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Infrared Absorption Spectra of the CO_2/H_2O Complex in a Cryogenic Nitrogen Matrix—Detection of a New Bending Frequency

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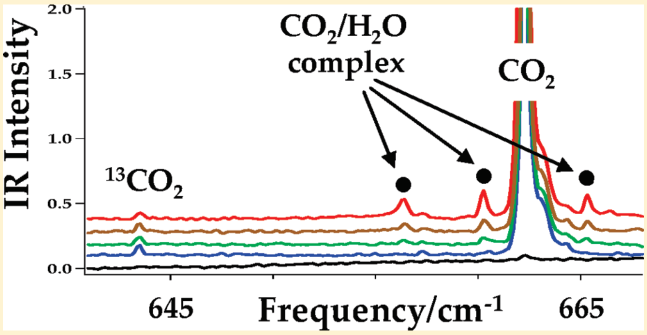
ABSTRACT: Infrared absorption spectra have been measured for the mixture of CO_2 and H_2O in a cryogenic nitrogen matrix. The 1:1 CO_2/H_2O complex has been observed. Each structure of this complex should have two bending frequencies corresponding to the CO_2 fundamental bending mode (ν_2). In this work, three bending frequencies corresponding to the CO_2 fundamental bending mode (ν_2) have been detected; one of them at 660.3 cm^{-1} is reported here for the first time. This finding helps confirm the existence of two structures for this complex. A new feature attributed to a CO_2 and H_2O complex is observed at 3604.4 cm^{-1} and is tentatively assigned to the CO_2/H_2O complex band corresponding to the CO_2 combination mode ($\nu_3 + 2\nu_2$). In addition, a band that belongs to a CO_2 and H_2O complex is detected at 3623.8 cm^{-1} for the first time and is tentatively assigned to the $(CO_2)_2/H_2O$ complex band corresponding to the symmetric stretching mode (ν_1) of H_2O.



INTRODUCTION

The interaction of carbon dioxide and water is an important topic in biochemical and atmospheric chemistry.[1,2] It may also play a key role on planetary bodies, such as the satellites of Jupiter and Saturn.[3] Complexes between carbon dioxide and water have been the subject of many investigations. The combination of matrix isolation and infrared (IR) absorption spectroscopy is a very useful method for studying the vibrational frequencies and structures of weak complexes. Jacox and Milligan[4] attempted to detect the CO_2 and H_2O complexes in CO_2 matrices, but were unsuccessful, likely due to the overwhelming CO_2 bands. The 1:1 CO_2/H_2O complex[5] was first observed[6] in a nitrogen matrix, and its matrix IR spectrum was collected by Fredin, et al. Two peaks in the CO_2 fundamental bending mode region (ν_2), 665.3 and 656.3 cm^{-1}, were attributed to the CO_2/H_2O complex. In addition, two bands in the CO_2 fundamental stretching regions (one each for symmetric (ν_1) and asymmetric (ν_3)) and three bands corresponding to the H_2O fundamentals (one each for ν_1, ν_2, and ν_3) were also assigned to the CO_2/H_2O complex. Small frequency shifts were measured from the fundamentals of CO_2 and H_2O monomers to those of the complex. Their findings suggested the existence of a non-hydrogen-bonded CO_2/H_2O complex with the water oxygen bound to the carbon dioxide carbon (C_2 or C_{2v} symmetry). No hydrogen-bonded complexes were observed based on the small shift for the fundamentals of the complexed water molecule. The T-shaped C_{2v} structure (structure **1** in Figure 1) was later confirmed and determined by Peterson and Klemperer from gas-phase radio frequency and microwave spectra.[7] Matrix isolation studies in other matrices have also been conducted.[8−11] In an O_2 matrix, studies suggested the existence of the T-shaped C_{2v} structure and a possible hydrogen-bonded isomer.[10,11] Several theoretical studies have been carried out to determine the structure, binding energy, and vibrational frequencies of the CO_2/H_2O complex. Most studies[1−3,12] predicted the T-shaped C_{2v} symmetry as the most stable structure with a stabilization energy of about 2 kcal/mol. However, Danten et al. found[13] the optimized structure of C_s symmetry (similar to structure **2** in Figure.1), with a stabilization energy of 1.5−1.8 kcal/mol using second-order Møller−Plesset perturbation theory (MP2) with the aug-cc-pVTZ basis set. Applying coupled cluster methods (CCSD(T)/aug-cc-pVTZ), Garden et al. obtained the optimized geometry as the T-shaped C_{2v} structure but was unable to identify the C_s structure as a minimum.[14] In another study, Altmann and Ford[15] computed the optimized structure to be the nonsymmetrical C_1 symmetry with a stabilization energy of about 1.8 kcal/mol using the MP2 level of calculations. Their structure with C_1 symmetry has the heavy atoms and one of the hydrogen atoms essentially coplanar, while the remaining OH bond projected out of this quasi-plane; it is similar to the one with C_s symmetry in Figure 1 except that one of the OH bonds projects out of the plane. The hydrogen-bonded structure of the CO_2/H_2O complex with a higher energy has also been found,[2] but could not be confirmed at higher theoretical levels.[3]

A recent matrix study by Schriver et al. reinvestigated the CO_2/H_2O complex in solid nitrogen using water isotopic

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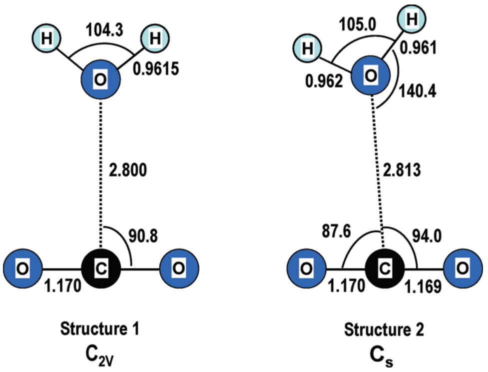

