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A Vibrational-Spectroscopic Study of the Species Present in the CO_2–H_2O System

A. R. Davis[1] and B. G. Oliver[1]

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Raman and infrared spectra have been recorded of water and heavy-water solutions of carbon dioxide, potassium bicarbonate, and potassium carbonate. The structures of the carbonate and bicarbonate ions and CO_2 (aqueous solution) have been determined from a consideration of Raman and infrared data. The results reveal the presence of solvent effects in the carbonate and CO_2 water solutions. No bands characteristic of H_2CO_3 were observed in the Raman spectrum of aqueous solutions of CO_2.

KEY WORDS: Raman; infrared; carbon dioxide; bicarbonate; carbonate; water; deuterium oxide; structure.

1. INTRODUCTION

The dissolution of carbon dioxide in water and the subsequent equilibrium processes involving carbonate and bicarbonate ion have been the subject of many publications.[1,2] The great number of these studies reflects, to a large extent, the importance of the role of the CO_2–H_2O equilibria in governing chemical and biological processes in natural waters.[3] Although considerable data have been collected on the kinetics and equilibrium constants of the system, there is no information on the structure of the aqueous species. Raman and infrared spectroscopy have been used with some success in structural interpretations of other oxyacid[4] and oxyanion[5,6] systems. Not only have the structures of these species been determined, but also detailed information about their interaction with cations and water has been deduced. These results suggested the use of Raman and infrared spectroscopy to obtain detailed information about the species involved in the following CO_2–H_2O equilibria. The first stage involves the slow uptake of CO_2 by H_2O. The CO_2

[1] Inland Waters Branch, Department of the Environment, Ottawa, Ontario, Canada.

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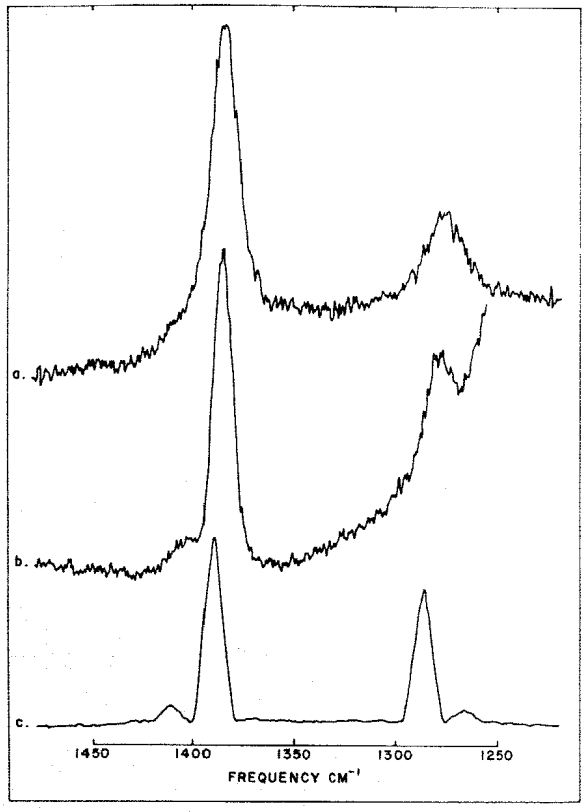

Fig. 1. Raman spectrum of CO_2 in the region 1250–1450 cm^{-1}. (a) Dissolved in H_2O; (b) dissolved in D_2O; (c) pure gas–pressure of CO_2 5 atm for each spectrum. Spectral silt width 10 cm^{-1} in each case.

Table I. Raman Frequencies for CO_2 in the Gaseous and Solution State

Gas[a]	Gas (5 atm)	Solution in D_2O	Solution in H_2O
1264.8	1266	—	—
1285.5	1286 (10.0)[b]	1279 (14.0)	1276 (23.5)
1388.3	1390 (10.2)	1386 (12.2)	1384 (16.9)
1409.0	1411	1405	—

[a] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand, Princeton, 1968), p. 274.
[b] Bandwidth at half-height in cm^{-1}.

