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Effect of humidity on the absorption continua of CO$_2$ and N$_2$ near 4 µm: Calculations, comparisons with measurements, and consequences for atmospheric spectra

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We present a theoretical study of the effects of collisions with water vapor molecules on the absorption, around 4 µm, in both the high frequency wing of the CO$_2$ ν$_3$ band and the collision-induced fundamental band of N$_2$. Calculations are made for the very first time, showing that predictions based on classical molecular dynamics simulations enable, without adjustment of any parameter, very satisfactory agreement with the few available experimental determinations. This opens the route for a future study in which accurate temperature-dependent (semi-empirical) models will be built and checked through comparisons between computed and measured atmospheric spectra. This is of interest since, as demonstrated by simulations, neglecting the humidity of air can lead to significant modifications of the atmospheric transmission (and thus also emission) between 2000 and 2800 cm$^{-1}$. Published by AIP Publishing. https://doi.org/10.1063/1.5019994

I. INTRODUCTION

To the best of our knowledge, radiative transfer codes for studies of the Earth’s atmosphere have, so far, disregarded most (if not all) of the effects of the presence of water vapor on the absorption spectra of other gases. There are several reasons for this situation: (i) The first is that the temperature-dependent pressure-broadening coefficients of the lines of the absorbing gas resulting from collisions with H$_2$O are not provided in the currently used databases. Although some data are available (e.g., Refs. 3–5 and those therein), these databases still provide complete sets of values for mixtures with dry air only. An effort is underway to extend the High-Resolution Transmission Molecular Absorption (HITRAN) database and some broadening coefficients by H$_2$, He, and CO$_2$, but not H$_2$O so far, are now available. (ii) The second is due to the relatively small mole fraction of H$_2$O in the Earth’s atmosphere and the fact that the broadening coefficients by H$_2$O and dry air are not so different. The errors induced by using only dry-air broadenings remain of the order of one percent or less. This assumption can thus be used in most atmospheric studies, where the errors that it induces are masked by other sources of uncertainty, except for those which aim at an extremely high accuracy. This is the case, for instance, of the space-borne remote sensing of greenhouse gases for which the broadening effect of collisions with H$_2$O may have to be taken into account for very humid atmospheres. (iii) Finally, when one considers the broadband continua resulting from collision-induced absorption (CIA) (e.g., those of N$_2$ in the far infrared and near 4 µm) or from the far line wings (e.g., those of the intense ν$_2$ and ν$_3$ bands of CO$_2$), no model is available (except for H$_2$O itself). The influence of humidity is, thus again, supposed to be negligible and all computations of the atmospheric continua of gases other than H$_2$O, and associated retrieval exercises, are made for dry air.

This last assumption may induce significant errors in the region around 4 µm, which is used for various observations (e.g., Refs. 11–16), where the Earth’s atmospheric absorption is largely due to N$_2$ continuum with a weaker contribution of the CO$_2$ far line wings. Indeed, Ref. 17 shows that, with respect to N$_2$–N$_2$ (or N$_2$–air) collisions, N$_2$–H$_2$O interactions considerably enhance the collision-induced absorption in the fundamental band of N$_2$ (a factor of nearly ten on the integrated band area). A similar result is obtained for the high frequency wing of the CO$_2$ ν$_3$ band, where the binary absorption coefficient for CO$_2$–H$_2$O is, around 2500 cm$^{-1}$, about one order of magnitude larger than that for CO$_2$–N$_2$. As can thus be expected (and is demonstrated in this paper), significant errors in computations of atmospheric spectra are induced by neglecting the effect of collisions with water vapor on the continua between roughly 3.6 and 4.2 µm. Unfortunately, there is no model so far and the (very few) measured data remain insufficient for atmospheric spectra calculations. Indeed, they were all obtained above 50°C and provide no reliable information on the temperature dependence. This results

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from the optical thicknesses attainable in laboratory experiments, which are limited, for the considered spectral region, by both the path lengths of the cells and the H₂O saturation pressure. Indeed, while very long optical paths can be obtained using high finesse cavities and cavity enhanced absorption spectroscopy (CEAS) or cavity ringdown spectroscopy (CRDS) techniques, the wavelengths that can be studied remain practically limited to below ≈2 μm due to mirror technology limits. These two constraints make laboratory experiments below ≈300 K extremely difficult if not infeasible. Using theoretical calculations to complete the available experimental information is thus, today, the only solution.