Figure 1. Structures of the CO_2/H_2O complex calculated with BSSE/MP2/aug-cc-PVTZ by Schriver et al. (ref 16). The bond length is in angstroms, and the bond angle is in degrees. For the structure with C_1 symmetry calculated using MP2/aug-cc-pVTZ (ref 15), the heavy atoms and one of the hydrogen atoms are essentially coplanar, and the remaining OH bond projects out of this quasi-plane; it is similar to C_s symmetry here except that one of the OH bonds projects out of the plane.

species.[16] In the symmetric (ν_1) as well as the asymmetric (ν_3) stretching regions of HOD, three features were detected and attributed to the CO_2/HOD complex. They are a doublet and a lower-frequency band with a shift larger than 4 cm^{-1} between the doublet and the lower-frequency feature. This result suggested the existence of two structures for the weakly bound CO_2/H_2O complex: one of C_{2v} and the other of C_s symmetry (see Figure 1). Force constant calculations and ab initio calculations were also used to support their findings. Their calculated energies of the two structures differ by less than 0.01 kcal mol^{-1}, with a stabilization energy of 1.97 kcal mol^{-1}. In the CO_2 bending mode region (ν_2), two features at 665.2 and 656.3 cm^{-1} were detected and assigned to the CO_2/H_2O complex, which are in good agreement with the results[6] by Fredin et al. In addition, one band in the CO_2 asymmetric stretching region (ν_3) and five bands corresponding to the H_2O fundamentals (two each for ν_1 and ν_3, and one for ν_2) were also observed and assigned to the CO_2/H_2O complex. Their results are in agreement with those of Fredin et al., except that more bands are detected by Schriver et al. due to their higher spectral resolution.

On the basis of the findings by Schriver et al., there should be four vibrational bands of the CO_2/H_2O complex corresponding to the fundamental bending mode (ν_2) of CO_2 (two for each structure). In the CO_2 monomer, the out-of-plane and in-plane bending modes are degenerate, but in the CO_2/H_2O complex, that degeneracy is broken. For each structure of the CO_2/H_2O complex, there are two frequencies corresponding to the fundamental bending mode (ν_2) of CO_2: out-of-plane and in-plane. Therefore, four bands should be observed for the two structures of the complex in the CO_2 bending mode region. However, only two were observed at 665.2 and 656.3 cm^{-1}. In this work, we report the detection of a third vibrational band at 660.3 cm^{-1} that belongs to the CO_2/H_2O complex in the CO_2 fundamental bending frequency region. In addition, the band at 3604.4 cm^{-1} is attributed to a CO_2 and H_2O complex and tentatively assigned to the CO_2/H_2O complex band corresponding to the CO_2 combination mode ($\nu_3 + 2\nu_2$). A feature that belongs to the CO_2 and H_2O complex at 3623.8 cm^{-1} is tentatively assigned to the $(CO_2)_2/H_2O$ complex band corresponding to the symmetric stretching mode (ν_1) of H_2O.

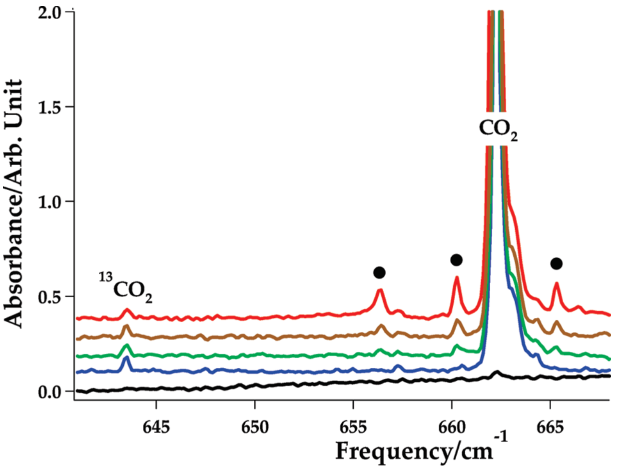

Figure 2. Spectra in the CO_2 bending mode (ν_2) region collected at 4.5 K after deposition at 10 K, with five different $[CO_2]:[H_2O]:[N_2]$ concentration ratios. From bottom to top: black trace, $[CO_2]:[H_2O]:[N_2] \cong 0:20:700$; blue trace, $[CO_2]:[H_2O]:[N_2] \cong 1:0:700$; green trace, $[CO_2]:[H_2O]:[N_2] \cong 1:1:700$; brown trace, $[CO_2]:[H_2O]:[N_2] \cong 1:3:700$; red trace, $[CO_2]:[H_2O]:[N_2] \cong 1:10:700$. The black bullets (●) indicate the CO_2/H_2O complex bands.