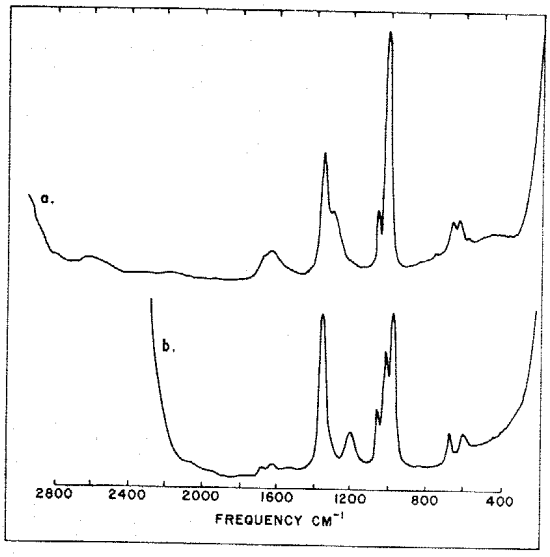

Fig. 3. Raman spectrum of 3.5 *M* $KHCO_3$ from 400–2800 cm^{-1}. (a) H_2O solution; (b) D_2O solution.

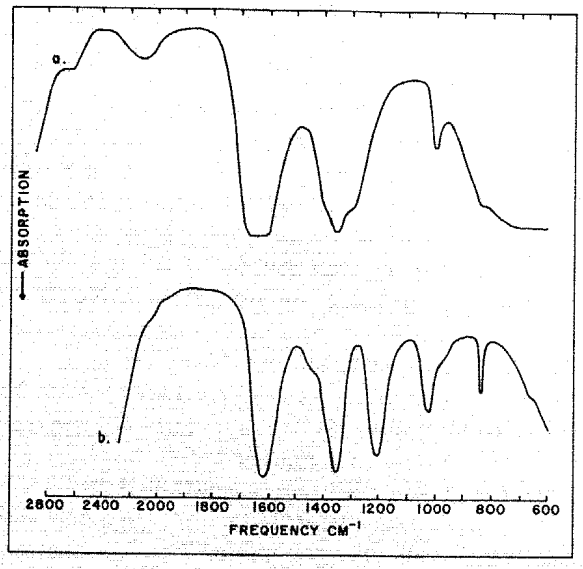

Fig. 4. Infrared spectrum of 3.5 *M* $KHCO_3$ from 600–2800 cm^{-1}. (a) H_2O solution; (b) D_2O solution.

and is observed only weakly in concentrated nitric acid solutions.[16,17] Since one depolarized and seven polarized bands are observed, then only the $C_s(\sigma_h)$ model is compatible with the results. On this basis the unseen torsional vibration would be depolarized. In order to unambiguously assign modes of vibration of the $C_s(\sigma_h)$ model to frequencies, the spectra of both HCO_3^- and DCO_3^- have been recorded (Figs. 3b and 4b and Table II). The modes of vibration associated with the OH part of the ion should undergo pronounced low frequency shifts on deuteration.

Initially a solution containing mainly DCO_3^- was prepared by dissolving $KHCO_3$ in D_2O. The Raman spectrum of this solution (Fig. 3b) contains bands at 1017 and 1302 cm^{-1}, indicative of HCO_3^-. A solution containing only DCO_3^- was prepared by adding a D_2O solution of DCl to K_2CO_3 dissolved in D_2O until the pD (actually measured using a pH meter) was 8.2. The Raman spectrum of this solution shows no bands at 1017 and 1302 cm^{-1} and contains no HCO_3^-. In all the Raman spectra of aqueous bicarbonate, a band is observed at 1064 cm^{-1}, which is assigned to the symmetric stretch vibration of the carbonate ion. Increasing the pH of a bicarbonate solution increases the CO_3^{2-} concentration, whereas decreasing the pH increases the HCO_3^- concentration. Figure 5 shows that as the pH of a bicarbonate solution is increased, the band