The present paper tests the ability of some theoretical models to predict the CO₂–H₂O and N₂–H₂O continua near 4 μm by comparing computed results with the available measurements. This is a first step before producing data at temperatures relevant for the Earth’s atmosphere and testing them by comparisons between measured and computed atmospheric spectra, which will be the subject of a future work. For the predictions, rigorous quantum mechanical approaches cannot be used for the considered molecular systems since they are far too complex. Hence, we here mostly use Classical Molecular Dynamics Simulations (CMDSs) with which very satisfactory agreements with measured values are obtained for both CO₂ and N₂ in H₂O vapor, opening the route to more extensive temperature-dependent predictions. The remainder of this paper is divided into four parts. Section II is devoted to the high frequency wing of the H₂O-broadened CO₂ v₃ band. It describes the theoretical approach and its input data and presents comparisons between calculated and experimental results. Similarly, the methods used for computations of the H₂O-induced absorption by N₂ in the fundamental band and comparisons between predictions and measurements are presented in Sec. III. The consequences of humidity on the atmospheric absorptions by CO₂ and N₂ around 4 μm are then simulated and discussed in Sec. IV before some concluding remarks and directions for future studies (Sec. V).

II. THE H₂O-BROADENED HIGH FREQUENCY WING OF THE CO₂ v₃ BAND

A. Classical molecular dynamics simulations and input data

The binary molecular absorption coefficient of CO₂ colliding with water vapor in the region of the v₃ band was calculated using a combination of the methods described in Refs. 20–22, as explained below.

1. Molecular orientations and positions

In Refs. 18 and 19, the purely binary CO₂–H₂O density-normalized absorption coefficient in the region beyond the v₃ band (2400-2600 cm⁻¹) was experimentally determined. For this, the contributions of local CO₂ and H₂O lines as well as those of the CO₂-broadened v₃ wing and of the water-vapor continuum were subtracted from measured spectra. The resulting sets of values deduced from measurements for various mixtures were then divided by the product of the corresponding H₂O and CO₂ densities and averaged. This exercise provides a binary absorption, normalized to H₂O and CO₂ partial densities of 1 amagat (Am, with 1 Am = 2.69 × 10¹⁹ molecule/cm³), that results only from interac-

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3. Absorption spectrum

Finally, the spectrum was computed from the Fourier transform of the full dipole ACF, multiplied by the proper radiative factor, shifted by the CO\textsubscript{2} \nu\textsubscript{3} vibrational frequency (2349 cm\textsuperscript{-1}) and scaled by the detailed balance correction \exp(2\pi\Delta\gamma/2k_B T), where \Delta\gamma is the distance from the band center. Following Ref. 22, the minor but not fully negligible contributions from the \nu\textsubscript{1} band of \textsuperscript{13}CO\textsubscript{2} and the \nu\textsubscript{3} + \nu\textsubscript{2} - \nu\textsubscript{2} band of \textsuperscript{12}CO\textsubscript{2} were included in the same way.

B. Comparison with measured values

Measured binary absorption coefficients (normalized by the product of the CO\textsubscript{2} and collision partner densities) beyond the band head of the \textsuperscript{12}CO\textsubscript{2} \nu\textsubscript{3} band for pure CO\textsubscript{2} and CO\textsubscript{2} in H\textsubscript{2}O are compared in Fig. 1 with the associated CMDS results from Ref. 22 (in which CO\textsubscript{2}--CO\textsubscript{2} interactions were of course taken into account) and the present work, respectively. As can be seen, the computations do quite well predict the magnitude and shape of both continua, despite that no correction (and the present work, respectively. As can be seen, the computations do quite well predict the magnitude and shape of both continua, despite that no parameter was adjusted. In particular, the fact that CO\textsubscript{2}--CO\textsubscript{2} collisions significantly enhance the absorption with respect to CO\textsubscript{2} collisions, with a ratio that increases with the detuning from the band center (at 2349 cm\textsuperscript{-1}), is reproduced. Note that although a large number of molecules were treated in the CMDS, the calculated results (Fig. 1) still carry a significant “noise.” This results from the fact that the predictions in this region, of very weak absorption with respect to that near the \nu\textsubscript{3} band center, are extremely sensitive to the exhaustivity with which the phase space is spanned and sampled. It is worth mentioning that the calculation of the H\textsubscript{2}O-broadened CO\textsubscript{2} far wing in Fig. 1 is the first one ever made. Considering the extreme complexity of the problem, the results obtained are, in our opinion, very satisfactory, although the difference between the predictions and measurements for CO\textsubscript{2} in H\textsubscript{2}O increases with frequency and the distance from band center. Concerning this increase, we have no clear explanation, but it may come from the intermolecular potential since the calculated values in the far band wings are very sensitive to details of the description of collisions at short time (and thus distance) scales.

