FTIR and ab Initio Study of the 1/1 Complex between Water and Carbon Dioxide in Solid Nitrogen

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Infrared spectra of the 1/1 complex between water and carbon dioxide isolated in a nitrogen matrix are reported. Isotopic substitution of water (HOD, D_2O) suggests the existence of two very weak complexes with a nearly T-shaped structure where the C atom is bonded to the water oxygen: one of C_{2v} symmetry and another one of C_s symmetry, in which a slight distortion results in a very weak interaction between one hydrogen atom of water and one oxygen atom of carbon dioxide. This result is supported by force constant calculations, consistent with a double, symmetrical, and unsymmetrical force field, and ab initio calculations. At the MP2/aug-cc-PVTZ level corrected from basis set superposition error the C_{2v} structure is a saddle point with an imaginary frequency for H_2O rocking, in contrast to a C_s structure, which would have nonequivalent hydrogen atoms. Nevertheless, the energies of both structures, with a stabilization energy of 1.97 kcal mol^{-1}, differ by less than 0.01 kcal mol^{-1} from each other. A comparison of calculated and observed frequency shifts allows us to suggest the presence in the matrix of both C_{2v} and C_s complexes.

Introduction

Due to their importance in the earth's atmosphere, the intermolecular interaction between water and carbon dioxide has been the object of several experimental[1−3] and theoretical works.[2,4−6] Structure determination has been one of the essential tasks in the early stages. The structure of the H_2O/CO_2 complex was first determined by Peterson and Klemperer from radio frequency and microwave spectra.[1] Analysis of these data showed the structure of the complex to be T-shaped with C_{2v} symmetry and with hydrogens pointing away from the CO_2. The barrier hindering the internal rotation of H_2O around its C_{2v} axis was estimated to be about 300 cm^{-1}, a value confirmed later by gas-phase high-resolution spectroscopy in the ν_{OH} asymmetric region.[2] Recent ab initio calculations[6] confirmed the T-shaped planar structure with the C atom attached to the oxygen atom of the water moiety but also predicted an H-bonded arrangement. Unfortunately, very few IR spectroscopic data are available for mixed binary water/carbon dioxide systems in the gas phase, and the IR spectrum of the complex in the gas phase has not been thoroughly characterized. Indeed, IR spectra in the gas phase are complicated by rotational fine structure of the species and the presence of hot bands. Use of a low-temperature matrix is a suitable technique for isolating weak complexes with a high concentration from deposition of a gas mixture where complexation occurs in the gas phase. Coupled with IR spectroscopy, this technique allows one to obtain information on these complexes. The vibrational spectrum of the nitrogen matrix isolated H_2O/CO_2 1/1 complex was first reported by Fredin et al.[7] It was consistent with a T-shaped structure with frequencies very weakly shifted from those of the parent molecules. Later, similar results were obtained for the complex isolated in oxygen[8] and argon matrices.[9,10] However, the equilibrium geometry could not be accurately determined in the absence of isotopic substitution in the water molecule. In this study, we have reinvestigated at high resolution the H_2O/CO_2 complex isolated in solid nitrogen using water isotopic species. Analysis of the data was performed with the help of force field and ab initio calculations.

Experimental Section

Matrix Isolation Studies. Water and D_2O (CEA 99% isotopic purity) were used after "freeze−pump−thaw" purification in a vacuum line. Nitrogen (Air Liquide N50 purity) was used without further purification. The gas mixtures containing N_2 as the matrix were made in a bulb by standard manometric techniques and sprayed through a one-inlet system onto a gold-plated mirror maintained at 17 K in a rotatable closed-cycle helium refrigerator (AIR Product Displex Model 202A) with CsI windows. The deposition rate was 8 mmol/h. A temperature controller (silicon diode 966-1) was used to maintain the chosen temperature within ±0.1 K. Spectra were recorded at 11 K in the 4000−400 cm^{-1} spectral region with a Bruker FTIR IFS 113 v spectrometer in the reflection mode (incidence angle of 5°) at a nominal resolution of 0.1 cm^{-1}. The optical path between the beam extractor and the cryostat was nitrogen purged to avoid atmospheric absorption by CO_2 and H_2O.

