ADVANCED QUANTUM PHYSICS
Duration : 3 hours

Infrared spectrum of carbon dioxide

In 1896, physicist Svante Arrhenius published an article highlighting the climatic impact of carbon dioxide (CO_2), whose vibrations absorb part of the black body radiation emitted by the Earth. A few years later, however, his theory was challenged by Knut Ångström, who argued that the atmosphere is already completely opaque to the infrared wavelength absorbed by CO_2. A variant of this argument is still used today by climate change deniers. The argument put forward is that the concentration of CO_2 already present in the atmosphere is sufficient to absorb all the radiation emitted by the Earth at the vibration frequency of the molecule, so that a further increase in CO_2 will have no consequence on the climate. While this claim is obviously erroneous, its refutation requires the use of a radiative transfer model of the atmosphere based on precise knowledge of the shape of the infrared absorption spectrum of CO_2. This is the spectrum that will be studied in the following.

The interaction between a CO_2 molecule and the oscillating electric field $\vec{\mathcal{E}}(t) = \vec{\mathcal{E}}_0 \cos \omega t$ associated with an infrared radiation of angular frequency ω can be treated using time-dependent perturbation theory. It is recalled that this interaction can give rise to a transition between an initial state $|i\rangle$ and a final state $|f\rangle$, provided that the frequency ω is very close to the transition frequency $\omega_{fi} = (E_f - E_i)/\hbar$. The transition probability can then be written as

$$\mathcal{P}_{i \to f} \propto |\langle f| \hat{\vec{\mu}} \cdot \vec{\mathcal{E}}_0 |i\rangle|^2, \tag{1}$$

where $\hat{\vec{\mu}}$ is the electric dipole operator of the molecule.

Exercise 1
CO_2 Vibration modes

CO_2 is a linear triatomic molecule composed of two oxygen atoms (isotope $^{16}_{8}O$) located on either side of the central carbon atom (isotope $^{12}_{6}C$), as shown in Fig. 1(a). Since the nuclear spins of the considered isotopes are zero and the molecule is assumed to always be in its electronic ground state, only the motion of the nuclei will be taken into account. The center of mass of the molecule, whose motion is irrelevant for infrared absorption, will be assumed to be stationary and positioned at the origin of the coordinate system. Finally, for this and the following exercise, the molecule will be assumed to be oriented along the z axis.
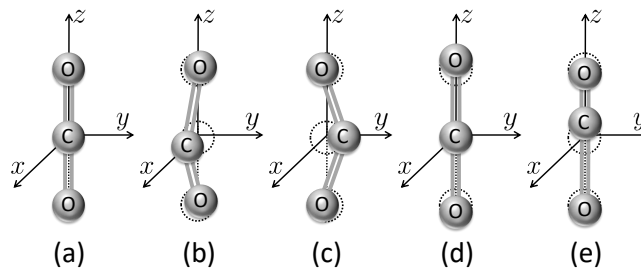

FIGURE 1 – (a) Equilibrium structure of the CO_2 molecule. (b) Bending mode along the x axis, with angular frequency ω_1. (c) Bending mode along the y axis, with angular frequency ω_1. (d) Symmetric stretching mode (along the z axis), with angular frequency ω_2. (e) Antisymmetric stretching mode (along the z axis), with angular frequency ω_3.

Under these assumptions, the motion of the nuclei can be decomposed into four independent *vibrational modes*, shown in Fig. 1, each described using a harmonic oscillator. First, there are two bending modes : one along the x axis (b) and the other along the y axis (c), both associated with a two-dimensional harmonic oscillator of angular frequency ω_1. Second, there are two stretching modes, in which the nuclei move along the z axis : the symmetric stretching mode (d), where the carbon nucleus remains stationary while the two oxygen nuclei oscillate symmetrically about the origin. This mode

is described as a one-dimensional harmonic oscillator with angular frequency ω_2. Finally, there is the antisymmetric stretching mode (e), in which the carbon nucleus moves in the opposite direction to the two oxygen nuclei. This mode is described as a one-dimensional harmonic oscillator with angular frequency ω_3. The vibrational frequencies are given as $\omega_1/(2\pi) \approx 20.0$ THz, $\omega_2/(2\pi) \approx 40.1$ THz, and $\omega_3/(2\pi) \approx 70.4$ THz, where 1 THz $= 10^{12}$ Hz.