Since the full dipole involves both an intrinsic, coming from the asymmetric vibration, and an interaction-induced component, its ACF results from the addition of a purely intrinsic \langle \vec{\mu}(t) \cdot \vec{\mu}(0) \rangle, a purely induced \langle \vec{\mu}(t) \cdot \vec{\mu}(0) \rangle, and a cross \langle \vec{\mu}(t) \cdot \vec{\mu}(0) + \vec{\mu}(t) \cdot \vec{\mu}(0) \rangle term. Figure 2 presents their respective contributions, denoted as PP, II, and PI + IP. This shows that, for CO\textsubscript{2}--H\textsubscript{2}O, the purely induced term is practically negligible (~4\% of the total) while the cross term (intra-collisional interference) is not (~20\% of the total), a situation close to that for pure CO\textsubscript{2}.22

III. THE N\textsubscript{2} FUNDAMENTAL BAND INDUCED BY COLLISIONS WITH H\textsubscript{2}O

A. Classical molecular dynamics simulations and input data

The binary absorption coefficient of N\textsubscript{2} colliding with H\textsubscript{2}O in the region of the fundamental band was calculated using a combination of the methods described in Refs. 20, 21, 27, and 38, as explained below.

1. Molecular orientations and positions

The molecular orientations and positions were obtained as described in Sec. II A 1 by replacing CO\textsubscript{2} by N\textsubscript{2} and setting the temperature to 352 K, which is one of the experiments.17 The method used and the N\textsubscript{2}--H\textsubscript{2}O intermolecular potential (including Coulombic, repulsive, and dispersive forces) retained are described in Ref. 21. As done for CO\textsubscript{2} (cf. Sec. II A 1), N\textsubscript{2} and H\textsubscript{2}O densities of 1 Am were used and the N\textsubscript{2}--N\textsubscript{2}
and H₂O–H₂O potentials were set to zero since Ref. 17 provides experimental values of the purely binary and density normalized contribution to the absorption.

2. Dipole moments

The dipole moment induced in colliding N₂–H₂O pairs, that leads to absorption in the fundamental band of N₂, was computed from knowledge of the positions and orientations of the molecules following the method described in Refs. 27 and 38. For this, we limited the induction terms to those associated with the following: (i) The isotropic and anisotropic polarizabilities of N₂ ((ν = 0) αN₂|ν = 1) = 0.375 a.u. and (ν = 0) γN₂|ν = 1) = 0.428 a.u.38 in the field of the static dipole of H₂O ((ν = 0) μH₂O|ν = 0) = 0.73 a.u.; see Ref. 30 and those therein) which is carried by the vector in between the two O–H bonds. (ii) The static isotropic polarizability of H₂O, (ν = 0|αH₂O|ν = 0) = 9.9 a.u. (see Sec. II A 2), in the electric fields of the N₂ quadrupole and hexadecapole, (ν = 0|θN₂|ν = 1) = 0.0583 a.u. and (ν = 0|ΦN₂|ν = 1) = −0.158 a.u.38 Other terms,35 such as those induced by the anisotropic polarizability of H₂O (γH₂O) in the fields of the N₂ quadrupole and hexadecapole, have been neglected because (ν = 0|γH₂O|ν = 0) is very small as mentioned in Sec. II A 2. In fact, tests show that the computed collision-induced absorption (CIA) is strongly dominated by the contributions associated with αN₂ and γN₂ in the field of μH₂O. These represent 80% of the computed integrated area of the CIA band, thanks to the very large water vapor dipole and the broad range of intermolecular distances over which this induction mechanism is efficient.

3. Absorption spectrum

Finally, the spectrum was computed27 from the Fourier transform of the full dipole ACF, multiplied by the proper radiative factor, shifted by the N₂ vibrational frequency, and scaled by the detailed balance correction exp(2πcΔσ/2kB T), where Δσ is the distance from the band center (2329 cm⁻¹).

B. Isotropic quantum model and K₂ line shape

CIA spectra have also been calculated for the N₂–H₂O pair in the region of the nitrogen fundamental band by using the model of Ref. 39, which is much simpler and less expensive than the CMDS. We here give only the relevant information on the model, the reader being invited to consult Refs. 40–43 for more details. The approach used is based on the so-called isotropic approximation which neglects the effect of the intermolecular potential anisotropy and thus assumes that the molecules rotate freely at all times. This is the most severe weakness of the model but it has the considerable advantage to enable us to write the absorption in terms of a superposition of independent components. Indeed, the binary absorption coefficient (i.e., the absorption normalized by the product of the densities of the two molecular species, in cm⁻¹/Am²) at wave number σ and temperature T is then given by