Computational Details. Full geometry optimizations were performed at the MP2 level BSSE corrected, using the Boys

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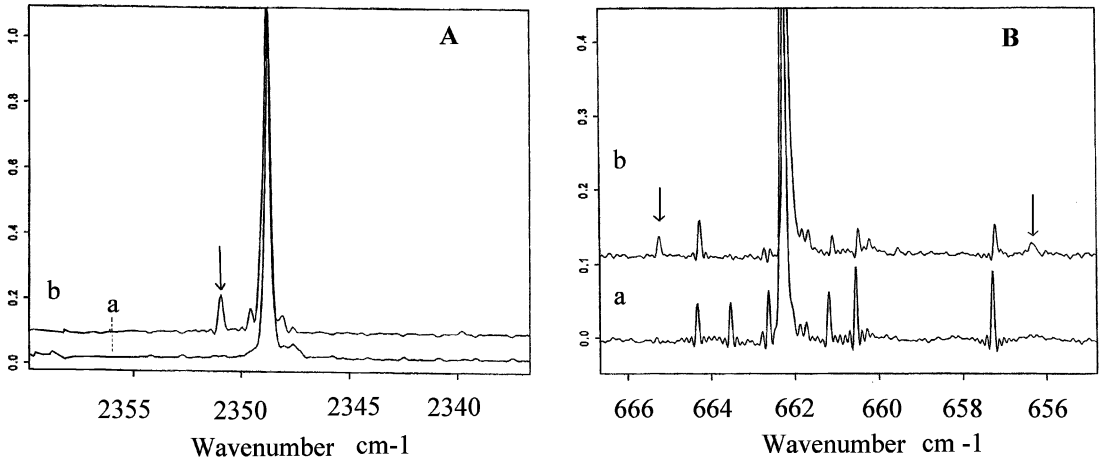

Figure 1. (A) Spectra recorded at 11 K in the ν_3 region of CO_2 of a $CO_2/H_2O/N_2 = 1/5/10\,000$ mixture: (a): after deposition at 17 K; (b) after weak annealing at 21 K. (B) Comparison in the ν_2 region of CO_2 at 11 K of the infrared spectra of CO_2 in nitrogen: (a) $CO_2/N_2 = 1/1000$; (b) $CO_2/H_2O/N_2 = 1/1/3000$. (a) and (b) were obtained after weak annealing at 20 K.

counterpoise method,[11] with the Dunning basis set, which includes a 2df/2pd set of polarization orbitals and a spdf/spd set of diffuse orbitals (aug-cc-pvTZ). Harmonic vibration frequencies were calculated after further optimization of internal parameters of CO_2 and H_2O moieties with increased convergence criteria (*tight* option). To emphasize the role of diffuse orbitals and of BSSE corrections, additional calculations were done at the BSSE/MP2/cc-PVTZ and MP2/aug-cc-PVTZ levels. The Gaussian 03[12] set of programs was used throughout this work.

Experimental Results and Discussion

Some experiments were carried out with various relative concentrations (high dilution in CO_2, high concentration in H_2O and the reverse situation). However, to identify only the 1/1 complex, in many cases, experiments were also performed using low concentrations, typically $CO_2/H_2O/N_2 = 1/5/10\,000$ and weak annealing after deposition. The complex will be described by first considering absorptions due to the perturbed CO_2 molecule and then the absorptions characterizing the H_2O (HOD, D_2O) submolecule in the complex.

CO_2 Submolecule in the Complex. In a nitrogen matrix, the vibrational spectrum of the CO_2 monomer is characterized by a strong absorption at 2349.0 cm^{-1}, assigned to the ν_3 asymmetric stretching vibration, a weak feature at 662.3 cm^{-1}, assigned to the ν_2 bending vibration, and two medium-intensity doublets assigned to the $\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$ combinations in Fermi resonance located at 3714.5−3711.6 and 3609.1−3607.0 cm^{-1}, respectively.[13] As displayed in Figure 1A, addition of H_2O to highly diluted CO_2 ($CO_2/N_2 = 1/10\,000$) gives rise, in the ν_3 region, to a new feature located at 2351.0 cm^{-1}. This band is close to that of the ν_3 absorption of the CO_2 dimer,[13] but this dimer is lacking from these highly diluted samples. Its intensity increases with the H_2O/CO_2 molar ratio. However, in this experiment, no band of complexed CO_2 was observed in the bending region, due to the difference in intensity of the two active fundamental vibrations of CO_2 and to high dilution in CO_2. To investigate the bending ν_2 region, the initial concentration of CO_2 was slightly increased ($CO_2/H_2O/N_2 = 1/1/3000$) and the deposition was followed by a weak annealing at 21 K. Trace b in Figure 1B shows the spectrum recorded at 11 K after annealing at 21 K with, for comparison, the spectrum of a CO_2/N_2 sample (without water) rich in carbon dioxide aggregates. It can be seen that the two absorptions at 665.2 and 656.3 cm^{-1} do not belong to carbon dioxide aggregates, and hence, they are assigned to CO_2 perturbed by one molecule of H_2O. As for the ν_3 mode, the absorptions of the ν_2 mode of CO_2 in the complex are close to the ν_2 absorptions of the CO_2 dimer located at 664.4 and 660.6 cm^{-1}. These results, as well as those in the ν_3 region, are in agreement with data reported by Fredin.[7]

