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

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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

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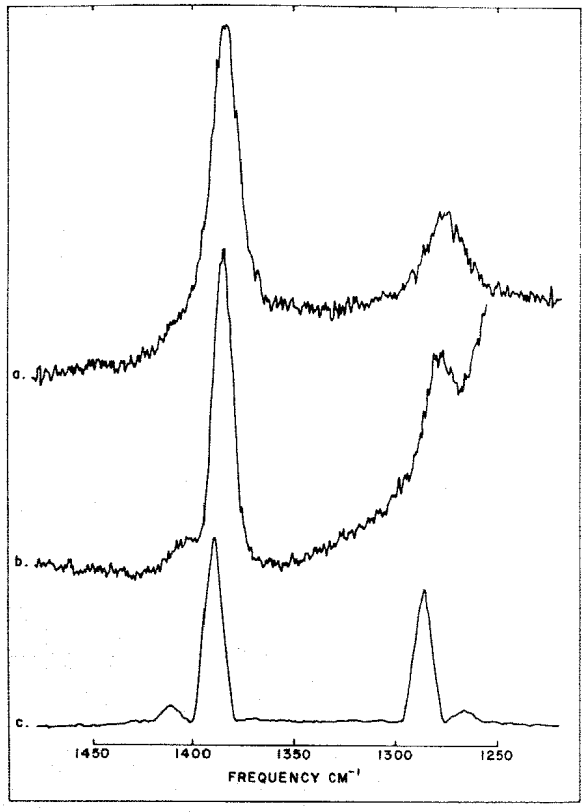


Fig. 1. Raman spectrum of CO_2 in the region 1250–1450 cm^{-1}. (a) Dissolved in H_2O; (b) dissolved in D_2O; (c) pure gas–pressure of CO_2 5 atm for each spectrum. Spectral silt width 10 cm^{-1} in each case.

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}.

then reacts slowly with H_2O to form carbonic acid ($k_1 = 1.67 \times 10^{-2}$/sec).[7]

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \qquad K = 2.6 \times 10^{-3}$$

The subsequent ionization equilibria are established in approximately 10^{-6} sec in dilute solution at 25°C.[8]

$$H_2CO_3 \rightleftarrows HCO_3^- + H^+ \qquad K_{a_1} = 1.7 \times 10^{-4}$$

$$HCO_3^- \rightleftarrows CO_3^{2-} + H^+ \qquad K_{a_2} = 5.6 \times 10^{-11}$$

In this study, vibrational spectroscopy has been used to obtain quantitative and structural information about CO_2, CO_3^{2-}, and HCO_3^- dissolved in water.

2. EXPERIMENTAL

Raman spectra were recorded on a Jarrell–Ash 25-300 Raman spectrometer with a spectral slit width of 10 cm^{-1}. The majority of spectra were recorded using the 488.0-nm line of a Coherent Radiation Model 54A argon laser. Some spectra were recorded using the 632.8-nm line of a Spectra Physics Model 125 helium–neon laser. The laser power at the sample was respectively 200 mW (488.0 nm) and 50 mW (632.8 nm). Depolarization measurements were carried out according to the technique of Allemand.[9] Infrared spectra were recorded on a Perkin Elmer Model 457 spectrometer using a 1.5 × normal slit programme. The samples were pressed between two silver chloride plates.

The Raman spectra of CO_2 dissolved in water were obtained using a cell of 0.7 cm O.D. pyrex tubing with an optical flat at one end and sealed off with a Quickfit Rotaflo valve. The pressure of CO_2 above the water was 5 atm. The cell was shaken to equilibrate the gaseous CO_2 with water.

Band contours were resolved with a du Pont curve resolver. A Lorentz–Gaussian distribution function was used as a basis for the component curves.