■ EXPERIMENT

The room-temperature gas mixture of CO_2 (Air Products, >99.9% pure), H_2O (distilled), and N_2 (Airgas, Ultra Pure Carrier grade, >99.9993%) was made in a 1.2 L volume reservoir with a pressure of 1.1 atm. The pressure was measured using a capacitance monometer. The mixture was injected through Teflon tubing (3/8 in. o.d. and 1/4 in. i.d.) onto a cold CsI window. The Teflon tubing was mounted to the vacuum shroud of an Advanced Research System (ARS) two-stage closed-cycle helium cryostat, approximately 2 cm away from the cryogenic CsI window. The flow (or the deposition rate) was adjusted with a needle valve; the deposition rate was roughly 24 mmol/h of the gas mixture. The cold CsI window was kept at 10.0 ± 0.5 K during the deposition and then cooled to 4.5 K for spectral collection. The infrared absorption spectra were measured using a Nicolet Magna 560 Fourier transform infrared spectrometer with a deuterated L-alanine-doped triglycine sulfate (DLaTGS) detector. The ARS cryostat is equipped with a pair of CsI side windows that are traversed by the IR beam. The spectra were collected at resolutions of 0.25 and 0.5 cm^{-1} with Happ-Genzel apodization. A typical data collection time is about an hour. For the annealing experiment, the matrix was warmed up to 20 K after deposition at 10 K, then cooled to 4.5 K for spectral collection.

■ RESULTS AND DISCUSSION

The experiments were conducted with different concentration ratios of a $CO_2/H_2O/N_2$ gas mixture. Figures 2−9 illustrate the IR spectra in different frequency ranges. Table 1 summarizes our measured vibrational frequencies of the CO_2/H_2O complex, the CO_2 monomer and dimer, H_2O monomer and dimer, and a possible $(CO_2)_2/H_2O$ complex.

CO_2 Vibrational Regions.

Bending Mode ν_2 *(640−670* cm^{-1}*).* Figure 2 shows the spectra collected at 4.5 K after deposition at 10 K, with five different $[CO_2]:[H_2O]:[N_2]$ concentration ratios. In this region,

Table 1. Fundamentals and Overtones of the CO_2/H_2O Complex, Carbon Dioxide (Monomer and Dimer), Water (Monomer and Dimer), and Possible $(CO_2)_2/H_2O$ Complex in a N_2 Matrix (4.5 K)[a]

	CO_2 fundamentals and overtones			H_2O fundamentals			
	CO_2 ($^{13}CO_2$)	CO_2/H_2O ($^{13}CO_2/H_2O$)	$(CO_2)_2$	H_2O	CO_2/H_2O	$(H_2O)_2$	$(CO_2)_2/H_2O$
ν_3 (asym str)	2348.5 (2283.1)	2351.1 (2285.2)	2351.1	3727.3		3714.5	
ν_2 (bending)	662.2 (643.6)	656.4	664.3	1597		1600.7	
		660.3	660.5			1619	
		665.3					
ν_1 (sym str)		1384.5 (T)	1384.8	3634.7	3632	3627.7	**3623.8 (T)**
					3632.7		
$2\nu_2$			1279.3				
$\nu_3 + \nu_1$	3711.7 (3632.6)						
	3714.5						
$\nu_3 + 2\nu_2$	3609.9	**3604.4 (T)**					
	3606.8						

[a] The bands in underlined bold are new observations. T: tentative assignment.

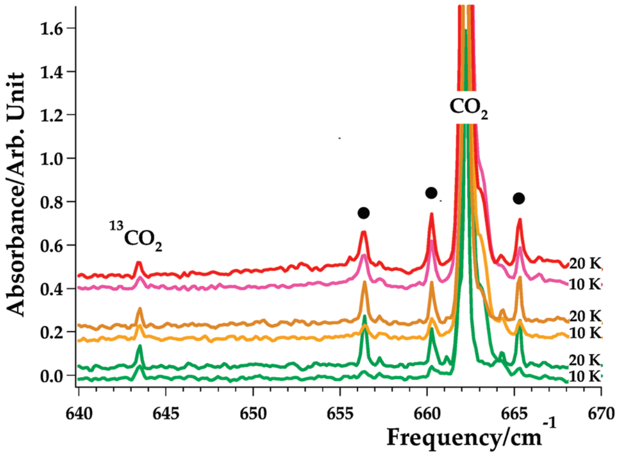

Figure 3. Spectra in the CO_2 bending mode (ν_2) region collected at 4.5 K after (1) deposition at 10 K and (2) deposition at 10 K, followed by warming up to 20 K. From bottom to top: light and dark green traces, $[CO_2]:[H_2O]:[N_2] \cong$ 1:1:700; yellow and brown traces, $[CO_2]:[H_2O]:[N_2]_2 \cong$ 1:3:700; pink and red traces, $[CO_2]:[H_2O]:[N_2] \cong$ 1:10:700. The black bullets (●) indicate the CO_2/H_2O complex bands.

the CO_2 monomer has a strong absorption at 662.2 cm^{-1} (643.6 cm^{-1} for $^{13}CO_2$). When only CO_2 is present along with N_2, two weak bands of the CO_2 dimer are also observed at 664.3 and 660.5 cm^{-1}, which have been reported previously.[6,16,17] The small peak at 657.3 cm^{-1} is also detected. A study[17] by Fredin et al. assigned this feature to the ν_2 band of the $^{12}C^{16}O^{18}O$ monomer, whereas another study[18] by Nxumalo et al. attributed it to the CO_2 dimer. Our preliminary results show that, when more CO_2 was added, this band increased in a trend similar to the $^{13}CO_2$ band, but not the CO_2 dimer bands; therefore, it is more likely from a monomer of CO_2. Because our result seems to support the assignment by Fredin et al., we assign the band at 657.3 cm^{-1} to the ν_2 band of the $^{12}C^{16}O^{18}O$ monomer.