The ν_1 symmetric stretching mode of CO_2, which is IR inactive, could be observed in the CO_2/H_2O complex. In a krypton matrix, using Raman spectroscopy, the absorption due to the ν_1 mode of CO_2 monomer was observed at 1277.9 cm^{-1}, in Fermi resonance with $2\nu_2$ located at 1382.0 cm^{-1}.[14] Unfortunately, no band belonging to the CO_2 submolecule in the complex was found in this region. The absence of any absorption band in the CO_2 ν_1 region suggests a weak perturbation of the CO_2 molecule, in agreement with the small ν_3 shift with respect to its value in the monomer ($\Delta\nu = 2$ cm^{-1}).

H_2O Submolecule in the Complex. Infrared spectra of all isotopic water monomers and dimers in nitrogen have been reported by Fredin et al.[15]

Deposition of a $CO_2/H_2O/N_2$ mixture ($CO_2/H_2O/N_2 = 1/1/3000$) led to the appearance of a doublet at 3725.5−3724.1 cm^{-1} in the ν_3 region, to a doublet located at 3632.4$_5$−3631.7 cm^{-1} in the ν_1 region, and to a band at 1598.4$_5$ cm^{-1} in the ν_2 region, as illustrated in Figure 2. These bands are situated at higher frequencies than those observed, in a water dimer trapped in nitrogen, for the water molecule acting as proton acceptor (3715, 3627.2, and 1601.1 cm^{-1} for ν_3, ν_1, and ν_2 respectively). It is worth noting from Figure 2 that the $\nu_3/\nu_2/\nu_1$ intensity ratio in the complex (0.32/1/0.37) is different from that of monomer water (1.3/1/0.1). This suggests a significant charge transfer upon complexation, as previously observed for other complexes,[16,17] despite very weak frequency shifts from the water monomer to the complexed water molecule. Due to a lower resolution, Fredin[7] could only observe in the ν_3 water region a distinct asymmetry of the water monomer band in the spectrum containing both water and carbon dioxide in nitrogen. By subtraction of the water spectrum in nitrogen from the water monomer band of a carbon dioxide containing matrix, a quite large peak at 3726.7 cm^{-1} was obtained and assigned to the asymmetric stretching mode of water complexed to carbon dioxide. In our spectra, a distinct weak doublet at 3725.5−3724.1 cm^{-1} was observed, and hence, it is assigned to the ν_3 fundamental of water perturbed by carbon dioxide.

D_2O and HOD Submolecules in the Complex. A series of similar studies with D_2O (70% deuterium enriched) provide results comparable to those for H_2O. In each D_2O fundamental

