions have been calculated.

Les spectres en Raman laser et en infrarouge des bicarbonates de Li, Na, K, Rb, et Cs, ainsi que

Results and Discussion

A typical Raman spectrum observed for carbonate solutions is shown in Fig. 1. The relative intensities of the major Raman bands are graphed as a function of concentration in Fig. 2. The plots are linear over the whole concentration range. The bands in the 600 and 1400 cm^{-1} regions have much lower relative intensities than the band in the 1000 cm^{-1} region; so low in fact that feeble water bands in these regions have sufficient intensity to make curve resolving more difficult. Using D_2O as the solvent does alleviate this problem to some extent. The Raman and infrared band positions for potassium carbonate at different concentrations in H_2O and D_2O are shown in Table 1. The carbonate frequencies are virtually independent of alkali metal cation. The Raman band positions are seen to change by a few wave numbers with concentration.

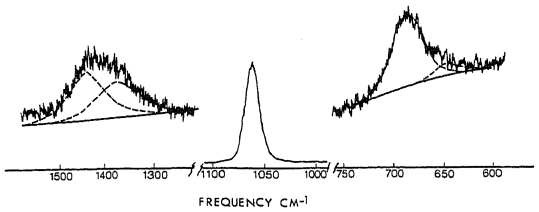

FIG. 1. Resolved Raman spectrum of 8 M Rb_2CO_3 in H_2O. Full scale equals 1×10^4 counts per s for the 100–1100 cm^{-1} region and 2×10^2 c.p.s. for the 600–750 cm^{-1} and the 1300–1500 cm^{-1} region. The weak Raman band at 880 cm^{-1} is observed only at high gain and is not shown in the figure.

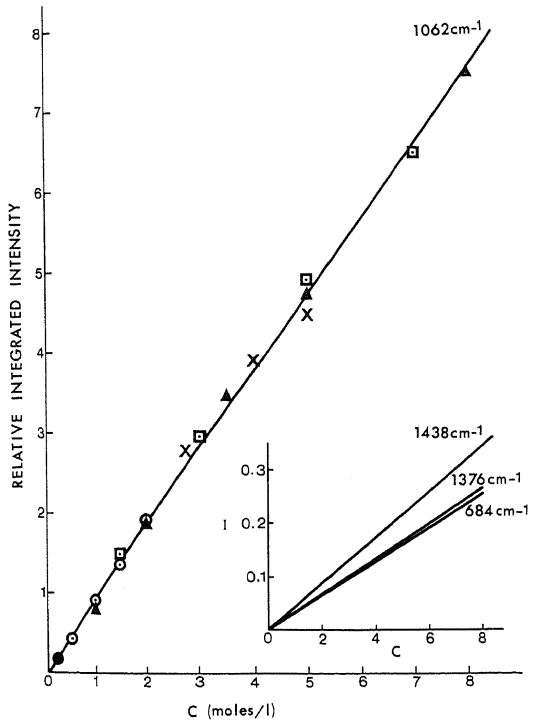

FIG. 2. A plot of relative integrated intensity *vs.* concentration for the major Raman bands of carbonate. ●, Li_2CO_3; ○, Na_2CO_3; △, K_2CO_3; □, Rb_2CO_3; ×, Cs_2CO_3. Only best fit lines shown for weaker bands for clarity.

The symmetry point group for an unperturbed carbonate ion is D_{3h} and the Raman and infrared activity of the expected vibrations are: $\nu_1(A_1')$ R ~1065 cm^{-1}, $\nu_2(A_2'')$ i.r. ~880 cm^{-1}, $\nu_3(E')$ i.r., R ~1400 cm^{-1}, and $\nu_4(E')$ i.r., R ~685 cm^{-1}. The vibrational spectrum of carbonate in aqueous solution is at variance with these selection rules. The infrared forbidden ν_1 band appears in the infrared spectrum of the concentrated solutions at 1052 cm^{-1}. Also the Raman forbidden ν_2 band appears in the Raman spectrum of the concentrated solutions at 880 cm^{-1}. In addition the $\nu_3(E')$ vibration appears to be split into two bands in both the infrared and Raman spectra at all concentrations.