When H_2O is added to the CO_2/N_2 mixture, three new bands are observed at 656.4, 660.3, and 665.3 cm^{-1}. Their intensities increase when more H_2O was added with the amount of CO_2 fixed. They are not visible when only H_2O/N_2 is present. In addition, the intensities of all three bands increase monotonically with increasing concentration ratio of $[CO_2]:[H_2O]$. Previously, two features have been observed and assigned to the 1:1 CO_2/H_2O complex at 656.3 and 665.3 cm^{-1} by Fredin, et al.,[6] and at 656.3 and 665.2 cm^{-1} by Schriver et al.[16] Two of the three bands detected here at 656.4 and 665.3 cm^{-1} are in good agreement with these earlier results. However, the third feature at 660.3 cm^{-1} has not been reported previously; here, we assign this band to the 1:1 CO_2/H_2O complex as well based on the above analysis and the following discussion. Figure 3 compares the spectra collected at 4.5 K after (1) deposition at 10 K and (2) deposition at 10 K, followed by warming up to 20 K. It shows that the intensities of all these three bands increase in a similar manner when the matrices were warmed up to 20 K from 10 K. The increase was not as significant for $[CO_2]:[H_2O]$ = 1:10 as for $[CO_2]:[H_2O]$ = 1:1 or 1:3. The likely reason is that, in the case of $[CO_2]:[H_2O]$ = 1:10, nearly the maximum amount of the CO_2/H_2O complex was formed at 10 K due to the large excess of H_2O. The annealing to 20 K, therefore, did not significantly increase the amount of the CO_2/H_2O complex formed. The annealing experiments also help eliminate the possibility that the band at 660.3 cm^{-1} is from matrix site splitting or a second site. In general, when a matrix is warmed up, then cools back down again, the bands from two different matrix sites will undergo significant changes in both intensities and frequencies. For example, two bands from two different sites may merge into one band or one band increases while the other decreases, and there are usually frequency shifts with these bands. However, here in this work, when the matrix undergoes annealing, all three bands, including the one at 660.3 cm^{-1}, increase in a similar manner as discussed earlier (see Figure 3), and there are no frequency shifts. In addition, when two bands result from two different matrix sites, in many cases, one band is more intense than the other (the second site). Here, all three bands have similar intensities. On the basis of these analyses, we conclude that the band at 660.3 cm^{-1} is not from matrix site splitting. To eliminate the possibility that the peak at 660.3 cm^{-1} belongs to the $(CO_2)_2/H_2O$ complex, we have collected spectra of $[CO_2]:[H_2O] \approx$ 10:10 to compare with those of $[CO_2]:[H_2O] \approx$ 1:10. The results show a proportionate increase

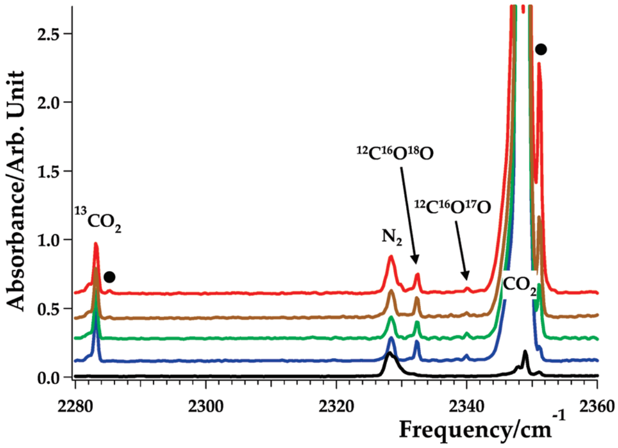

Figure 4. Spectra in the CO_2 asymmetric stretching mode (ν_3) region collected at 4.5 K after deposition at 10 K, with five different $[CO_2]$:$[H_2O]$:$[N_2]_2$ concentration ratios. From bottom to top: black trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 0:20:700; blue trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:0:700; green trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:1:700; brown trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:3:700; red trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:10:700. The black bullets (●) indicate the CO_2/H_2O complex bands.

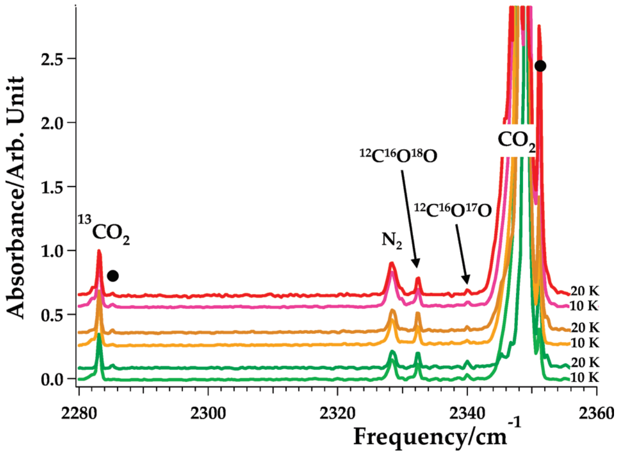

Figure 5. Spectra in the CO_2 asymmetric stretching mode (ν_3) region collected at 4.5 K after (1) deposition at 10 K and (2) deposition at 10 K, followed by warming up to 20 K. From bottom to top: light and dark green traces, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:1:700; yellow and brown traces, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:3:700; pink and red traces, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:10:700. The black bullets (●) indicate the CO_2/H_2O complex bands.

in the intensities of all three peaks from the spectra of $[CO_2]$:$[H_2O]$ $\approx$ 1:10 to those of $[CO_2]$:$[H_2O] \approx$ 10:10. Consequently, we assign the band at 660.3 cm^{-1} to the 1:1 CO_2/H_2O complex.

Our detection of three CO_2/H_2O complex bands in this region further confirms that there are two structures of the CO_2/H_2O complex in a N_2 matrix. As discussed previously, four frequencies should exist corresponding to the bending mode of CO_2 monomer. We observed three of the four in this work. One possible reason that the fourth band has not been detected is that its frequency is very close to the CO_2 monomer band; therefore, it is obscured by the large CO_2 monomer peak.