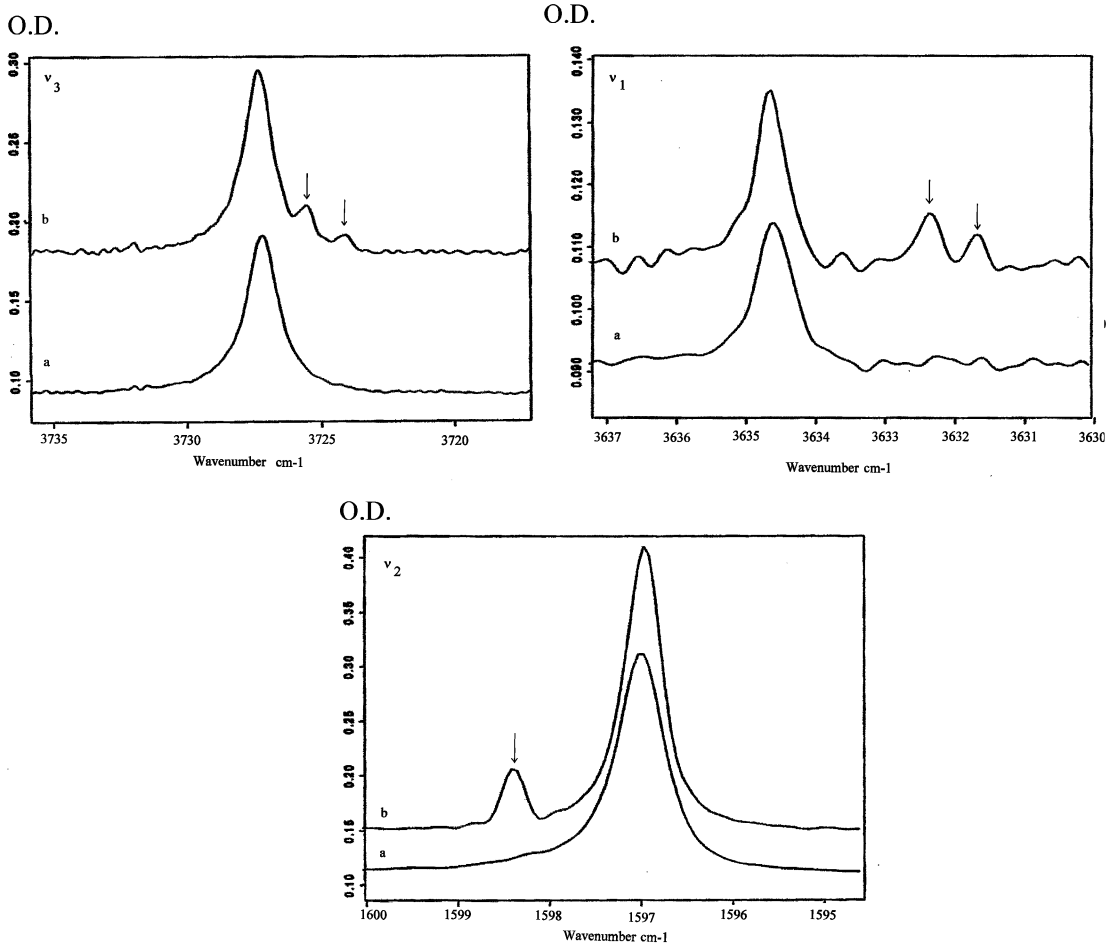

Figure 2. Spectra recorded at 11 K in the three fundamental water regions of a $CO_2/H_2O/N_2 = 1/2/5000$ mixture: (a) after deposition at 17 K; (b) after weak annealing at 21 K.

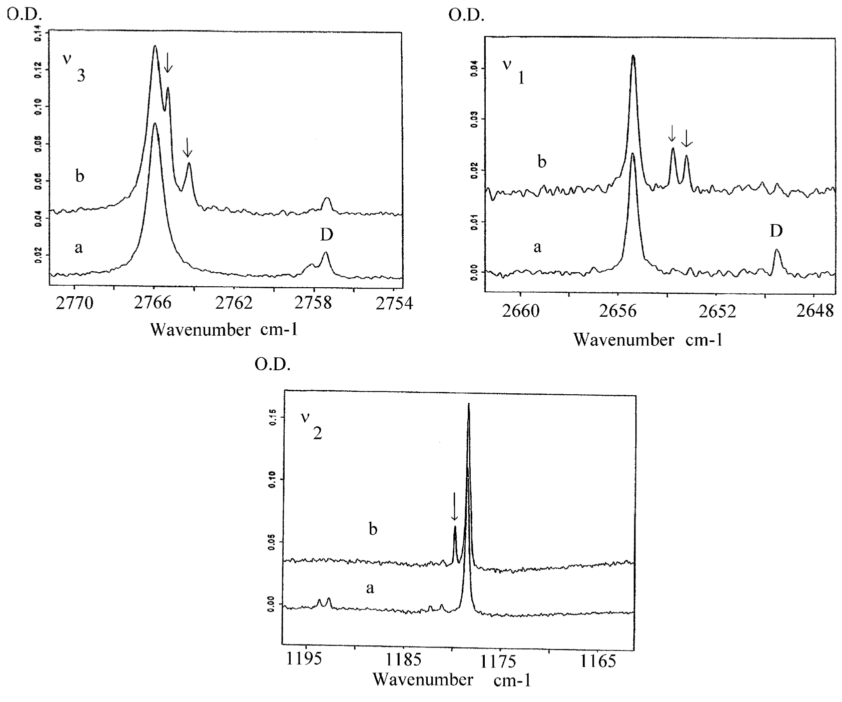

Figure 3. Comparison in a nitrogen matrix at 11 K of infrared spectra: (a) D_2O ($D_2O/N_2 = 1/500$); (b) $CO_2 + D_2O$ ($CO_2/H_2O/N_2 = 1/2/5000$). D/H = 3/1; D = dimer.

region, new bands with a fine structure were observed in the proximity of the monomer fundamentals, as illustrated in Figure 3. They were found at 2765.3−2764.2, 2653.7$_5$-2653.2, and 1179.8 cm^{-1} in the ν_3, ν_1, and ν_2 regions, respectively. These vibrations have H_2O/D_2O frequency ratios of 1.347, 1.369, and 1.355, respectively, values in good agreement with the usual