$$\alpha(\sigma) = \frac{4\sigma^2}{3} \alpha_0 \eta_0^2 \sum_{i_1,i_2} \sum_{f_1,f_2} S_k(T, i_1, f_1, i_2, f_2) \times G_k(T, \sigma - \sigma_{i_1i_2} - \sigma_{f_1f_2}).$$

where α₀ is the fine structure constant, a₀ is the Bohr radius, and n₀ is the number density at standard temperature and pressure (i.e., at 1 Am). The index k identifies the various components of the induced dipole,35 S_k is the corresponding strength for the (i_1, i_2) → (f_1, f_2) transition, where i and f denote the initial and final states and the indices 1 and 2 refer to N₂ and H₂O, respectively. Finally, G_k(T, σ - σ_{i_1i_2} - σ_{f_1f_2}) is a normalized profile discussed below.

As mentioned above, for the N₂–H₂O pair, the dominant induction mechanisms are the dipole-induced dipole components. Among these, an example is given by the dipole arising from the isotropic polarizability of N₂ (αN₂) in the field of the H₂O dipole (μH₂O). The corresponding component is associated with anisotropic polarizabilities and the electric quadrupole and hexadecapole; see Sec. III A 2, and the associated positions σ_{i_1f_1} = σ_{v=0,j=0} of the transitions, can be easily calculated for all needed values of the rotational quantum numbers J and J’. They have analytical expressions43 in terms of the vibrational matrix elements ⟨ν = 0|ν = 1⟩, of the vibrational energy and of the rotational constants. For H₂O, with rotational quantum numbers J, K_a, and K_c, while the ⟨ν = 0, J, K_a, K_c|0|ν = 0, J’, K_a’, K_c’⟩ = αH₂OβJ,J’|0⟩δK,K’|K,K’⟩ is trivial, the terms (ν = 0, J, K_a, K_c|μH₂O|ν = 0, J’, K_a’, K_c’) cannot be easily computed. However, since they are directly involved in the integrated intensities of the absorption lines of the rotational band, they were deduced from the associated values provided by the HITRAN2012 database.44 The latter also gives the positions σ_{i_2f_2} = σ_{v=0,j=0}K_a,K_c,K_a’ K_c’ and the energies of the levels for the calculation of the relative populations ρ_{v=0,J,K_a,K_c}(T).

Note that, when the N₂–H₂O pair absorbs a photon and N₂ makes a vibrational transition, H₂O can be simultaneously deexcited rotationally. This corresponds, for this molecule, to a dipole transition at a negative frequency for which there is no data in HITRAN. However, since one has σ_{i_2f_2} = −σ_{i_1f_1} and (f_2|μH₂O|i_2) = (2I_{J_0} + 1)/(2I_{J_0} + 1) (i_2|μH₂O|i_2), the needed parameters for the transition f_2 ↔ i_2 can be deduced from those for the i_2 ↔ f_2 line which is present in HITRAN.

Concerning the line shape, many models have been proposed, the most widely used being that of Birnbaum and Cohen.45 We have preferred to retain here the so-called K₂ line shape46 because it can be completely determined a priori. G_k(T,Δσ), which is area normalized, is then given by

$$G_k(T, \Delta\sigma) = \frac{2}{3\pi\eta_k(T)} \left[ \frac{\Delta\sigma}{\eta_k(T)} \right]^2 \left[ 1 + \exp \left( -\frac{\hbar c \Delta\sigma}{k_B T} \right) \right]^{-1} \times K_2 \left[ \Delta\sigma/\eta_k(T) \right],$$

where K₂ denotes a modified Bessel function of the second kind and η_k(T) is a temperature-dependent parameter. The latter can be determined46 from the chosen isotropic intermolecular potential and dipole component k (i.e., λ_1, λ_2, Λ, and λ). The associated values at 350 K, calculated for a 12-6
TABLE I. Computed values (in cm$^{-1}$) of the $\eta_\phi$ parameters of the $K_2$ line shape at 350 K. See Sec. III A 2 for the definition and retained values of the tensors and Ref. 35 for the associated sets of $A_1$, $A_2$, $\Lambda$, $L$ (indices 1 and 2 refer to N$_2$ and H$_2$O, respectively).

| Tensors | $\eta_\phi$ |
|---------|-------------|
| $\phi_{N_2}$, $\mu_{N_2}$ | (0.1, 1.2) | 12.1 |
| $\gamma_{N_2}$, $\mu_{N_2}$ | (2.1, 1.2), (2.1, 2.2), (2.1, 3.2) | 12.1 |
| $\theta_{N_2}$, $\mu_{N_2}$ | (2.0, 2.3) | 18.0 |
| $\phi_{N_2}$, $\mu_{N_2}$ | (4.0, 4.5) | 26.4 |

Lennard-Jones potential (with $\varepsilon = 97$ K and $\sigma = 3.28$ Å, consistent with the angular average of that used for the CMDS), are given in Table I for all retained components of the induced dipoles.