The CO_2 dimer band at 660.5 cm^{-1} and the CO_2/H_2O complex band at 660.3 cm^{-1} are very close to each other. When H_2O was added to the CO_2/N_2 mixture, the CO_2/H_2O band at 660.3 cm^{-1} grew, which overshadowed the CO_2 dimer band at 660.5 cm^{-1}. Because the intensity of the feature at 660.3 cm^{-1} increased when more H_2O was added while the CO_2 dimer band at 664.3 cm^{-1} did not, the band at 660.3 cm^{-1} is not a CO_2 dimer band.

Asymmetric Stretching Mode ν_3 *(2280−2360 cm^{-1}).* Figure 4 illustrates the spectra collected at 4.5 K after deposition at 10 K, with five different $[CO_2]$:$[H_2O]$:$[N_2]$ concentration ratios. In this region, the CO_2 monomer has a strong absorption at 2348.5 cm^{-1} (2283.1 cm^{-1} for $^{13}CO_2$). Previous studies[19] have also reported a CO_2 dimer band at around 2351.1 cm^{-1}, which can be seen in our spectrum when only CO_2 is present along with N_2. Weak bands at 2340.1, 2332.5, and 2328.4 cm^{-1} are also detected. Fredin et al. attributed two features at 2339.6 and 2331.9 cm^{-1} to the ν_3 band of $^{12}C^{16}O^{17}O$ and $^{12}C^{16}O^{18}O$ monomers, respectively.[17] Our preliminary results show that, when more CO_2 is added, the bands at 2340.1, 2332.5, and 2328.4 cm^{-1} increase in proportion to the $^{13}CO_2$ band, but not the CO_2 dimer bands. In addition, the integrated intensities of the 2340.1 ($^{12}C^{16}O^{17}O$), 2332.5 ($^{12}C^{16}O^{18}O$), and 2283.1 cm^{-1} ($^{13}C^{16}O_2$) bands are in the ratio of about 0.2:1.1:3.1, which is in reasonable agreement with the expected ratio of 0.2:1.0:2.7 for $^{12}C^{16}O^{17}O/^{12}C^{16}O^{18}O/^{13}C^{16}O_2$ based on the natural abundances.[17] Consequently, we assign the signals at 2340.1 and 2332.5 cm^{-1} to the ν_3 band of $^{12}C^{16}O^{17}O$ and $^{12}C^{16}O^{18}O$ monomers, respectively.

Previously, the relatively broad band at 2328.1 cm^{-1} was assigned[17] by Fredin et al. to the N−N stretching frequency of N_2, which is IR-activated in the presence of CO_2. The study by Nxumalo et al. attributed[18] the features at both 2328.4 and 2332.0 cm^{-1} to the ν_3 band of the $^{12}C^{16}O^{18}O$ monomer. Our result seems to support the assignment by Fredin et al. for the following reasons. In Figure 4, the relatively broad feature at about 2328.4 cm^{-1} can also be seen in the H_2O/N_2 only spectrum; its frequency is very close to that in the CO_2/N_2 only spectrum. This is likely the N−N stretching band of N_2, which is activated by the presence of H_2O. In the $CO_2/H_2O/N_2$ spectra, when more H_2O is added with a similar amount of CO_2, the signal at 2328.4 cm^{-1} shows some increase, especially when the $[CO_2]$:$[H_2O]$ ratio reaches 1:10, which indicates that the N−N stretching band of N_2 is activated not only by CO_2 but also by H_2O. In addition, if both features at 2332.5 and 2328.4 cm^{-1} belong to the ν_3 band of the $^{12}C^{16}O^{18}O$ monomer, the integrated intensities of the $^{12}C^{16}O^{17}O$ (2340.1 cm^{-1}), $^{12}C^{16}O^{18}O$ (2332.5 and 2328.4 cm^{-1}), and $^{13}C^{16}O_2$ (2283.1 cm^{-1}) bands would be in the ratio of about 0.2:3.1:3.1, which would not agree with the expected ratio of 0.2:1.0:2.7 based on the natural abundances.[17] Consequently, we assign the band at 2328.4 cm^{-1} to the N−N stretching frequency of N_2, which is IR-activated in the presence of CO_2 and/or H_2O.

When H_2O was added to the CO_2/N_2 mixture, the intensity of the feature at 2351.1 cm^{-1} increased substantially. Its intensity increased when more H_2O was added with a fixed amount of CO_2. The intensity was negligible when only H_2O/N_2 was present. Previous studies[6,16] have detected the CO_2/H_2O band at 2351.0 cm^{-1}, which is very close to the CO_2 dimer band. Here, we assign the band at 2351.1 cm^{-1}, which coincides with the CO_2 dimer band, to the CO_2/H_2O complex. The $^{13}CO_2/H_2O$ complex band at 2285.2 cm^{-1} is also detected; it has been observed[6] by Fredin et al. previously at 2284.8 cm^{-1}. Figure 5 compares the spectra collected at 4.5 K after (1) deposition at 10 K and (2) deposition at 10 K, followed by warming up to 20 K. It shows that the intensities of both CO_2/H_2O and $^{13}CO_2/H_2O$ complex bands at 2351.1 and 2285.2 cm^{-1}, respectively, increase when the matrices were warmed up to 20 K from 10 K. Again, the