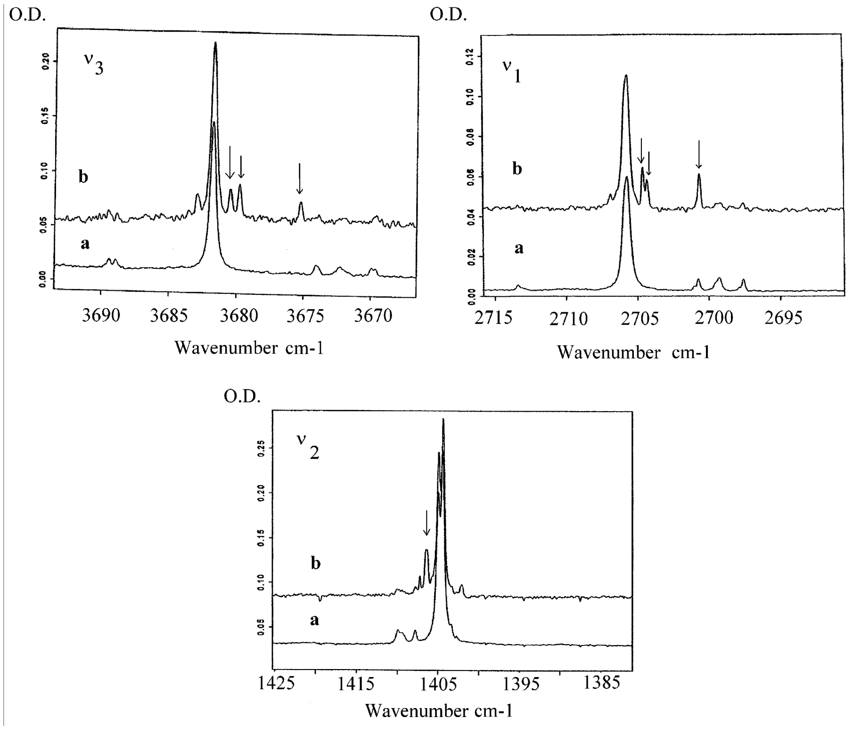

Figure 4. Comparison in a nitrogen matrix at 11 K of infrared spectra: (a) HOD; (b) CO_2 + HOD ($CO_2/H_2O/N_2$ = 1/2/5000). D/H = 3/1.

TABLE 1: Fundamentals of the Water Carbon Dioxide Complex, Carbon Dioxide, and Water Monomer (11 K)

	CO_2 fundamentals		H_2O fundamentals					
	CO_2	CO_2/ H_2O	H_2O	H_2O/ CO_2	HOD	HOD/ CO_2	D_2O	D_2O/ CO_2
ν_3	2349.0	2351.0	3727.4	3725.5 3724.1	3681.7	3680.4 3679.8 3675.5	2765.9	2765.3 2764.2
ν_1			3634.9	3632.4_5 3631.7	2705.7	2704.6 2704.3 2700.5	2655.4	2653.7_5 2653.2
ν_2	662.3	665.2 656.3	1597.0	1598.4_5	1405.0	1406.3	1178.5	1179.8

TABLE 2: Anharmonicity Coefficients and Correction Coefficients for Anharmonic Frequencies for the Various Isotopic Species

	H_2O	D_2O		HOD	
ν_i	α_i	$\bar{\alpha}_i$	$1 - \bar{\alpha}_i/(1 - \alpha_i)$	$\bar{\alpha}_i$	$1 - \alpha_i/(1 - \alpha_i)$
ν_1	0.048	0.035	1.0142	0.048	1
ν_2	0.033	0.025	1.0079	0.029_5	1.0037
ν_3	0.048	0.035_5	1.0129_5	0.036_5	1.0120

ones found for other weak water complexes. Several additional bands were also observed in each spectral region of HOD (formed by the simultaneous presence of hydrogen and deuterium in the 70% deuterium enriched water), as shown in Figure 4. They are measured at 3680.4, 3679.8, and 3675.5 cm^{-1} in the ν_{OH} region and at 2704.6, 2704.3, and 2700.5 cm^{-1} in the ν_{OD} region. In the bending region a new feature was located at 1406.3 cm^{-1}. Table 1 summarizes the frequencies of the new bands observed in CO_2 and H_2O (HOD, D_2O) regions, respectively. The fundamentals of the carbon dioxide and the water monomers are also given.

The multiplicity of new bands in the OH and OD stretching regions of HOD is not due to a 2/1 complex, $(CO_2)_2$/HOD, nor to a 1/2 complex, $CO_2/(HOD)_2$, as evidenced by several experiments where the relative concentrations of CO_2 and D_2O were varied without significant effect. The presence of a doublet and a lower frequency feature in ν_3 and ν_1 regions of HOD (with a shift larger than 4 cm^{-1} between the doublet and the lower feature) suggests the existence of the two isotopomers DOH/CO_2 and HOD/CO_2 in which the two oscillators OH and OD are not equivalent, due to a weak bond between one hydrogen and one oxygen atom of the carbon dioxide molecule. However, to check such an assumption and to assign the complex bands, force field calculations were performed separately on the water submolecule in the complex, assuming no vibrational coupling between H_2O and CO_2, as justified by the weakness of the intermolecular forces.