1. We consider initially only the antisymmetric stretching mode, with angular frequency ω_3. The stretching is characterized by the real quantity $\zeta = z_c - (z_1 + z_2)/2$, where z_c is the coordinate of the carbon nucleus, and z_1 and z_2 are the coordinates of the oxygen nuclei. We work within the state space $\mathcal{E}_3 = \mathcal{L}^2(\mathbb{R})$ and introduce the annihilation operator

$$\hat{a}_3 = \frac{1}{\sqrt{2}} \left(\sqrt{\frac{m_r \omega_3}{\hbar}} \hat{\zeta} + i \frac{\hat{p}_\zeta}{\sqrt{m_r \hbar \omega_3}} \right), \tag{2}$$

where $\hat{\zeta}$ and $\hat{p}_\zeta$ are the position and momentum observables. The quantity $m_r = 2 m_O m_C / (2 m_O + m_C)$ is the reduced mass, with m_O and m_C being the masses of the oxygen and carbon nuclei, respectively. The Hamiltonian associated with this vibrational mode can then be written as :

$$\hat{H}_3 = \hbar \omega_3 \left(\hat{a}_3^\dagger \hat{a}_3 + \frac{\hat{I}}{2} \right), \tag{3}$$

where $\hat{I}$ is the identity operator. The eigenstates of $\hat{H}_3$ will be denoted as $|n\rangle$, with $n \in \mathbb{N}$. Recall the values and degeneracies of the energy levels.

2. Using a numerical application, show that for this mode it is justified to consider that only the ground state $|0\rangle$ is populated at the temperature of the Earth's atmosphere ($T = 288$ K).

3. Show that the dipole operator associated with the antisymmetric stretching mode reads

$$\hat{\vec{\mu}} = \mu_3 \left(\hat{a}_3 + \hat{a}_3^\dagger \right) \vec{u}_z, \tag{4}$$

where $\vec{u}_z$ is a unit vector along the z axis. Express the real quantity μ_3 in terms of the problem's parameters and the partial charge δq carried by the carbon atom.

4. Using eq. 1, identify the only transition associated with the antisymmetric stretching mode that can be excited by the infrared field and provide the corresponding transition frequency.

5. We now consider the symmetric stretching mode. What can be said about the dipole observable $\hat{\vec{\mu}}$ in this case ?

6. Comment Fig. 2, which represents the infrared absorption spectrum of CO_2. Among the 4 vibration modes considered above, which are relevant in the context of the climate impact of CO_2 ?
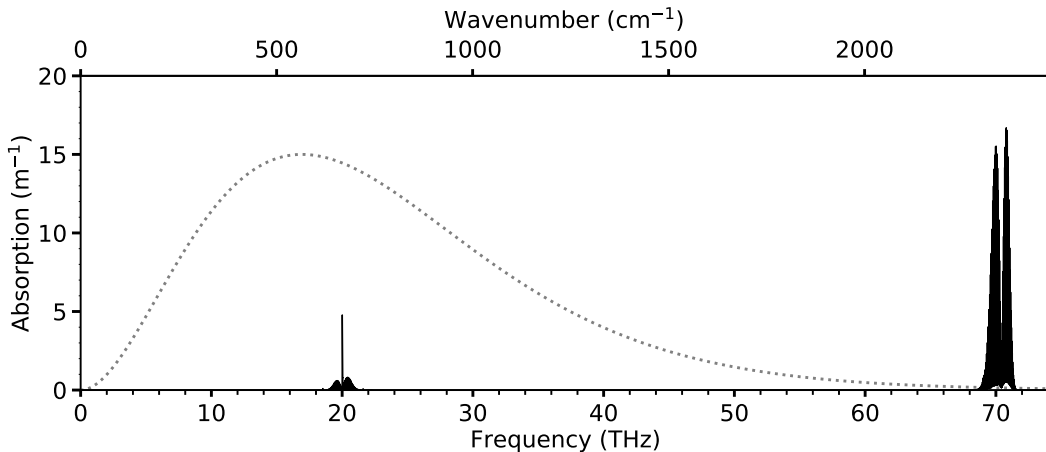

FIGURE 2 – Absorption spectrum of CO_2 in the mid-infrared range, for a CO_2 concentration of 426 ppm in air at atmospheric pressure and at a temperature of $T = 288$ K. The dashed line represents, in arbitrary units, the black body emission spectrum for $T = 288$ K.