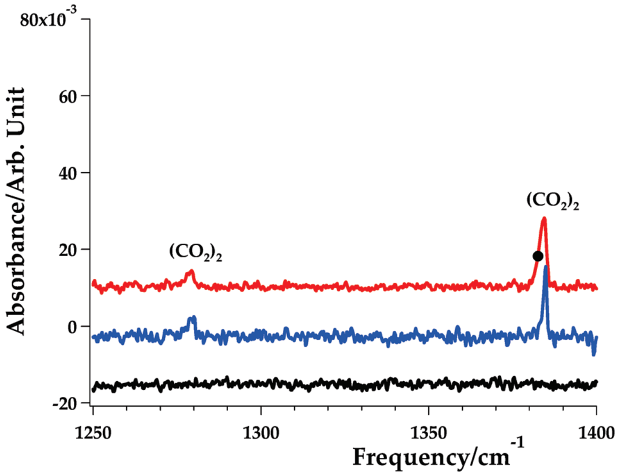

Figure 6. Spectra in the CO_2 symmetric stretching mode (ν_1) region collected at 4.5 K after deposition at about 10−30 K with three different $[CO_2]$:$[H_2O]$:$[N_2]$ concentration ratios. From bottom to top: black trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 0:20:700 and deposition at 10 K; blue trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 9:0:610 and deposition at 20 K; red trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 10:12:630 and deposition at 30 K. The black bullet (●) indicates the CO_2/H_2O complex band.

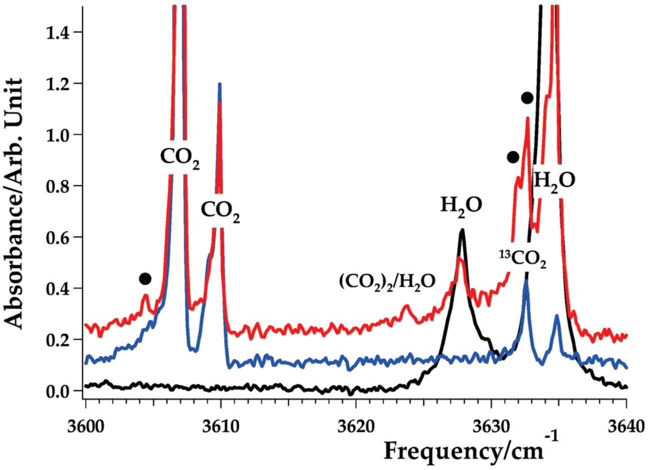

Figure 7. Spectra in the 3600−3640 cm^{-1} region collected at 4.5 K after deposition at 10−20 K with three different $[CO_2]$:$[H_2O]$:$[N_2]$ concentration ratios. From bottom to top: black trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 0:20:700 and deposition at 10 K; blue trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 9:0:610 and deposition at 20 K; red trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 12:9:600 and deposition at 20 K. The black bullets (●) indicate the CO_2/H_2O complex bands.

increase was not as significant for $[CO_2]$:$[H_2O]$ = 1:10 as for $[CO_2]$:$[H_2O]$ = 1:1 or 1:3 for the same reason discussed earlier. A small CO_2 monomer band at 2348.5 cm^{-1} still appears in the H_2O/N_2 spectrum, which indicates that trace amounts of CO_2 exist in the H_2O/N_2 mixture.

Symmetric Stretching Mode ν_1 (1250−1400 cm^{-1}). In this region, the CO_2 monomer has a symmetric stretching mode (ν_1), which is IR-inactive. Previously, in a krypton matrix using Raman spectroscopy,[20] ν_1 of the CO_2 monomer was detected at 1382.0 cm^{-1}, in Fermi resonance with $2\nu_2$ at 1277.9 cm^{-1}. In our experiment, when the concentration of CO_2 was small (e.g., $[CO_2]$:$[N_2]$ = 1:700), no signal was observed in this region.

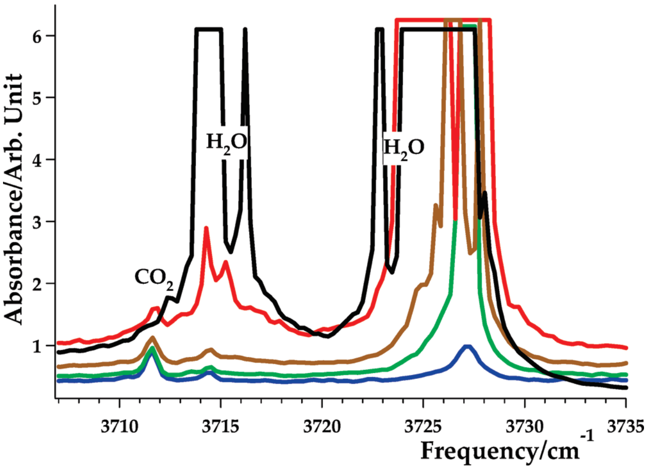

Figure 8. Spectra in the 3707−3735 cm^{-1} region collected at 4.5 K after deposition at 10 K, with five different $[CO_2]$:$[H_2O]$:$[N_2]$ concentration ratios. Black trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 0:20:700; blue trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:0:700; green trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:1:700; brown trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:3:700; red trace, $[CO_2]$:$[H_2O]$:$[N_2] \cong$ 1:10:700.