3. RESULTS AND DISCUSSION

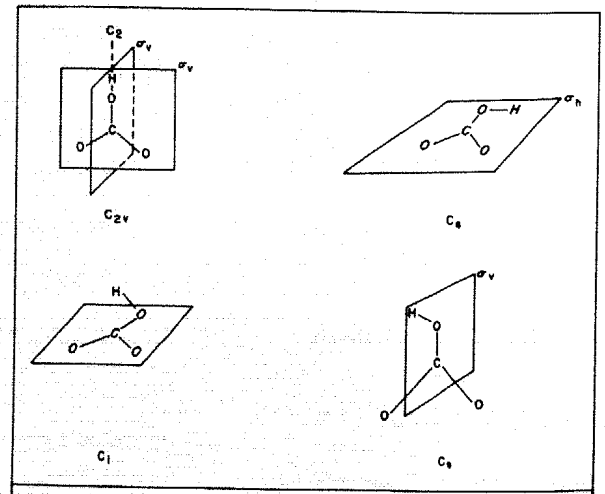
3.1. Carbon Dioxide–Water System

Raman spectra of gaseous CO_2, CO_2 dissolved in H_2O, and D_2O are shown in Fig. 1. The band positions and half-widths are tabulated in Table I. The two prominent Raman bands observed (1286 and 1390 cm^{-1}) result from a Fermi resonance between $2\nu_2$ and ν_1 of the CO_2 molecule. At a pressure of 5 atm the solubility of CO_2 in water is 0.17 M.[10] The dissolution of CO_2 in water produces little H_2CO_3, the prominent species being molecular CO_2. Table I shows that there is a pronounced lowering of frequencies on going from the gaseous to the solution phase and a smaller shift on going from D_2O to H_2O. A similar trend has been observed for the infrared spectra of gaseous CO_2 and SO_2 dissolved in water.[11] Raman band half-widths show a more pronounced

Table II. Assignment of the Normal Modes of Vibration of the HCO_3^- and DCO_3^- Ions According to the $C_s(\sigma_h)$ Model

HCO_3^-		DCO_3^-		
Raman	Infrared	Raman	Infrared	Species and description of vibration
—	—	—	—	$\nu_9(A'')$ OH torsional vibration
632[a] (0.65)[b]	—	600 (0.40)	—	$\nu_7(A')$ (OH) CO bend
672 (0.35)	—	672 (0.30)	670	$\nu_6(A')$ CO_2 bend
841 (0.75)	840	841 (0.75)	835	$\nu_8(A'')$ CO_3 out-of-plane deformation
1017 (<0.1)	1000	980 (<0.1)	975	$\nu_5(A')$ C–OH stretch
1302 (<0.1)	1300	1030 (<0.1)	1025	$\nu_4(A')$ COH bend
1360 (<0.1)	1355	1360 (<0.1)	1355	$\nu_3(A')$ symmetric CO stretch
1630 (0.50)	1620	1630 (0.70)	1620	$\nu_2(A')$ asymmetric CO stretch
1684 (0.20)	—	1684 (0.20)	—	$(2 \times \nu_8)(A')$
2650 (0.50)	2620	2030 (0.50)	2020	$\nu_1(A')$ OH stretch

[a] Frequencies in cm^{-1}, average of results using 488.0 nm and 632.8 nm.
[b] Depolarization ratio in parentheses.



Model	Infrared	Raman	Coincidences	Polarized	Depolarized
C_{2v}	9	9	9	4	5
$C_{s(\sigma_v)}$	9	9	9	6	3
$C_{s(\sigma_h)}$	9	9	9	7	2
C_1	9	9	9	9	0

Fig. 2. Four possible geometries of the bicarbonate ion and their resultant infrared and Raman activity.

effect: they increase in the series pure gas, D_2O solution, H_2O solution. The slight dependence of CO_2 Raman frequencies on the use of D_2O or H_2O as a solvent may not be significant. Nevertheless the marked change in band half-width deserves some comment. The half-width may be considered as reflecting the distribution of vibrational energies associated with a particular mode of vibration. The larger half-width associated with CO_2 in H_2O, both 1276 and 1384 cm^{-1}, is indicative of a wider distribution of vibrational energies than in the case of D_2O. This would be in agreement with the concept of D_2O as a more structured liquid than H_2O.[12] The effect of increased structure in liquid D_2O would produce a more orderly and well-defined environment for the dissolved CO_2. This would lead to a smaller distribution of vibrational energies for a particular molecular motion and hence narrower band half-widths. This view is clarified by a consideration of line broadening and the lifetime of a vibrational state. The relationship between these two is such that a shortening of a vibrational lifetime results in line broadening.[13] From our experimental data it can be concluded that the vibrational lifetime of CO_2, before a collision occurs, is shorter in H_2O than D_2O. This would imply that the CO_2 molecule is more mobile in H_2O than in D_2O. This deduction is supported by the experimental observation that the self-diffusion rate for H_2O is greater than D_2O.[14]

The similarity of the Raman spectra of CO_2 in the gaseous and solution state and the absence of new bands implies that the structure is unaltered in passing from the gaseous to the solution state. Therefore, in aqueous solution the CO_2 molecule is linear and of $D_{\infty h}$ molecular symmetry.