7. It can be read from Fig. 2 that absorption α at angular frequency ω_1 is approximately 4.8 m^{-1}. Knowing that the resulting transmission after propagation over a distance L is given by $\exp(-\alpha L)$, deduce the value of L required for the photon transmission probability to be less than 10^{-6}. Comment on this result.

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Exercice 2

Fermi Resonance

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This exercise deals with the bending motion shown in Fig. 1(b) and (c).

1. Two-dimensional harmonic oscillator

Given the small value of the bending angle, we can assume that the nuclei move within horizontal planes. Let (x, y) represent the coordinates of the carbon nucleus relative to the projection of the two oxygen nuclei in the xy-plane. We introduce the observables $\hat{x}$ and $\hat{y}$ associated with these coordinates, as well as the corresponding momentum observables $\hat{p}_x$ and $\hat{p}_y$. Operator $\hat{a}_x$ (respectively $\hat{a}_y$) can then be constructed using an equation similar to eq. 2, by replacing ω_3 with ω_1, and substituting $\hat{\zeta}$ and $\hat{p}_\zeta$ with $\hat{x}$ and $\hat{p}_x$ (respectively $\hat{y}$ and $\hat{p}_y$). We work in the state space $\mathcal{E}_1 = \mathcal{L}^2(\mathbb{R}^2) = \mathcal{L}^2(\mathbb{R}) \otimes \mathcal{L}^2(\mathbb{R})$, and the Hamiltonian of the system is expressed as $\hat{H}_1 = \hat{H}_x + \hat{H}_y$, where $\hat{H}_x = \hbar\omega_1\left(\hat{a}_x^\dagger \hat{a}_x + \hat{I}/2\right)$ and $\hat{H}_y = \hbar\omega_1\left(\hat{a}_y^\dagger \hat{a}_y + \hat{I}/2\right)$.

1.1 Explain why $\hat{H}_x$ and $\hat{H}_y$ can be co-diagonalized, and show that the eigenvalues of $\hat{H}_1$ are $E_n = (n + 1)\hbar\omega_1$, with $n \in \mathbb{N}$. Specify the associated denegeracies.

1.2 Let us introduce operators $\hat{a}_\pm = (\hat{a}_x \mp i\hat{a}_y)/\sqrt{2}$, which commute with each other and, along with their adjoints, satisfy the usual commutation relations of annihilation and creation operators associated with a one-dimensional harmonic oscillator. Show that $\hat{H}_1 = \hbar\omega_1\left(\hat{N}_+ + \hat{N}_- + \hat{I}\right)$, where $\hat{N}_\pm = \hat{a}_\pm^\dagger \hat{a}_\pm$. Recover with this alternative method the eigenvalues of $\hat{H}_1$ and their degeneracies.

1.3 We note $\hat{K} = \hbar(\hat{N}_+ - \hat{N}_-)$ the projection of the angular momentum along the z-axis of the molecule. Explain the physical reason why $\hat{K}$ commutes with $\hat{H}_1$.

1.4 We consider the common eigenbasis of the ECOC $\{\hat{H}_1, \hat{K}\}$ for the eigenvalues $(n + 1)\hbar\omega_1$ and $k\hbar$, which will simply be denoted as $\{|n, k\rangle\}$ throughout the rest of this text. Show that $|n, k\rangle$ is an eigenvector of $\hat{N}_+$ and $\hat{N}_-$ for the eigenvalues n_+ and n_-, which will be expressed in terms of n and k.

1.5 Show that k is an integer with the same parity as n and belonging to the interval $[-n, n]$.

1.6 Show that $\hat{a}_\pm |n, k\rangle \propto |n - 1, k \mp 1\rangle$ and $\hat{a}_\pm^\dagger |n, k\rangle \propto |n + 1, k \pm 1\rangle$.