These observations are in many ways similar to those made for alkali metal nitrates by Irish and Davis (3). They interpreted their data in terms of nitrate–water and nitrate–metal interactions. The persistent splitting of the $\nu_3(E')$ band in dilute carbonate solutions where interionic effects should be small, probably indicates that this splitting is due to carbonate–water interaction. This is supported by the fact that the splitting of the $\nu_3(E')$ band is different in the solvent D_2O. Also the band positions in the 1400 cm^{-1} and the 600 cm^{-1} region are different in the two solvents, another indication that the dilute solution spectrum is that of the solvated carbonate ion. The weak bands at 1052 cm^{-1} in the infrared and at 880 cm^{-1} in the Raman could also be features of the solvated carbonate ion spectrum. The weak band at 650 cm^{-1} which is present only in the ultraconcentrated solutions can be assigned to a carbonate ion–water restricted rotation or libration similar to modes found in pure water (9) and those observed for the solvated nitrate ion (3).

Lee and Wilmshurst (10) also observed that the $\nu_3(E')$ band of aqueous K_2CO_3 was split but attributed this to ion-pair formation. Previous studies of aqueous alkali metal nitrates (3, 5, 6)

TABLE 1. Concentration variation of the Raman and infrared band positions of the carbonate ion dissolved in H_2O and D_2O*

Concentration (mol/l)	Spectra (cm^{-1})						
			Raman for H_2O solutions				
8.0	(650)	684	880	1062	1376	1438	1762
6.0	—	684	880	1063	1377	1437	1762
4.0	—	684	—	1065	1379	1436	1761
2.0	—	686	—	1066	1380	1435	1762
1.0	—	687	—	1067	1380	1434	1761
0.1	—	—	—	1069	—	—	—
0.01	—	—	—	1069	—	—	—
			Raman for D_2O solutions				
8.0	—	702	880	1062	1398	1451	1759
2.0	—	703	—	1065	1395	1446	1760
0.1	—	—	—	1068	—	—	—
			Infrared for H_2O solutions				
8.0	—	—	880	1056	~1375	~1430	—
2.0	—	—	880	1060	1370	1425	—
0.1	—	—	—	—	1374	1427	—
			Infrared for D_2O solutions				
8.0	—	695	877	1052	~1390	~1445	1750
2.0	—	—	877	1056	1385	1434	—
0.1	—	—	—	—	1386	1436	—

*For detailed assignment see ref. 2.

have shown that the $\nu_4(E')$ band is split into two bands when contact ion-pairs are present. Only a single band was observed in the $\nu_4(E')$ region for the aqueous carbonate solutions. Bates, Brooker, Quist, and Boyd (11) have shown that the $\nu_4(E')$ band is not split even for molten alkali metal carbonates. Therefore, the spectral results indicate that contact ion-pairs may not be formed in this system. However, the results do not rule out the possibility of ion-pair formation. The $\nu_4(E')$ band is extremely weak in carbonates so recording and resolving the spectrum in this region is difficult. It could be that the $\nu_4(E')$ band for carbonate is split but to a much smaller extent than for nitrate. In any case, it is evident that in these solutions the carbonate ion symmetry has been altered by solvent and possibly cation interactions.

The Raman spectrum for bicarbonate in H_2O is shown in Fig. 3. The 1067 cm^{-1} Raman band is due to carbonate. About 10% of the bicarbonate decomposes to CO_2 and carbonate when it is dissolved in water at 25 °C.

$$[1] \qquad 2HCO_3^- \rightarrow CO_2 + CO_3^{2-} + H_2O$$

Therefore, twice the carbonate concentration, determined from Raman relative intensity data

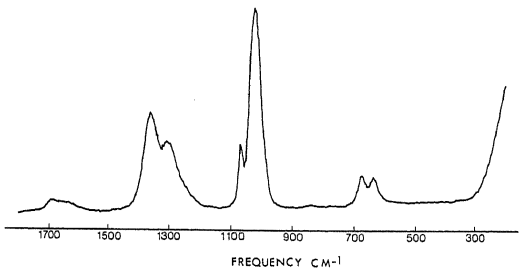

FIG. 3. Raman spectrum of 4 *M* $CsHCO_3$ in H_2O.

(Fig. 2), must be subtracted from the bicarbonate concentration, determined by weight, to obtain the correct concentration of bicarbonate in the aqueous solutions. The relative intensities of the major Raman spectral bands of potassium bicarbonate are plotted against this corrected concentration in Fig. 4. Three other fundamentals at 841, 1630, and 2650 cm^{-1} and one overtone band at 1684 cm^{-1} are also present in the Raman spectrum, but they are very weak. The plots are linear over the whole concentration range.

