On the significant enhancement of the continuum - collision induced absorption in $\text{H}_2\text{O}+\text{CO}_2$ mixtures.

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Abstract

The IR spectra of water vapor–carbon dioxide mixtures as well as the spectra of pure gas samples have been recorded using a Fourier-transform infrared spectrometer at a resolution of 0.1 cm^{-1} in order to explore the effect of colliding CO_2 and H_2O molecules on their continuum absorptions. The sample temperatures were 294, 311, 325 and 339 K. Measurements have been conducted at several different water vapor partial pressures depending on the cell temperature. Carbon dioxide pressures were kept close to the three values of 103, 207 and 311 kPa (1.02, 2.04 and 3.07 atm). The path length used in the study was 100 m. It was established that, in the region around 1100 cm^{-1} , the continuum absorption coefficient $C_{\text{H}_2\text{O}+\text{CO}_2}$ is about 20 times stronger than the water-nitrogen continuum absorption coefficient $C_{\text{H}_2\text{O}+\text{N}_2}$. On the other hand, in the far wing region (2500 cm^{-1}) of the ν_3 CO_2 fundamental band, the binary absorption coefficient $C_{\text{CO}_2+\text{H}_2\text{O}}$ appears to be about one order of magnitude stronger than the absorption coefficient $C_{\text{CO}_2+\text{CO}_2}$ in pure carbon dioxide. The continuum interpretation and the main problem of molecular band shape formation are discussed in light of these experimental facts.

Keywords: Atmospheric absorption; water vapor IR spectra; continuum absorption; collision induced absorption.

1. Introduction

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The water-vapor continuum is a significant contributor to the total absorption of IR-radiation in atmospheric windows, and plays an important role in the radiative-transfer processes of the Earth's atmosphere [1]. However, this absorption is still not well studied and understood [2, 3]. Carbon dioxide weak continuum and collision induced absorptions in window and micro-window regions are also important in many applications such as Earth remote sensing or radiative transfer in planetary atmospheres [4, 5].

There is the additional motivation for the presented study given below. Controversial explanations of the continuum as absorption by “far line wings” or absorption by water dimers are the subject of discussion during many past decades. Recently the water-vapor continuum alternate interpretation in terms of collision induced absorption (CIA) processes [3] has been proposed and discussed.

It is well known that in binary mixture of gases “*a*” and “*b*” (oxygen and nitrogen, for example) the collision induced absorption coefficient $K_{CIA}(\nu, \Theta)$ can be expressed as:

$$K_{CIA}(\nu, \Theta) = -\ln T(\nu, \Theta)L^{-1} = C_a(\nu, \Theta)\rho_a^2 + [C_{ab}(\nu, \Theta) + C_{ba}(\nu, \Theta)]\rho_a\rho_b + C_b(\nu, \Theta)\rho_b^2, \quad (1)$$

where ν is the wavenumber, Θ is the temperature, T is the transmittance, L is the path length, ρ_a and ρ_b are the partial densities of the two gases. C_a and C_b are the binary absorption coefficients of the pure gases whereas C_{ab} and C_{ba} stand for the mutual influence of gases on absorption in regions of their CIA bands. The first letter in the subscripts denotes an absorbing molecule in a colliding pair.

The idea of this current research is based on two well-established experimental facts. The first one is the significant absorption enhancement in the oxygen fundamental collision-induced band after the addition of carbon dioxide to a sample of pure O₂ [6].

The absolute integrated band intensity $S_{O_2+CO_2}^{1\leftarrow 0}(\Theta) = \int_{1175}^{1925} C_{O_2+CO_2}(\nu, \Theta) d\nu$ was found to be 5 times stronger than the band intensity $S_{O_2+O_2}^{1\leftarrow 0}$ in pure oxygen at $\Theta = 270$ K. A second similar fact is that in a N₂+H₂O mixture the band integrated intensity $S_{N_2+H_2O}^{1\leftarrow 0}$ [7] is about

14 times stronger than the intensity $S_{N_2+N_2}^{1\leftarrow 0}$ in pure nitrogen [8]. Because of these facts and the proposed continuum interpretation [3], one can expect that there will be a significant influence of carbon dioxide on the water vapor continuum absorption. Mixed H_2O+CO_2 spectra at comparatively high gas densities and long optical paths will be saturated in many broad spectral regions. Nevertheless, micro- and macro-windows of the water vapor spectrum in the regions around 1150 cm^{-1} and 2700 cm^{-1} , where carbon dioxide absorption is weak, are expected to be suitable for measurements of the continuum enhancement due to the presence of CO_2 .