However, when the CO_2 concentration was increased, two peaks were detected. Figure 6 shows the spectra collected at 4.5 K after deposition at about 10−30 K, with three different $[CO_2]$:$[H_2O]$:$[N_2]$ concentration ratios. When only CO_2/N_2 was present, two bands were observed at 1384.8 and 1279.3 cm^{-1}. According to an earlier study[21] by Castano et al., they belong to ν_1 and $2\nu_2$ of the CO_2 dimer, respectively. When H_2O is added to the CO_2/N_2 mixture, the band at 1384.8 cm^{-1} is broadened toward lower frequencies, which may result from the CO_2/H_2O complex band growing in. The study[6] by Fredin et al. tentatively assigned a weak band at 1384.5 cm^{-1} to the CO_2/H_2O complex in a N_2 matrix. Our result seems to support their finding. The matrix temperature increase from 20 to 30 K is unlikely to be the source of this broadening, especially considering that the peak at 1279.3 cm^{-1} did not show a similar broadening. However, more investigations are needed to confirm this assignment. These bands do not appear in the spectrum with only H_2O/N_2.

Combination Bands: $\nu_3 + 2\nu_2$ (3600−3620 cm^{-1}) and $\nu_3 + \nu_1$ (3707−3720 cm^{-1}). Figure 7 shows the spectra collected at 4.5 K after deposition at 10−20 K, with three different $[CO_2]$:$[H_2O]$:$[N_2]$ concentration ratios. In the CO_2/N_2 only spectrum, two peaks at 3606.8 and 3609.9 cm^{-1} are assigned to the $\nu_3 + 2\nu_2$ combination band of the CO_2 monomer, according to previous studies.[16,19] When H_2O is added, the signal at 3604.4 cm^{-1} grows in, and it only appears when both H_2O and CO_2 are present. Therefore, it is tentatively assigned to the CO_2/H_2O complex band corresponding to the $\nu_3 + 2\nu_2$ combination band of the CO_2 monomer. This CO_2/H_2O complex band has not been observed previously. More studies are needed to confirm this assignment. In the CO_2/N_2 only spectrum of Figure 7, the peak at 3632.6 cm^{-1} is attributed to the $\nu_3 + \nu_1$ combination band of the $^{13}CO_2$ monomer.[16,19] In addition, in Figure 7, it can be seen that a trace amount of H_2O exists in the CO_2/N_2 only spectrum, indicated by the small feature at 3634.7 cm^{-1}, which is attributed to the symmetric stretching mode (ν_1) of the H_2O monomer (discussed later). Figure 8 illustrates the spectra collected at 4.5 K after deposition at 10 K, with five different

[CO_2]:[H_2O]:[N_2] concentration ratios. In the CO_2/N_2 only spectrum, two features at 3711.7 and 3714.5 cm^{-1} are assigned to the $\nu_3 + \nu_1$ combination band of the CO_2 monomer, which is in Fermi resonance with the $\nu_3 + 2\nu_2$ band.[16,19]

H_2O Vibrational Regions.

Symmetric Stretching Mode $\boldsymbol{\nu_1}$ *(3620–3640 cm^{-1}).* In the H_2O/N_2 only spectrum of Figure 7, the strong band at 3634.7 cm^{-1} comes from the symmetric stretching mode (ν_1) of the H_2O monomer, while the weaker band at 3627.7 cm^{-1} is assigned to the H_2O dimer corresponding to the ν_1 mode of the H_2O monomer.[22] When both H_2O and CO_2 are present, two new features appear at 3632.0 and 3632.7 cm^{-1}, which are assigned to the CO_2/H_2O complex corresponding to the ν_1 mode of the H_2O monomer. This assignment is based on the study[16] by Schriver et al., who attributed the two bands at 3631.7 and 3632.4 cm^{-1} to the same vibrational mode. Fredin et al. only observed one feature at 3632.1 cm^{-1} for this mode, which is likely due to their lower spectral resolution.[6]

Another small signal at 3623.8 cm^{-1} also grows in when both H_2O and CO_2 are present. It has not been observed previously. We attribute this weak feature to a possible $CO_2/(H_2O)_2$ or $(CO_2)_2/H_2O$ complex. In the $CO_2/(H_2O)_2$ complex, hydrogen bonds exist between the two H_2O molecules as well as between one H_2O and CO_2 molecules, according to the theoretical study[3] by Chaban et al.; consequently, large frequency shifts[3] (about 165 and 45 cm^{-1}) are expected for the O–H symmetric stretching modes of complexed H_2O molecules with respect to the H_2O monomer. However, in the $(CO_2)_2/H_2O$ complex, only one hydrogen bond is predicted between the H_2O molecule and one CO_2 molecule based on the ab initio investigation[13] by Danten et al.; thus, a relatively small frequency shift[13] (about 13 cm^{-1}) can be expected for the O–H symmetric stretching mode of the complexed H_2O molecule. Here, the shift is 10.9 cm^{-1} from the weak feature at 3623.8 cm^{-1} to the O–H symmetric stretching band (3634.7 cm^{-1}) of the H_2O monomer. Therefore, we tentatively assign the small signal at 3623.8 cm^{-1} to the O–H symmetric stretching mode of the $(CO_2)_2/H_2O$ complex.

Because there are two structures of the CO_2/H_2O complex in the N_2 matrix, two CO_2/H_2O complex bands[16] should exist, corresponding to the ν_1 mode of the H_2O monomer; the two features at 3632.0 and 3632.7 cm^{-1} have been assigned to those bands. Furthermore, if the 3623.8 cm^{-1} band belonged to the CO_2/H_2O complex, the shift from the corresponding CO_2 monomer band (3634.7 cm^{-1}) would be unusually large (11 cm^{-1}) compared with the shifts of other modes (<6 cm^{-1}). Therefore, it is unlikely that the feature at 3623.8 cm^{-1} belongs to the CO_2/H_2O complex. However, more investigations are needed to confirm the assignment.