3.2. Bicarbonate Ion–Water System

The infrared and Raman spectra of crystalline potassium bicarbonate have been interpreted in terms of cyclic dimers of the HCO_3^- species.[15] For this species, 17 in-plane vibrations are predicted. A brief examination of Table II reveals only 9 Raman-active bands for the bicarbonate ion dissolved in water. The small number of bands observed indicates the absence of hydrogen-bonded dimers in aqueous solution. Some possible geometries for the simple monomeric bicarbonate ion are shown in Fig. 2. The predicted infrared and Raman activities for these models are also shown in Fig. 2. It is noteworthy that for these models all nine bands are infrared and Raman-active, and the only method of distinguishing between them is by a measurement of depolarization ratios. Raman and infrared spectra of aqueous potassium bicarbonate are shown in Figs. 3a and 4a, and band frequencies are tabulated in Table II. The polarized Raman band at 1684 cm^{-1} is the first overtone of the weak depolarized line at 840 cm^{-1}. Thus only 8 fundamental vibrations of the bicarbonate ion are observed. The torsional rotation of the OH group around the OC bond is not observed by us in this system. This vibration is also not observed in bisulfate solutions of higher concentration[5]

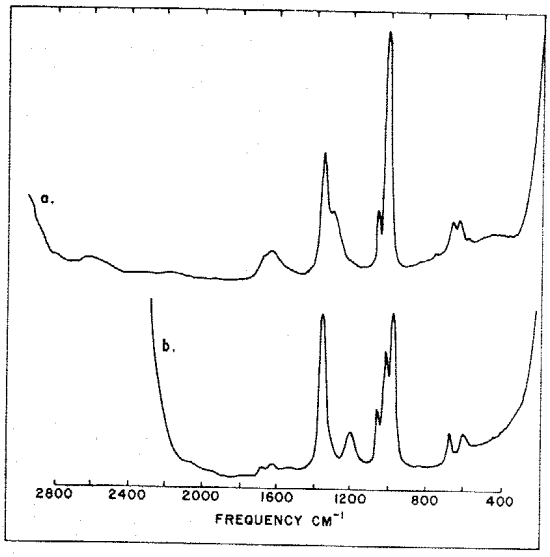


Fig. 3. Raman spectrum of 3.5 *M* $KHCO_3$ from 400–2800 cm^{-1}. (a) H_2O solution; (b) D_2O solution.

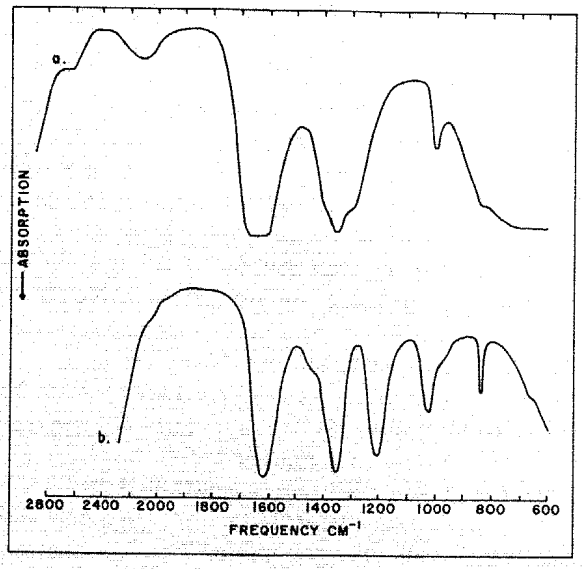


Fig. 4. Infrared spectrum of 3.5 *M* $KHCO_3$ from 600–2800 cm^{-1}. (a) H_2O solution; (b) D_2O solution.

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

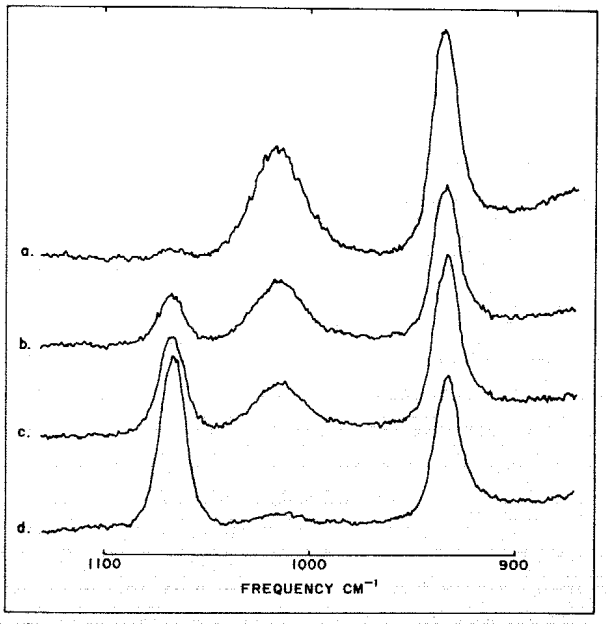


Fig. 5. Effect of pH change on the Raman spectrum of a 0.2*M* $KHCO_3$ solution over the range 900–1100 cm^{-1}. (a) pH 8.25; (b) pH 9.27; (c) pH 9.72; (d) pH 10.49.