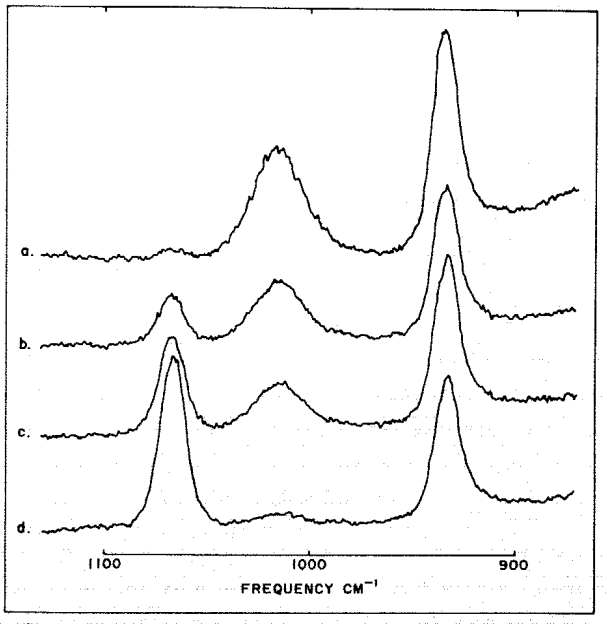

Fig. 5. Effect of pH change on the Raman spectrum of a 0.2*M* $KHCO_3$ solution over the range 900–1100 cm^{-1}. (a) pH 8.25; (b) pH 9.27; (c) pH 9.72; (d) pH 10.49.

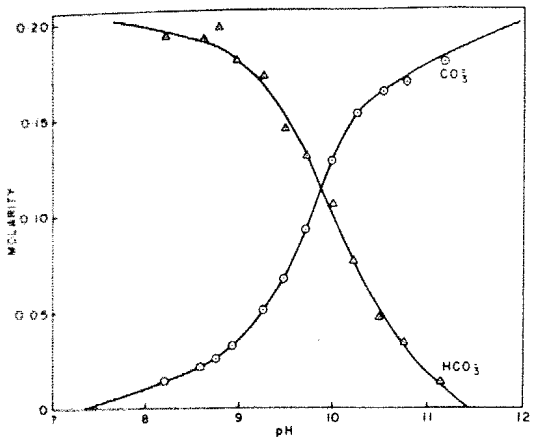

Fig. 6. Molar concentrations of CO_3^{2-} and HCO_3^- as a function of pH, measured using Raman-intensity data.

at 1064 cm^{-1} (CO_3^{2-}) increases in intensity, whereas the band at 1017 cm^{-1} (HCO_3^-) decreases in intensity. The band at 938 cm^{-1} originates from perchlorate ion, added as an internal standard. These results are shown quantitatively in Fig. 6. Since the band intensities are proportional to carbonate and bicarbonate concentrations, they may be used to quantitatively analyze bicarbonate–carbonate mixtures.

3.3. Carbonate–Water System

The vibrational spectrum of an isolated carbonate ion, of D_{3h} symmetry, has four fundamental modes of vibration (Fig. 7). The infrared and Raman spectra of an 8 *M* aqueous solution of potassium carbonate are shown in Figs. 8 and 9 and tabulated in Table III. These spectra are at variance with the predictions based on an isolated carbonate ion. The infrared forbidden symmetric stretch vibration occurs at 1052 cm^{-1} in the infrared spectrum and is as intense as the allowed in plane deformation at 695 cm^{-1} for a D_2O solution of K_2CO_3. Also, the asymmetric stretch at around 1400 cm^{-1} is resolvable into two bands. The Raman forbidden out-of-plane deformation occurs in the Raman spectrum at 880 cm^{-1}, and once again the $\nu_3(E')$ mode may be resolved into two bands. Since the splitting of the $\nu_3(E')$ mode for carbonate has been observed from dilute solutions through the molten salts, this effect has been attributed to the interaction of carbonate ion with the environment.[18] The $\nu_4(E')$ of the carbonate ion has not been observed to split for any of the solutions which we have studied. These results are in many ways very similar to those observed in the vibrational spectra of the alkali metal nitrates.[6] Vibrational

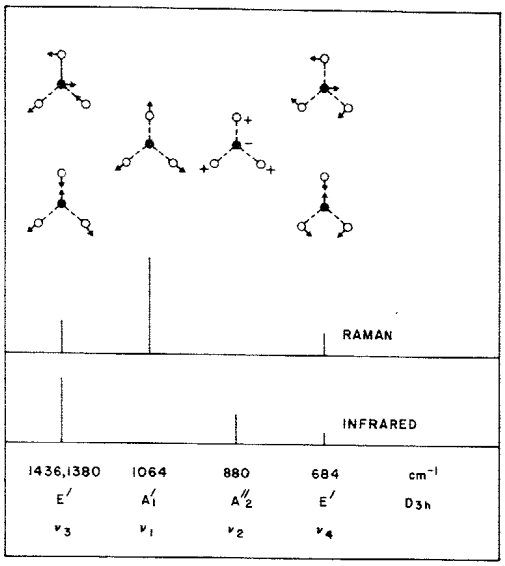

Fig. 7. Fundamental modes of vibration and infrared and Raman activity for a D_{3h} carbonate ion.