Asymmetric Stretching Mode ν_3 (3710–3735 cm^{-1}). The ν_3 band of the H_2O monomer at 3727.3 cm^{-1} is very strong, which can be seen in the H_2O/N_2 only spectrum of Figure 8. The strong feature at 3714.5 cm^{-1} comes from the H_2O dimer based on the study[6] by Fredin et al.; this feature is the asymmetric stretching mode ν_3 of the H_2O molecule, which is the proton acceptor in the H_2O dimer. Again, a trace amount of H_2O can be seen in the CO_2/N_2 only spectrum of Figure 8, indicated by the small band at 3727.3 cm^{-1}. No CO_2 and H_2O complex bands are detected in this region partly due to the saturation of the H_2O bands. More spectra with different [CO_2]:[H_2O]:[N_2] concentration ratios need to be studied to detect the CO_2/H_2O complex bands in this region. Schriver et al. reported[16] two features in this region that belong to the CO_2/H_2O complex at 3725.5 and 3724.1 cm^{-1}, whereas Fredin et al. only detected[6] one band at 3724.8 cm^{-1} due to their lower spectral resolution.

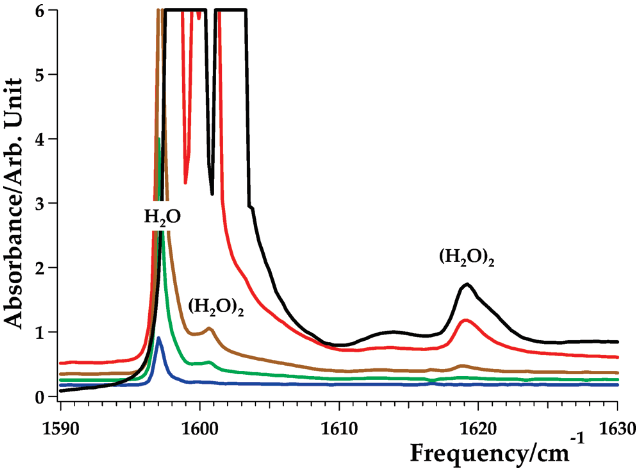

Figure 9. Spectra in the H_2O bending mode (ν_2) region collected at 4.5 K after deposition at 10 K, with five different [CO_2]:[H_2O]:[N_2] concentration ratios. Black trace, [CO_2]:[H_2O]:[N_2] ≅ 0:20:700; blue trace, [CO_2]:[H_2O]:[N_2] ≅ 1:0:700; green trace, [CO_2]:[H_2O]:[N_2] ≅ 1:1:700; brown trace, [CO_2]:[H_2O]:[N_2] ≅ 1:3:700; red trace, [CO_2]:[H_2O]:[N_2] ≅ 1:10:700.

Bending Mode ν_2 (1590–1630 cm^{-1}). Figure 9 illustrates the spectra collected at 4.5 K after deposition at 10 K, with five different [CO_2]:[H_2O]:[N_2] concentration ratios. It shows a very strong ν_2 band of the H_2O monomer at 1597.0 cm^{-1}. Two features at 1600.7 and 1619 cm^{-1} are attributed to the H_2O dimer based on the study[22] by Fredin et al. Again, a trace amount of H_2O can be seen in the CO_2/N_2 only spectrum of Figure 9, indicated by the small band at 1597.0 cm^{-1}. No CO_2 and H_2O complex bands are detected in this region partly due to the saturation of the H_2O bands. More spectra with different [CO_2]:[H_2O]:[N_2] concentration ratios need to be collected to observe the CO_2/H_2O complex bands in this region. One band at 1598.4 cm^{-1} was reported[16] to belong to the CO_2/H_2O complex by Schriver et al., and a band at 1598.1 cm^{-1} was assigned[6] to the CO_2/H_2O complex by Fredin et al.

SUMMARY

We have detected three CO_2/H_2O complex bands in the bending mode region of CO_2, which confirms that there are two structures of the CO_2/H_2O complex in a N_2 matrix. One of the three bands at 660.3 cm^{-1} is reported here for the first time. As for the two structures of the CO_2/H_2O complex, one of them most likely has the T-shaped C_{2v} symmetry, which has been determined by molecular beam electric resonance spectroscopy as well as a number of calculations. The second structure could have C_s or C_1 symmetry, both of which have been identified theoretically. The CCSD(T) studies[14] by Garden et al. and the more recent MP2 calculations[15] by Altmann and Ford suggest that the second structure is more likely to have C_1 symmetry than C_s symmetry. However, more studies are needed to determine the second structure. In addition, we have detected a new feature at 3604.4 cm^{-1} that belongs to a CO_2 and H_2O complex and tentatively assigned it to the CO_2/H_2O complex band corresponding to the CO_2 combination mode ($\nu_3 + 2\nu_2$). Furthermore, we have made the first observation of a CO_2 and H_2O complex band at 3623.8 cm^{-1}, which we tentatively assign to the O−H symmetric stretching mode of H_2O for the $(CO_2)_2/H_2O$ complex.

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(3) Chaban, G. M.; Bernstein, M.; Cruikshank, D. P. *Icarus* **2007**, *187*, 592 Note: The calculated 165 cm^{-1} shift seems quite high for the O−H symmetric stretching modes of complexed H_2O molecules in the $CO_2/(H_2O)_2$ complex with respect to H_2O monomer. Considering the similar shift in the H_2O dimer (~50 cm^{-1}), we would expect this shift in the $CO_2/(H_2O)_2$ complex to be around 50 cm^{-1}. This issue certainly needs to be reinvestigated.

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(5) Note: From now on, the 1:1 complex will be written as CO_2/H_2O and the 2:1 complex as $(CO_2)_2/H_2O$, etc.

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