On the other hand, the region beyond the ν_3 CO_2 band “head” ($2400\text{ cm}^{-1} \leq \nu \leq 2600\text{ cm}^{-1}$) is perfect for measurements of additional absorption induced by collisions of carbon dioxide and water molecules. The nature of this absorption is still not clear despite numerous experimental and theoretical studies. Usually it was interpreted in terms of “far wings of lines” (or “mixed lines”) composing the band. This interpretation contradicts the fact that the ν_3 CO_2 weak collision-induced “sub-band” exists as its natural component and this component should not be related to lines of allowed transitions [3]. Thus it was interesting to explore the influence of water vapor on weak continuous absorption in carbon dioxide. The expected experimental results could be significant in a discussion on the continuum origin and on physical mechanisms of molecular band profile formation.

It should be noted that the contribution by local permitted lines to the measured transmittance values may be significant in many micro-windows. Of course, this contribution must be estimated and subtracted from the experimental results in the same way as it was in our previous works [3, 9].

2. Experimental

Measurements were made at NIST using a BOMEM DA3-002 FTIR spectrometer² with a 2 m base-length multi-pass cell, which has been described in detail elsewhere [10]. Instrumental settings and experimental conditions are listed in Table 1. The spectra were recorded at four temperatures and different combinations of H₂O and CO₂ partial pressures as given in Table 1. The experimental procedures and the data acquisition sequence were almost identical to that described for the case of H₂O+N₂ mixtures in Ref. [11]. Note only that in this earlier study we did not vary nitrogen partial pressure, keeping it constant in all measurements at the level of about 4.1 atm.

3. Results

Figure 1 shows an example of the spectra of pure water vapor (1), pure CO₂ (2) and a mixture of both species (3) over two spectral regions around 1200 cm⁻¹ and in the vicinity of 2550 cm⁻¹.

The upper panel of Fig. 1 clearly shows that the presence of CO₂ significantly increases the absorption in the micro windows between 1100 and 1200 cm⁻¹ where the absorption from CO₂ is quite small. But a far more interesting fact is observed in the lower panel where significant enhancement of the absorption of the far wing of the permitted ν_3 band of CO₂ is observed. Note that the water-vapor pressure (52.4 Torr) is about 30 times less than the pressure of the CO₂ in the sample and should not significantly affect the half-width of the CO₂ lines in the ν_3 band. The fact that there is significantly increased absorption beyond the ν_3 band “head” at 2397 cm⁻¹ certainly may influence the discussion [3] on physical mechanisms of permitted molecular band-shape formation.

² Certain commercial equipment instruments or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

The effect of colliding H₂O and CO₂ molecules on the continuous absorption has been measured in a set of 48 spectral intervals located mostly in micro-windows (or windows) suitable for measurement. Seventeen of them fall in the region between 1098 and 1331 cm⁻¹. The others are located in the region between 2500 and 3268 cm⁻¹. The spectral transmittance values were first corrected for “the contribution from local lines” calculated with the use of the HITRAN-08 data base [12]³. Since broadening coefficients of water-vapor lines by carbon dioxide are necessary for this calculation, we assumed these coefficients to be proportional to the nitrogen broadening parameters with a multiplying factor of 1.5 which was determined approximately by comparison (fitting) of the observed spectra with a calculated spectrum. The factor of 1.5 was a variable parameter in that comparison. It is close to the value of 1.67 determined on the base of complex Robert-Bonamy calculations and reported in Ref. [13] for the water vapor rotational band spectral region.