Force Constant Calculations. Bonding between CO_2 and H_2O in the 1:1 Complex. Force field constants were calculated by an iteration method using the program of McIntosh and Peterson derived from Wilson's GF technique.[18] For the deuterated species, anharmonicity corrections were performed in the same framework as that in ref 19. Calculated isotopic frequencies have been multiplied by $(1 - \bar{\alpha}_i)/(1 - \alpha_i)$, where α_i is the anharmonicity coefficient of the ith vibrational mode and the bar corresponds to another isotopic species. Coefficients were calculated from the frequencies of the water monomer observed in our spectra and from α_i for H_2O taken from the gas phase. Values are reported in Table 2. Iterations allowed us to obtain eigenvalues with an error less than 2×10^{-3}.

As shown in Table 3, a good fit is observed between calculated and some observed frequencies, assuming two slightly different force constants for OH and OD stretchings and, hence, a slightly dissymmetrical structure. Thus, the feature measured at 3675.5 cm^{-1} should characterize a weakly H-bonded OH oscillator in a first isopotomer DOH/CO_2 (**4** in Figure 5) and the band at 2700.5 cm^{-1} should arise from the corresponding OD oscillator in another isopotomer HOD/CO_2 (**3** in Figure 5). Consequently, higher components of the doublets at 3680.4 and 2704.6 cm^{-1} are assigned to free OH and OD oscillators, respectively. For H_2O and D_2O, corresponding bands of hydrogen-bonded OH and OD are calculated at 3723.7 cm^{-1}

TABLE 3: Comparison of Calculated and Experimental Frequencies (cm^{-1}) of the Water Moiety in the CO_2/H_2O Complex of C_s Symmetry Trapped in Nitrogen[a]

$H_2O\cdots CO_2$		$HOD\cdots CO_2$		$DOH\cdots CO_2$		$D_2O\cdots CO_2$	
obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
3724.1	3723.66	3680.4	3680.99	3675.5	3675.95	2764.2	2763.60
3631.7	3631.20	2700.5	2701.28	2704.6	2704.96	2653.2	2652.51
1598.4_5	1598.12	1406.3	1406.46	1406.3	1406.46	1179.8	1179.90

[a] Force constants (mdyn $Å^{-1}$): $fr_1 r_1 = 7.574$, $fr_2 r_2 = 7.553$, $fr_1 r_2 = -0.069$, $fr_{1\theta} = 0.288$, $fr_{2\theta} = 0.301$, $f_{\theta\theta} = 0.727$.

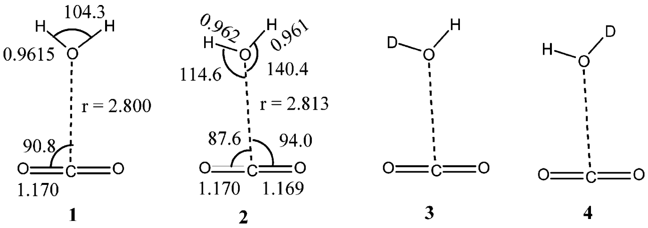

Figure 5. Optimized stationary points of T-shaped CO_2/H_2O complexes and CO_2/H_2O isotopomers (lengths in Å and angles in deg). Note the slight angle variation of each monomer (−1.6° for CO_2 and +0.2° for H_2O).

TABLE 4: Comparison of Calculated and Experimental Frequencies (cm^{-1}) of the Water Moiety in the CO_2/H_2O Complex of C_{2v} Symmetry Trapped in Nitrogen[a]

$H_2O\cdots CO_2$		$H(D)O\cdots CO_2$		$D_2O\cdots CO_2$	
obsd	calcd	obsd	calcd	obsd	calcd
3725.5	3725.49	3679.8	3680.07	2765.3	2764.97
3632.4_5	3632.45	2704.3	2704.23	2653.7_5	2653.66
1598.4	1598.45	1406.3	1406.52	1179.8	1179.92

[a] Force constants (mdyn $Å^{-1}$): $fr = 7.570$, $frr = -0.0702_5$, $fr_\theta = 0.288$, $f_{\theta\theta} = 0.725_6$.