In summary, as for the CMDS of Sec. III A, this model contains no adjustable parameter and enables calculations of the CIA spectra for N$_2$–H$_2$O mixtures in the region of the N$_2$ fundamental band.

C. Comparisons with measured values

Measured collision-induced binary absorption coefficients (normalized by the product of the N$_2$ and collision partner densities) in the fundamental band of N$_2$ for pure N$_2$ and N$_2$ in H$_2$O are compared in the main panel of Fig. 3 with the associated CMDS results from Ref. 38 and the present work, respectively. As can be seen, the computations do well predict the magnitude and shape (except for the central region of the N$_2$–H$_2$O CIA which is discussed at the end of this section) of both continua, despite the fact that no parameter was adjusted. Just as experiments, calculations show that N$_2$–H$_2$O collisions significantly enhance the CIA with respect to N$_2$–N$_2$ interactions, with a ratio that strongly increases when going toward the wings. A good agreement is obtained for the integrated CIA areas, with measured values of $5.1 \times 10^{-3}$ cm$^{-2}$/Am$^2$ for N$_2$–H$_2$O and $3.7 \times 10^{-4}$ cm$^{-2}$/Am$^2$ for N$_2$–N$_2$ with associated CMDS predictions of $5.1 \times 10^{-3}$ cm$^{-2}$/Am$^2$ and $3.2 \times 10^{-4}$ cm$^{-2}$/Am$^2$, respectively. Finally, the inset of Fig. 3 demonstrates that CMDS predictions for N$_2$–H$_2$O at various temperatures are largely within the experimental uncertainties of such difficult experiments.

A comparison between experiments and theory for the N$_2$–H$_2$O CIA now including the predictions of the isotropic quantum model with the $K_2$ line shape is shown in the main panel of Fig. 4 (similar comparisons for pure N$_2$ can be found in Refs. 43 and 49). As can be seen, this approach significantly underestimates the absorption with an error of a factor of nearly two on the integrated CIA area. This is consistent with the results of previous similar calculations for N$_2$–H$_2$O, but in opposition with the good agreement between experiments and predictions obtained in pure N$_2$ and N$_2$ in O$_2$. These results can be explained by the use of the isotropic approximation in which one assumes that the colliding molecules interact through an isotropic intermolecular potential (which drives the translational motion while the molecules rotate freely). Indeed, for pure N$_2$ around room temperature, it was shown that this approximation is very reasonable, thanks to the moderate anisotropy of N$_2$–N$_2$ interactions, explaining the quality of the predictions in Refs. 43 and 49. For N$_2$–H$_2$O collisions, a significantly different situation results from the very strong and anisotropic long-range quadrupole-dipole interaction. In this case, the isotropic approximation leads to a significant underestimation of the CIA (as also predicted for pure CO, where quadrupole-quadrupole interactions are strong). This is demonstrated by the inset in Fig. 4 which shows that the CMDS results calculated assuming isotropic interactions are about twice smaller than those (shown in Fig. 3 and reproduced in the main panel of Fig. 4) obtained when the anisotropy is taken into account. Furthermore, the integrated CIA area of these isotropic CMDS predictions ($3.32 \times 10^{-3}$ cm$^{-2}$/Am$^2$) is also perfectly consistent with that ($3.23 \times 10^{-3}$ cm$^{-2}$/Am$^2$).
obtained with the isotropic quantum model with the K\textsubscript{2} line shape (shown in the inset).

The fact that CMDSSs lead to a N\textsubscript{2}–H\textsubscript{2}O CIA carrying a strong Q branch at its center (Figs. 3 and 4) is explained by the libration motion included in the classical rotation of H\textsubscript{2}O. This motion leads, through the polarization of N\textsubscript{2}, to an induced dipole that also librates. The Fourier transform of its ACF thus leads to a peak at frequency zero (that is then shifted to the frequency of the N\textsubscript{2} fundamental vibration; see Sec. III A 3) which is broadened due to the limited life time of the induced dipole. In the real (quantum) world, the situation is different and the Q transitions allowed by the H\textsubscript{2}O static dipole are not centered at frequency zero. Indeed, Fig. 5 shows that the relevant transitions, extracted from the HITRAN2012 database, are significantly shifted from \(\sigma = 0\) cm\textsuperscript{-1}. The most intense ones peak below –20 cm\textsuperscript{-1} and above +20 cm\textsuperscript{-1} and one can thus expect that the N\textsubscript{2}–H\textsubscript{2}O CIA should not carry a peak at its center but, rather, a dip (as shown by the results of the isotropic quantum model with the K\textsubscript{2} line shape in Fig. 4).