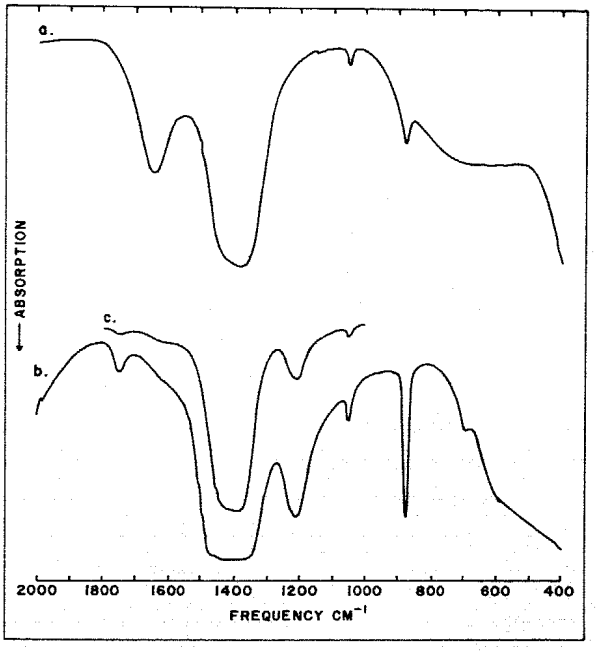

Fig. 8. Infrared spectra of aqueous potassium carbonate, 400–2000 cm^{-1}. (a) 8 *M* in H_2O; (b) 8 *M* in D_2O (c); 4 *M* in D_2O.

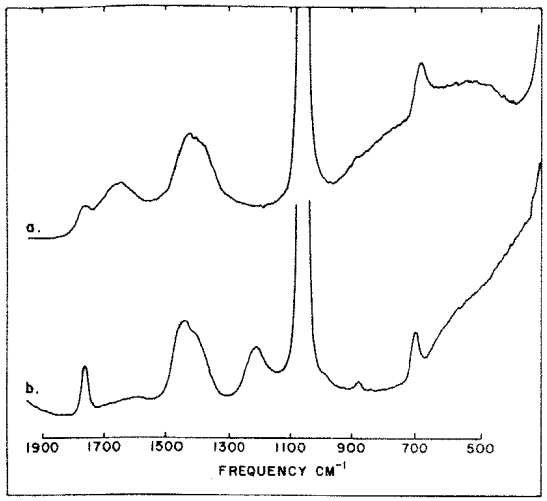

Fig. 9. Raman spectra of 8 *M* potassium carbonate, 500–1900 cm^{-1}. (a) H_2O solution; (b) D_2O solution.

Table III. Assignment of the Normal Modes of Vibration of the Carbonate Ion According to the D_{3h} Point Group

H_2O		D_2O		
Raman	Infrared	Raman	Infrared	Assignment
684 (0.74)[a]	Obscured	702 (0.73)	695	$\nu_4(E')$
880	880	880	877	$\nu_2(A_2'')$
1064 (0.03)	1056	1063 (0.03)	1052	$\nu_1(A_1')$
1380 (0.57)	~1375	1398 (0.55)	~1390	$\nu_3(E')$
1436 (0.70)	~1430	1451 (0.75)	~1445	
1761 (0.10)	Obscured	1759 (0.10)	1750	$2 \times \nu_2(A_2'')$

[a] Depolarization ratio in parentheses.

spectra of the nitrate ion were interpreted in terms of solvation and contact ion-pairing effects. The appearance of a band at 740 cm^{-1} for nitrate solutions was used as evidence for ion-pair formation. Solutions of lithium[19] and sodium[20] nitrate have revealed two bands—one generated by the ion pair and the other by solvated nitrate ions. The effect is especially pronounced when the mole fraction of water is low or when excess metal ion is added. If contact ion-pairing does occur in the potassium carbonate solutions, the Raman-spectral effects are certainly not as pronounced as for lithium and sodium nitrate. It should be noted that ion pairs have not been clearly identified by Raman

spectroscopy for potassium nitrate. The Raman and infrared spectra of the aqueous carbonate ion may therefore be interpreted in terms of a planar D_{3h} species slightly distorted by solvent and possibly cation interactions.

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