and at 3631.2, 2763.6, and 2652.5 cm^{-1} in the ν_3 and ν_1 regions of H_2O and D_2O, values in good agreement with the frequencies of the lower component of the observed doublets. Such a fine structure has been previously observed for some complexes in a matrix[20] and interpreted as due to differences in trapping sites. This assumption appears unlikely for the observable splittings in our spectra for three reasons: (i) no splitting was observed for hydrogen-bonded OH and OD oscillators of HOD; (ii) no temperature effect was evidenced; (iii) sets of calculations taking into account the different components of doublets were inconsistent. Consequently, we have assumed the existence of another structure with two equivalent OH oscillators for the 1:1 complex. As can be seen in Table 4, calculations allowed us to assign other absorptions at 3725.5, 3632.4_5, 1598.45 cm^{-1} (H_2O/CO_2), 3679.8, 2704.3, 1406.3 cm^{-1} (HOD/CO_2), and 2765.3, 2653.7_5, 1179.8 cm^{-1} (D_2O/CO_2) to complexes with C_{2v} symmetry.

Finally, the H_2O/CO_2 complexes share a T-shaped heavy-atom framework, involving a C···O linking due mainly to a charge transfer from the water oxygen atom to the C atom, as probed by very weak water complex shifts and the 9 cm^{-1} split of degeneracy of the CO_2 bending vibration. Nevertheless, experimental results using HOD species reveal the existence of two different structures for the H_2O/CO_2 complex (Figure 5), the first one with C_{2v} symmetry and the second one with C_s symmetry, slightly tilted from the C···O axis due to a very weak interaction between one hydrogen and one oxygen atom of carbon dioxide. Such structure has been observed for water/ozone[21] and water/nitrous oxide complexes.[22] The vibrational properties of these two complexes in H_2O and D_2O regions are nearly similar. Only weak shifts of 1.4 cm^{-1} between the two different structures are observed for the ν_3 mode of the H_2O submolecule.

TABLE 5: Calculated Harmonic Frequencies (cm^{-1}) for C_{2v} and C_s Structures 1 and 2 of Figure 5 at the MP2/aug-cc-PVTZ+BSSE Correction Level

C_{2v} **1**	C_s **2**	assignt
23.6i	24.9	H_2O rotation in plane
103.1	87.8	H_2O rotation out of plane
107.4	104.2	C···O stretching
132.3	148.4	H_2O twisting
159.5	163.8	O···C═O def
650.1	650.1	CO_2 bending
663.0	662.7	CO_2 bending
1328.5	1328.5	CO_2 stretching
1627.7	1626.1	HOH bending
2404.4	2404.6	CO_2 stretching
3820.0	3818.7	H_2O stretching
3944.8	3947.7	H_2O stretching

[a] Absolute energies (au): **1**, −264.654 886; **2**, −264.654 901. Fundamentals for isolated species (cm^{-1}): 3947.7, 3821.9, 1628.4 (H_2O); 2401.6, 1325.9, 658.9 (CO_2).

Generally, D bonds are preferred to H bonds, as reported for other complexes with water.[23,24] In the CO_2/HOD case, both complexes are observed. To compare the relative stabilities of H and D bonds, the intensity ratio between ν_1 (CO_2/HOD) and ν_3 (CO_2/DOH) was compared to the intensity ratio of ν_1 and ν_3 of the HOD monomer. It was found that the D bond ratio was twice the H bond ratio. This indicates a very weak energy difference between D- and H-bonded complexes and, thus, a weak difference of the zero-point energy contribution from the intermolecular vibrations between the two isopotomers. These conclusions are supported by further ab initio calculations.

Ab Initio Calculations on the H_2O/CO_2 Complex

Several ab initio calculations have been performed on the H_2O/CO_2 complex,[2,6,] which all predict a T-shaped structure as the absolute minimum, though another minimum was found, corresponding to a hydrogen-bonded O═C═O/H−O−H complex. Most of them did not take into account BSSE corrections. This correction was used by Sadlej et al.[6] to compute at a high level large parts of the H_2O/CO_2 potential energy surfaces, assuming nevertheless a frozen geometry of both CO_2 and H_2O moieties, which did not allow the calculation of their vibrational frequencies. These authors concluded a C_{2v} structure as the minimum, with a stabilization energy of 2.62 kcal mol^{-1}.

On the other hand, calculated vibration frequency shifts of H_2O and CO_2 in a C_{2v} complex at the MP2/6-311+G(2d,2p) level[2] are in reasonably good agreement with those observed experimentally, but such a structure is unable to explain the features observed in HOD/CO_2 complexes.