In order to semi-empirically improve the CMDS predictions, the following procedure was applied: (i) A fit of the CMDS-calculated CIA in Fig. 3 was first made using three Lorentzians in order to represent the narrow central peak and the broader ones on its low and high frequency sides. Figure 6(a) shows that this leads to a quite satisfactory fit. (ii) In a second step, the Q branch was removed from the original CMDS spectrum by subtracting the corresponding Lorentzian, leading to the “Q-branch free” CIA shown by the blue line in Fig. 6(a) (the small peak in the central trough is due to a not fully perfect removal of the original Q branch). (iii) Finally, a more realistic contribution of the Q transitions of H\textsubscript{2}O was calculated and added to the “Q-branch free” spectrum. It was obtained by simply summing of the transitions in Fig. 5, each having a Lorentzian shape. The half widths at half maximum used for this have been fixed to the value (23.3 cm\textsuperscript{-1}) obtained, in step (i), from the Lorentzian fit of the original Q branch. The overall area of the result was scaled to that (24.5 cm\textsuperscript{-1}) retrieved from the same fit. The spectrum obtained from this exercise is compared with the measured one in Fig. 6(b). As can be seen, the agreement with the measurement is now quite good, although the predicted central trough between 2290 and 2370 cm\textsuperscript{-1} (which we believe is true) does not appear in the measurements. A possible explanation for this difference may be the perturbative absorption by the \(v_3\) band of traces of CO\textsubscript{2} present in the measured spectra\textsuperscript{17} from which the N\textsubscript{2}–H\textsubscript{2}O CIA was retrieved. Note that Fig. 6(b) presents not only a satisfactory prediction of the N\textsubscript{2}–H\textsubscript{2}O CIA spectrum but the very first one of the kind.

It is worth mentioning that the half-width obtained from the Lorentzian fit of the Q branch (23.3 cm\textsuperscript{-1}) is in very good agreement with that (24.5 cm\textsuperscript{-1}) of the K\textsubscript{2} line shape calculated for the relevant induced-dipole component (for which \(\eta = 12.1\); see Table I). This agreement, together with the facts that K\textsubscript{2} line shape turns out to be close to Lorentzian and that the curves in the inset of Fig. 4 have practically the same

FIG. 5. Distribution of the intensities [i.e., \(\rho_{J,K_a,K_c}(T)\) \((v = 0, J, K'_a, K'_c)\mid \rho_{\text{H}_2\text{O}}(v = 0, J, K_a, K_c)\)] of the \((v = 0, J, K'_a, K'_c) \leftarrow (v = 0, J, K_a, K_c)\) rotational Q transitions of H\textsubscript{2}O obtained from the HITRAN2012 database. See the end of the 2nd paragraph of Sec. III B for explanations on the transitions at negative frequencies.

FIG. 6. N\textsubscript{2}–H\textsubscript{2}O binary collision-induced absorption coefficients at 352 K. (a) The circles represent the raw CMDS-calculated results and the red line their fit (see text) by three Lorentzians. The blue line is what is left from the former after subtraction of the fitted Lorentzian Q-branch. (b) The blue circles are the measured values\textsuperscript{17} while the black and red lines denote the CMDS-computed CIA before and after the correction of the Q-branch (see text).
areas, further demonstrates the consistency of the CMDs and quantum models when both use the isotropic approximation.

Finally, the fact that the peak and area of the N₂–H₂O CIA are much larger than those for pure N₂ can be explained by considering the dominant induction mechanisms, which are associated with the polarizability of N₂ in the fields of the H₂O dipole and N₂ quadrupole, respectively. For instance, the ratio of the amplitudes of the associated contribution to the absorption resulting from the isotropic part of N₂ polarizability scales as \( \langle \sqrt{3} R \rangle [v = 0] / [\mu (\text{H}_2O) [v = 0] / [\Theta (\text{N}_2) [v = 0]]^2 \), where \( R \) is the intermolecular distance. This leads, with \( [v = 0] / [\mu (\text{H}_2O) [v = 0] = 0.73 \) a.u. (see Sec. III A 2) and \( [\Theta (\text{N}_2) [v = 0] = -1.13 \) a.u., \( 0.35 \) to a ratio of 0.28\( R^2 \) with \( R \) in atomic units. For a typical distance of 3.5 Å, this leads to a factor of about 12. This enhancement in the N₂–H₂O pair is further increased by the anisotropy of the intermolecular potential, whose effect on the CIA is larger for this system that for pure N₂, as discussed above. Finally, the fact that the N₂ spectrum induced by collisions with H₂O is much broader than when collisions with N₂ are involved (see Fig. 3) simply comes from the much larger spectral spreading of the H₂O transitions (resulting from the larger rotational constant).