The Raman and infrared band positions for bicarbonate in H_2O and D_2O are compiled in Table 2. The structure of bicarbonate in a concentrated $KHCO_3$ solution and the assignment

TABLE 2. Raman and infrared band positions for a 3.5 *M* solution of $KHCO_3$ in H_2O and D_2O*

Raman (cm^{-1})		Infrared (cm^{-1})	
H_2O	D_2O	H_2O	D_2O
632	600	—	—
672	672	—	670
841	841	840	835
1017	980	1000	975
1302	1030	1300	1025
1360	1360	1355	1355
1630	1630	1620	1620
1682	1682	—	—
2650	2030	2620	2020

*For detailed assignment see ref. 2.

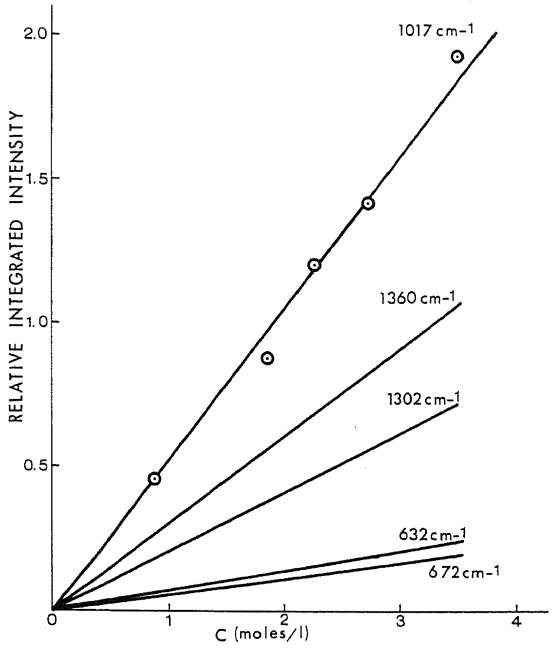

FIG. 4. A plot of relative integrated intensity *vs.* concentration for the major Raman band of potassium bicarbonate. Only best fit lines shown for weaker bands for clarity.

of frequencies to approximate modes of vibration has been deduced from the band positions, band shifts on deuteration, and Raman depolarization ratios (2). The replacement of $KHCO_3$ with Li, Na, Rb, or Cs bicarbonate proved to have little effect on the Raman or infrared band positions or the Raman relative intensities. Changing the bicarbonate molarity essentially has no effect on the spectra either. Thus it appears that the $C_s(\sigma_h)$ structure deduced for bicarbonate in concentrated $KHCO_3$ solutions holds for all concentrations and for all alkali metals. Certainly there is no evidence for ionic interactions from the vibrational spectrum.

The bicarbonate ion has an ionizable hydrogen atom which is replaceable by deuterium. This can occur when the bicarbonate ion is dissolved in D_2O and then the vibrations of the OH part of the ion will shift to lower frequencies due to the formation of OD. The 2650 cm^{-1} line shifts to 2030 cm^{-1} in D_2O, the 1302 cm^{-1} to 1030 cm^{-1}, the 1017 cm^{-1} to 980 cm^{-1}, and the 632 cm^{-1} to 600 cm^{-1}. Since the concentration of HCO_3^- in any solution can be found from the Raman intensity data (Fig. 4), it is possible to follow the hydrogen–deuterium exchange on the bicarbonate ion in H_2O–D_2O mixtures. The 900–1100 cm^{-1} region of the Raman spectrum of 2.9 *M* K_2CO_3 in H_2O–D_2O mixtures is shown in Fig. 5. The solution containing only DCO_3^- (spectrum (*d*)) was prepared by adding DCl to a D_2O solution of K_2CO_3 until no carbonate was detected in the Raman spectrum. Four bands appear in this region of the spectrum: the easily resolvable 1067 cm^{-1} carbonate band, the 1017 cm^{-1} HCO_3^- band, and the 980 and 1030 cm^{-1} DCO_3^- bands. The overlap of the latter three bands makes curve resolving difficult. But if it is kept in mind that both the 980 cm^{-1} and the 1030 cm^{-1} bands are generated by DCO_3^- and since it is possible to set the shapes of the two bands using the DCO_3^- spectrum, the total band contour for the two bands can be