In Table 5 we report the calculated frequencies of stationary points **1** and **2** described in Figure 5. In the first step, the optimization was carried out in a constrained C_{2v} symmetry, yielding structure **1**, which has an imaginary frequency of 23.6i cm^{-1} for the H_2O rotation in the plane of the complex. When, in the second step, any geometric constraint was removed, a zero-order stationary point was found for the C_s structure **2**, possessing nonequivalent hydrogen atoms. Nevertheless, the energy difference between these structures is less than 0.01 kcal mol^{-1} (1.5×10^{-5} au), which is almost insignificant and indicates a very flat potential surface for this motion. For the C_s structure **2**, the calculated van der Waals bond length $r = 2.813$ Å and dipole moment of 1.99 D are close to the experimental values from Petersen and Klemperer,[1] respectively: $r = 2.836$ Å and 1.8515 D.

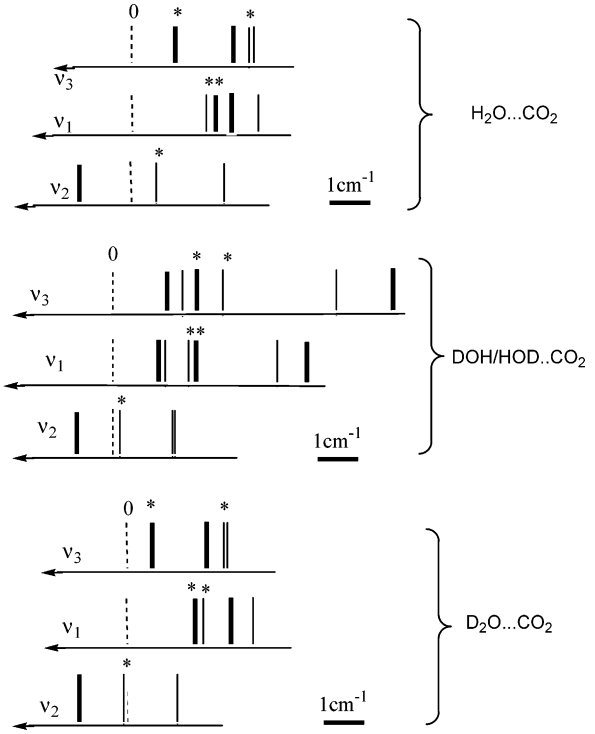

Figure 6. Experimental (bold lines) and calculated (thin lines) patterns for H_2O/CO_2, DHO/CO_2, and D_2O/CO_2 fundamentals of the water moiety. Dotted lines (- - -) refer to the monomer frequency. Solid lines marked with an asterisk refer to the symmetrical C_{2v} structure, and other solid lines refer to the C_s structure.

It is worth noting that the optimized structure symmetry is rather dependent on the calculation method: removing the diffuse basis set results in another C_s structure ($r = 2.897$ Å) with a symmetry plane perpendicular to CO_2 and slightly bent H_2O; removing the BSSE correction yields a structure close to **2** with a shortened bond ($r = 2.775$ Å).

The complexation energy has been found as 1.97 kcal mol^{-1} at the CCSD(T) level, including BSSE and ZPE corrections, slightly less than from previous calculations (2.26 kcal mol^{-1} [2] and 2.63 kcal mol^{-1} [6]).

The calculated frequency shifts of the CO_2 moiety, 3.0 cm^{-1} (ν_3) and 3.8 and -8.5 cm^{-1} (ν_2), are in good agreement with experimental values: 2.0, 2.9, and -6 cm^{-1}, respectively. For H_2O, calculations predict a red shift for all three vibrations for structure **1** as well as for structure **2**, whereas a blue shift of 1.2 cm^{-1} is measured for ν_2. It could arise from a calculation artifact: in fact, additional calculations showed that ν_2 is more sensitive to the rotation angle of the water molecule than the other modes. The very low energy difference between structures **1** and **2** allows us to consider that they are possibly both present, as suggested by the preceding discussion. To this end, we compare in Figure 6 the respective patterns for the fundamentals of H_2O (upper part) and D_2O (lower part), from experimental and calculated frequency shifts, assuming a mixture of the two complexes. Dealing with HOD/CO_2, three species are now expected: structures **3** and **4** and the symmetrical structure **1**. The calculated and experimental results are displayed in the middle part of Figure 6. From the calculations one therefore expects that the complex tunnels rapidly between the two minima and has an effective C_{2v} symmetry, as was found by Petersen and Klemperer.[1] Thus, the experimental results are dependent on the interaction between the complex and the nitrogen matrix and it is possible to interpret the experimental data for the C_{2v} complex as due to such a rapidly tunneling complex.

The energy difference between the HOD/CO_2 complex **3** and DOH/CO_2 complex **4** mainly arises from very weak differences in zero-point vibrational energy, which is calculated as 1.3×10^{-5} au, finally leading to a ΔG difference of less than 10 cal mol^{-1} at 12 K in favor of the HOD/CO_2 complex **3**. Under these conditions, a **3** ↔ **4** equilibrium constant of ca. 1.2 is found, in agreement with experimental results.

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