IV. CONSEQUENCES FOR TRANSMISSIONS IN THE EARTH’S ATMOSPHERE

A. Simulations and data used

In order to evaluate the influence of humidity on atmospheric absorption near 4 μm, we have simulated transmission spectra representative of those that can be recorded using ground-based solar occultation measurements. For this, vertical profiles of temperature, \( T(z) \), and total pressure, \( p_{\text{Tot}}(z) \), representative of a standard tropical atmosphere\(^{55} \) were used [with temperatures of \( T(0 \text{ km}) = 300 \text{ K at ground level and of } T(17 \text{ km}) = 195 \text{ K at the tropopause}. The CO₂ and N₂ volume mixing ratios were set constant and equal to 4 \times 10^{-4} \) and 0.78, respectively, while standard vertical profiles\(^{55} \) were used for all other species except water vapor. For H₂O, three profiles were constructed, with no water vapor above the tropopause and values in the troposphere corresponding to constant percentages of humidity of 0%, 20%, and 100%. In other words, the H₂O mole fraction at altitude \( z < 17 \text{ km} \) is given by \( \chi (z) = A \times p_{\text{sat}}(T(z)) / p_{\text{tot}}(z) \) with \( A = 0.2, \) or 1.0, where \( p_{\text{sat}}(T) \) is the saturation pressure at temperature \( T \). In the 100% humidity case, the H₂O fraction at ground level is 3.5% and the total precipitable water inside a vertical column is 6.7 g/cm² (i.e., 67 mm).

The atmospheric absorbance integrated (by steps of 1 km) over a vertical column was computed in the 2000-2800 cm⁻¹ spectral region by taking the contributions of CO₂, N₂, H₂O, N₂O, CH₄, and CO into account. The needed line positions and integrated intensities were all taken from the HITRAN2012 database.\(^{44} \) Voigt line shapes were retained with a cutoff 3 cm⁻¹ away from line-centers, except for CO₂ transitions for which the corrective \( \chi \) factors of Refs. 56 and 18 were applied for CO₂-(dry air) and CO₂–H₂O collisions, respectively. For all species, dry air line-broadening coefficient from HITRAN2102 was used, except for CO₂ for which the broadening by H₂O was taken into account using the data of Ref. 57. The continuum absorption of water vapor was disregarded. This was done for simplicity, but also because its contribution between 2200 and 2800 cm⁻¹ is relatively small\(^{10,54} \) and still uncertain (see Secs. 3.5.4 and 4.3 of Ref. 58). For the N₂ CIA in dry air, a refined version of the software+data package of Ref. 59, now extending up to 2830 cm⁻¹ and down to 1930 cm⁻¹, was created by using the data of Ref. 47. For the N₂–H₂O CIA, a simple temperature-dependent model was constructed, between 1930 and 2830 cm⁻¹, from CMDs-calculated values at 250, 300, and 350 K. The raw CMDs were used and the semi-empirical correction discussed at the end of Sec. III C was not applied. As seen from Fig. 3, this gives a good enough (for the present study) representation of this CIA, except in the central region of the band. Fortunately, this is of no consequences for the present simulations since the atmospheric transmission is negligible in this region (see below) thanks to the very strong absorption by CO₂. More refined data for the N₂–H₂O CIA will be constructed and used in a future study for comparisons between calculated and measured atmospheric spectra.

B. Results and discussion

The computed atmospheric high-resolution absorbances (integrated over a vertical column) of CO₂ and N₂ around 4.3 μm are plotted in Fig. 7 for the fully dry and fully humid cases. As can be seen, humidity does have a significant influence, as could be expected from the results of Secs. II and III. In order to be more specific, let us denote by \( A^D(\sigma) \) and \( A^H(\sigma) \) the dry and humid atmospheric absorbances in Fig. 7, with which the difference between the associated transmissions for an airmass of \( M \) is exp \[ -A^D(\sigma) M \] – exp \[ -A^H(\sigma) M \]. This difference would be detectable in measurements provided that it is greater than a few 10⁻². This requires simultaneously have \[ A^H(\sigma) – A^D(\sigma) \] \( M \) greater than a few 10⁻² and exp \[ -A^D(\sigma) M \] not too small. It can easily be concluded from Fig. 7 that, for airmasses between 1 and 10, there are several

![Fig. 7. Computed CO₂ and N₂ absorbances, integrated over a vertical atmospheric column. The black and magenta lines are for N₂ in atmospheres with 0% and 100% humidity (see Sec. IV A), respectively, while the corresponding results for CO₂ are the blue and red lines.](image-url)
regions where the effects of humidity on atmospheric transmissions could be observable, as is confirmed later. Note that this statement applies to the N₂ contribution and not to that of the CO₂ band wings where the effects are too small and completely masked by the N₂ absorption.