Note that for most of the selected intervals, the “local line” contribution was quite small and the possible uncertainties in the calculated values should not strongly affect the final results and conclusions. Broadening coefficients of CO₂ lines by water vapor pressure were less important in the spectral modeling. In this case, we also used nitrogen broadening coefficients from the HITRAN data base with the same multiplying factor of 1.5. The calculated values were not sensitive to this factor within the range 1 to 2.

As demonstrated in Eq. (1), the absorption coefficient $K_{CIA}(\nu, \Theta)$ at a constant water vapor density ρ_a linearly depends on the carbon dioxide density ρ_b after subtracting the pure CO₂ contribution (and vice-versa). Fig. 2 gives the density dependence of the “reduced” absorption coefficients, $-\ln(T_{H_2O+CO_2}/T_{CO_2})$, obtained in the micro-window 1128.6 cm⁻¹ region with an initial water vapor partial density of 0.0575 kg/m³ equal to a pressure of 64.8 Torr at 325.3K. The plot looks quite linear and its slope

³ The experimental part of the work and primary calculations were made at NIST in 2011 prior the publication of the current edition of the HITRAN data base.

permits one to estimate the binary absorption coefficient $C_{H_2O+CO_2}$ with a statistical uncertainty of 6%.

Fig. 3 is a similar plot showing dependence of the “reduced” absorbance $-\ln(T_{CO_2+H_2O}/T_{H_2O})$ at 2550 cm^{-1} in the wing of the ν_3 CO_2 fundamental band on the water vapor density. The slope of the plot yields the binary absorption coefficient $C_{CO_2+H_2O}$ (carbon dioxide is the major absorbing molecule at 2550 cm^{-1}) with a statistical uncertainty of about 6%. All the data taken for the set of 48 micro-windows were used to get $C_{ab}+C_{ba}$ values via the “least squares method”.

4. Analysis and discussion

Fig. 4 shows the spectral behavior of the water-carbon dioxide continuum in the 1200 cm^{-1} region. This graph presents the binary absorption coefficients, averaged over all four temperatures since there was no clear and distinct temperature dependence detected, as is seen in the insert. An additional reason for averaging was a desire to get more realistic and representative spectral behavior of the absorption coefficients. These results agree with our expectations. The binary absorption coefficients in the left part of the plot (for example at 1128.6 cm^{-1} , where water molecules are the major contributors to the total absorption) are much stronger than those in the case of H_2O+N_2 [14, present study, 3], i.e.

$$C_{H_2O+H_2O} : C_{H_2O+CO_2} : C_{H_2O+N_2} = 375:20:1.$$

The absorption coefficient for pure water vapor $C_{H_2O+H_2O}$ is taken at a temperature of 326K.

The weak spectral feature clearly exhibits itself in the right portion of the plot. Certainly it should be attributed to the low-frequency component of the CO_2 Fermi-dyad ($\nu_1, 2\nu_2$) at 1285 cm^{-1} . The feature looks broader than the corresponding spectral feature in pure CO_2 (the lower trace in Fig. 4) [6] and can be assumed as a CIA band being

composed of P-, Q-, and R-like branches. Unfortunately we cannot extend the measurements toward higher wavenumbers because of saturated absorption in the recorded spectra.

The experimental results in the 3 to 4 μm spectral region are shown in Fig. 5. Here we also present the binary absorption coefficients averaged over all temperatures because of the absence of distinct and sufficient temperature dependence in the data as is seen in the insert. Just as in the wing region of the ν_3 CO_2 fundamental band at 2525 cm^{-1} , a quite weak (comparable with the data uncertainty) negative temperature dependence has been detected. Assuming minimal contribution to the continuum in the 2800 to 2900 cm^{-1} spectral range from CO_2 molecules, we have found a similar ratio for binary absorption coefficients at 2806 cm^{-1} [9, present study, 11]: $C_{\text{H}_2\text{O}+\text{H}_2\text{O}} : C_{\text{H}_2\text{O}+\text{CO}_2} : C_{\text{H}_2\text{O}+\text{N}_2} = 122:15:1$, which is quite expectable. The weak spectral feature arises in the region from 2950 to 3250 cm^{-1} . The deep dip at 3105 cm^{-1} seems not to be an artifact. Initially it was detected just as one low experimental point at 3105.2 cm^{-1} , shown on the figure in black. To double-check the result, additional data were taken in neighboring microwindows at 3098.1 and 3111.2 cm^{-1} . These data points are shown as white dots and confirm the existence of this dip.