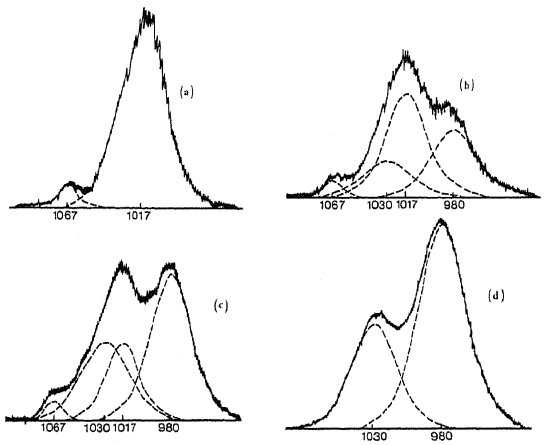

FIG. 5. Resolved Raman spectra of the 900–1100 cm^{-1} region for 2.9 *M* $KHCO_3$ in (*a*) H_2O, (*b*) 50 mol% H_2O – 50 mol% D_2O, (*c*) 25 mol% H_2O – 75 mol% D_2O, and (*d*) D_2O.

TABLE 3. Species concentrations and concentration quotients determined by Raman spectroscopy for the system $KHCO_3$–H_2O–D_2O*

Solution	$[HCO_3^-]$	$[DCO_3^-]$	$[H_2O]$	[HOD].	$[D_2O]$	Q_3	Q_4
2.9 *M* $KHCO_3$ in 50 mol% H_2O – 50 mol% D_2O	1.57	1.33	14.66	27.25	13.33	1.73	0.46
2.9 *M* $KHCO_3$ in 25 mol% H_2O – 75 mol% D_2O	0.96	1.94	4.06	21.42	29.72	1.46	0.38
2.9 *M* $KHCO_3$ in 10 mol% H_2O – 90 mol% D_2O	0.37	2.52	0.87	11.82	42.47	1.90	0.50

*Mean concentration quotients $Q_3 = 1.7 \pm 0.2$, $Q_4 = 0.45 \pm 0.05$.

treated as a single band and the missing gap filled with the 1017 cm^{-1} band. In this way it was possible to obtain excellent reproducible fits for the experimental spectrum. The concentration of HCO_3^- was then determined from the 1017 cm^{-1} band intensity and the concentration of DCO_3^- obtained by subtraction. A check on the accuracy of the determination was made using the 1302 cm^{-1} band intensity. The HCO_3^- concentrations from both regions of the spectrum were found to be in good agreement.

The important reactions for the exchange equilibrium are as follows

[2] $H_2O + D_2O \rightleftarrows 2HOD$

$$Q_2 = [HOD]^2/[H_2O][D_2O]$$

[3] $HCO_3^- + D_2O \rightleftarrows DCO_3^- + HOD$

$$Q_3 = [DCO_3^-][HOD]/[HCO_3^-][D_2O]$$

[4] $HCO_3^- + HOD \rightleftarrows DCO_3^- + H_2O$

$$Q_4 = [DCO_3^-][H_2O]/[HCO_3^-][HOD]$$

The value of the concentration quotient Q_2 for reaction 2 at 25 °C is 3.8 (12).

Since $[HCO_3^-]$ and $[DCO_3^-]$ have been obtained experimentally there are five unknowns in the equations: $[H_2O]$, $[D_2O]$, [HOD], Q_3, and Q_4. It is possible to write equations for the known total concentration of hydrogen and deuterium in the solutions.

[5] $[H]_{total} = 2[H_2O] + [HOD] + [HCO_3^-]$

[6] $[D]_{total} = 2[D_2O] + [HOD] + [DCO_3^-]$

From these five equations it is now possible to calculate the concentration quotients Q_3 and Q_4. The species concentrations obtained from Raman intensity data for three 2.9 *M* $KHCO_3$ solutions in H_2O–D_2O mixtures and the calculated concentration quotients are shown in Table 3. The experiment was repeated for 1 *M* $NaHCO_3$ solutions in two H_2O–D_2O mixtures and the quotients, $Q_3 = 1.9 \pm 0.2$, $Q_4 = 0.50 \pm 0.05$, are in close agreement with the $KHCO_3$ results. Therefore, the concentration quotients appear to be independent of cation and molarity.

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