The differences in Fig. 7 between the absorbances for the dry and humid atmospheres in the N₂ CIA and the wing of the CO₂ ν₃ band can be quantitatively explained as follows. In these regions, the absorbance at wave number σ for species X is given by

\[
A_X(\sigma) = \int_0^\infty dz \left[ n_X(z)n_{air}(z)C_X \cdot air[\sigma, T(z)] + n_X(z)n_{H₂O}(z)C_X \cdot H₂O[\sigma, T(z)] \right],
\]

where \(T(z)\) and \(n_Y(z)\) denote the temperature and the density of species Y (=N₂, CO₂, air, or H₂O) at altitude z, respectively, while \(C_{X-Y}(\sigma, T)\) is the normalized (i.e., divided by the product of the densities of X and Y) binary absorption coefficient due to species X colliding with Y (e.g., Figs. 1 and 3). If one assumes, for simplicity, that the latter is independent on temperature (quite reasonable), the relative difference between the humid and dry atmospheres absorbances for species X is

\[
\frac{A_{X-H₂O}^D(\sigma) - A_{X-H₂O}^D(\sigma)}{A_{X-H₂O}^D(\sigma)} = \frac{C_X \cdot H₂O(\sigma)}{C_X \cdot air(\sigma)} \int_0^\infty n_X(z)dz - n_{H₂O}(z)dz \int \frac{n_X(z)n_{H₂O}(z)dz}{n_X(z)n_{air}(z)dz}.
\]

For the tropical atmosphere described in Sec. IV A, the (last) ratio of integrated densities products in Eq. (4) is equal to 0.016 in the 100% humidity case. It is then quite easy to see that the effects of humidity shown in Fig. 7 are consistent with the difference between the pure N₂ and N₂–H₂O CIAs in Fig. 3 and the fact that the H₂O-broadened far wing of the CO₂ ν₃ band is much larger than that for CO₂ in dry air. For a factor of ten between \(C_X \cdot H₂O(\sigma, T)\) and \(C_X \cdot air(\sigma, T)\), for instance, the relative error on the absorbance induced by neglecting the effect of humidity is 16%.

Figure 8 displays synthetic atmospheric transmissions spectra for various values of the airmass (i.e., of the solar zenith angle in ground-based solar-occultation measurements) and humidity. It enables us to compare results obtained with and without the inclusion of the influence of water vapor on the spectra of CO₂ and N₂. As can be seen, this influence is often obvious and likely detectable in adapted measurements, although there are parts of the spectrum where it is masked by the absorption by other gases. It is the case on the low and high frequency sides of the displayed window where the absorption is dominated by lines of H₂O, while N₂O is responsible for the P and R branches around 2469 and 2560 cm⁻¹. Finally, analysis shows that, as predicted from Fig. 7, the influence of H₂O on the wings of the CO₂ bands is too small or masked to be detectable and that the differences between the transmissions in Fig. 8 are due to the N₂ CIA only. Checking these predictions using real atmospheric spectra will be our next step on this research topic.

V. CONCLUSION AND DIRECTIONS FOR FUTURE STUDIES

The results presented in this paper show that classical molecular dynamics simulations can be reliably used for predictions of the effects of collisions with water vapor on the absorption in both the wings of the CO₂ ν₃ band and the fundamental collision-induced band of N₂ (provided that, for N₂, the simple to implement correction described at the end of Sec. III C is made). This opens the route for the creation of relevant and reliable data at temperatures of the Earth’s atmosphere for which laboratory measurements are very difficult, if not impossible, to carry. This is of practical interest since simulations show that neglecting the effect of humidity in computations of atmospheric absorption by N₂ around 4 µm leads to a significant overestimation of the transmission. A study, in which predictions and the available measurements will be used to construct the best possible model, will be the subject of a future work, together with its subsequent test by comparisons between measured and calculated spectra of the Earth’s atmosphere. Note that while we have shown that data on the absorption continua of CO₂–H₂O mixtures are not needed for the Earth’s atmosphere (at least near 4 µm),
they are of crucial importance for planetology research. It is the case for studies of the current or past climates of several planets with atmospheres containing significant amounts of both CO and H₂O (e.g., Refs. 61–63 and those therein), for which including both the effects of collisions with H₂O on CO₂ absorption and of collisions with CO₂ on H₂O spectra is required.

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