The interpretation of the extracted feature is not clear. Exteriorly it resembles the feature at 3130 cm^{-1} observed in the self-continuum profile (lower trace on the figure) [9, 15], but is shifted (meaning major maximums) for about 35 cm^{-1} toward lower wavenumbers. Note that the feature at 3130 cm^{-1} in the self-continuum was suggested to be a water dimer manifestation [15]. However, for the feature observed in this study we have not detected a distinct temperature dependence (see the upper plot on the inset, for example), perhaps because of the narrow temperature range covered in the study. Additionally, the observed structure in $\text{H}_2\text{O}+\text{CO}_2$ continuum looks even slightly broader than the feature in the H_2O self-continuum. This suggests that the discussed structure may not be related to dimeric absorption only and has a more complicated origin.

The increase of the water-vapor-carbon dioxide continuum in the 2500 to 2575 cm^{-1} range no doubt should be attributed to the wing of the ν_3 CO_2 fundamental band. Assuming that CO_2 molecules are the major contributor to the total absorption in that region, we have compared the observed absorption coefficients with the other experimental data for the ν_3 CO_2 band far wing. The absorption in that region was a subject of laboratory studies for the first time by Winters, Silverman and Benedict [16] in 1964. Later measurements and theoretical modeling of observed data in terms of “far line wing” and (or) “line mixing” were undertaken again and again, see for example Refs. [17-19] and literature therein. The comparison of absorption coefficients beyond the ν_3 CO_2 band “head” is presented in Fig. 6. We used for the plot a limited number of more reliable experimental data from Refs. [20-23]. The most important result shown in this figure is that water vapor produces additional absorption in the region beyond the band “head” much more effectively than other gases used in the other experiments [20-23]. For example, the $\text{CO}_2+\text{H}_2\text{O}$ binary absorption coefficient at 2525 cm^{-1} appears to be about 8 times stronger than that for pure CO_2 and about 15 times stronger than the absorption coefficient in a CO_2+N_2 mixture. This provides evidence for the assumption that the observed absorption belongs not to “far wings of lines” (or “mixed lines”), but rather to the wing of the ν_3 CO_2 collision induced “sub-band”. Discussing this problem it should be noted first that lines in molecular spectra may have far wings caused by Doppler broadening only. The widely used terms “far line wings” and “line mixing” are unfortunate in molecular spectroscopy. They contradict each other and can not be used simultaneously. “Far line wing” approaches may be convenient instruments for practical use in spectra modeling but not for scientific representation of physical mechanisms of band-shape formation. The second term also seems to be not good because lines may not be mixed. If we consider a single interaction of two molecules, and one of them absorbs a quantum of electro-magnetic energy, we will observe just one single pixel in a future spectrum and all mixing effects are included in it. This pixel and a variety of the others may not interfere or be mixed because they are a result of independent, separated in space

and time events – molecular interactions. So, to be exact, we have to talk about mixing (or interference) of molecular quantum states. The important consequences follow from this conclusion. 1. Quantum states are mixed in colliding molecules independently of absorption or emission events. 2. Quantum state mixing is inherent to all molecules such as O₂ and CO, for example. 3. Quantum state mixing may manifest itself in collision induced spectra as well as in allowed molecular band profiles. So, this is still an open question as to what absorption was studied in different theoretical models, based on “line mixing” formalism. As is noted in Ref. [3], detailed analysis of a dipole moment autocorrelation function and correct mathematical solution for a spectrum should provide its whole profile including a collision induced “sub-band”.

5. Conclusions

The data presented in this study confirm our expectations of significant mutual enhancement of continuous absorption in H₂O+CO₂ mixtures. The effect of carbon dioxide on the water-vapor continuum in the micro- and macro-windows in 1200 and 2800 cm⁻¹ regions is 20 and 15 times stronger than that produced by nitrogen. Similarly, we found a significant influence of water vapor on absorption in the high-frequency far wing of the allowed ν_3 CO₂ fundamental band. The binary absorption coefficients $C_{CO_2+H_2O}$ measured in that region exceed the results for pure carbon dioxide $C_{CO_2+CO_2}$ by about one order of magnitude. This result for the far wing of the band is very impressive if one bares in mind that the low partial pressure of water vapor used in this study might not affect significantly half-widths of the CO₂ lines composing the band. This leads to the question: - does this absorption really belong to far wings of lines, or it is a far wing of the ν_3 collision-induced “sub-band”? The second option seems to be more realistic. Certainly, transitions, which form the band far wing, occur between strongly perturbed, not stationary states. These states and their wave-functions may have nothing in common with states and wave-functions of isolated molecules. They may have more or less lost symmetry properties and quantum number identification. Transitions between those states

form an underlying collision-induced “sub-band”, but should not be attributed to individual allowed lines.

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Figure captions.

Fig. 1. The absorption spectra of water vapor (1), carbon dioxide (2), and a mixture of both species (3) in two spectral regions.

Fig. 2. Reduced absorbance $-\ln(T_{H_2O+CO_2}/T_{CO_2})$ in the micro-window at 1128.6 cm^{-1} plotted versus the carbon dioxide density. The water vapor density is 0.0517 kg/m^3 .

Fig. 3. Reduced absorbance $-\ln(T_{CO_2+H_2O}/T_{H_2O})$ in the ν_3 CO₂ band wing region at 2550 cm⁻¹ plotted versus water vapor density. Carbon dioxide density is 3.365 kg/m³.

Fig. 4. Spectral behavior of the water-carbon dioxide continuum in the 7 to 9 μm region. The data are a result of averaging over all four temperatures. The insert represents the temperature dependence of the binary absorption coefficients at four selected wavenumbers, designated in the plot by arrows. The thin solid line shows the spectral behavior of the MT_CKD [11] self-continuum fitted to the experimental point at 1128 cm⁻¹ and scaled to the experimental data. The lower trace represents the pure CO₂ CIA spectrum in arbitrary units.

Fig. 5. Spectral behavior of the water-carbon dioxide continuum in the 3 to 4 μm region. The data are a result of averaging over all four temperatures. The insert represents the temperature dependence of the binary absorption coefficients at three selected wavenumbers, designated in the plot by arrows. The bottom solid line shows the spectral behavior of the self-continuum [11] scaled roughly to the experimental data.

Fig. 6. Binary absorption coefficients beyond the ν_3 CO₂ band “head”.

Fig. 1. The absorption spectra of water vapor...

Fig. 2. Reduced absorbance $-\ln(T_{\text{H}_2\text{O}+\text{CO}_2}/T_{\text{CO}_2})$ in the micro-window at 1128.6...

Fig. 3. Reduced absorbance $-\ln(T_{\text{CO}_2+\text{H}_2\text{O}}/T_{\text{H}_2\text{O}})$ in the ν_3 CO_2 band wing...

Fig. 4. Spectral behavior of the water-carbon dioxide continuum in the 7 to 9 μm ...

Fig. 5. Spectral behavior of the water-carbon dioxide continuum in the 3 to 4 μm region.

Fig. 6. Binary absorption coefficients...

Table 1. Instrumental settings and experimental conditions.

Instrumental settings: MCT detector, KBr beamsplitter, Res.=0.1 cm ⁻¹ .				
Temperature K (± 0.5 K)	H ₂ O partial pressures, kPa (torr)	CO ₂ partial pressures, kPa (atm)	Number of spectra of H ₂ O/H ₂ O+CO ₂	Number of pure CO ₂ spectra
339	7.32, 14.4 (54.9, 108)	103, 207, 310 (1.02, 2.04, 3.06)	28	7
325	4.32, 7.01, 8.64 (32.4, 52.6, 64.8)	103, 207, 310 (1.02, 2.04, 3.06)	45	14
311	2.72, 4.00, 5.29 (20.4, 30, 39.7)	103, 207, 310 (1.02, 2.04, 3.06)	27	9
295	1.36, 2.00 (10.2, 15.0)	103, 207, 310 (1.02, 2.04, 3.06)	24	9