1.7 In the rest of this exercise, we assume that the infrared field is polarized along the x axis. We consider the Cartesian component along this axis of the dipole operator, $\hat{\mu}_x = \delta q\, \hat{x}$. Express $\hat{\mu}_x$ in terms of the operators $\hat{a}_\pm$ and their adjoints, and then show that if the system is initially in the state $|n, k\rangle$, the infrared field can induce a transition to final state $|n', k'\rangle$ only if $n' = n \pm 1$ and $k' = k \pm 1$.

We will say that the transition follows the selection rule $\Delta n = \pm 1$ and $\Delta k = \pm 1$.

2. Anharmonic coupling between vibrational modes

We are interested in the anharmonic coupling between the bending modes and the symmetric stretching mode, a coupling that is exacerbated by what is called a *Fermi resonance*. This results from the near-equality between $2\omega_1/(2\pi) = 40.0$ THz and $\omega_2/(2\pi) = 40.1$ THz. For simplicity, we will replace ω_2 by $2\omega_1$ in this part. Moreover, the antisymmetric stretching mode will not be considered, which amounts to working in the space $\mathcal{E}_1 \otimes \mathcal{E}_2 = \mathcal{L}^2(\mathbb{R}^2) \otimes \mathcal{L}^2(\mathbb{R})$. We will use the tensorial basis $\{|n_1, k; n_2\rangle = |n_1, k\rangle \otimes |n_2\rangle\}$, where $\{|n_1, k\rangle\}$ is the common eigenbasis of $\hat{H}_1$ and $\hat{K}$ introduced in the previous part (with $k \in \{-n_1, -n_1 + 2, \cdots, n_1\}$), and where $\{|n_2\rangle\}$ is the eigenbasis of the Hamiltonian $\hat{H}_2$ of the harmonic oscillator with frequency $\omega_2 = 2\omega_1$ associated with the symmetric stretching mode. The anharmonic coupling will be taken into account with an additional term $\hat{W}$ to be added to the unperturbed Hamiltonian $\hat{H}_1 + \hat{H}_2$. The effect of $\hat{W}$ will be treated at first order in time-independent perturbation theory. By symmetry, we will assume that all diagonal terms of the form $\langle n_1, k; n_2| \hat{W} |n_1, k; n_2\rangle$ are zero.

2.1 Write the action of $\hat{H}_1 + \hat{H}_2$ on $|n_1, k; n_2\rangle$, then express the energy of the first three levels in terms of $\hbar\omega_1$ (in the absence of perturbation). For each level, provide the vectors of the tensorial basis that generate the corresponding eigenspace.

2.2 By proceeding as in question 2 of exercise 1, show that the probability of finding the system in the first excited state is not completely negligible.

2.3 Explain why operator $\hat{K}$ commutes with $\hat{W}$.

2.4 Calculate $\langle n_1, k; n_2 | [\hat{W}, \hat{K}] | n_1', k'; n_2' \rangle$ in two different ways, and then deduce that the matrix elements $\langle n_1, k; n_2 | \hat{W} | n_1', k'; n_2' \rangle$ are zero whenever $k \neq k'$.

2.5 Show that $\hat{W}$ has no effect on the first two energy levels (as first order).

2.6 We now consider the effect of $\hat{W}$ on the third energy level, still to first order in perturbation theory. By appropriately ordering the basis vectors, show that the matrix to be considered is block-diagonal, then determine the new position of the energy levels as well as the corresponding eigenbasis. We will denote $\hbar\Omega = \langle 2, 0; 0 | \hat{W} | 0, 0; 1 \rangle$, a quantity which will be assumed to be real.

2.7 Represent on a diagram the position of the states discussed in 2.5 and 2.6, taking into account the effect of the perturbation $\hat{W}$. For each state, the horizontal position of the level will correspond to the value of k, while the vertical position of the level will correspond to its energy. Using the selection rules established in 1.7, represent with arrows the transitions allowed under the action of the infrared field.

2.8 The absorption spectrum of CO_2 near the frequency ω_1 is shown in Fig. 3. Here, we focus only on the main lines indicated by vertical dashed lines (the interpretation of the much narrower lines appearing on either side of these main lines will be addressed in the next exercise). Using the energy level diagram constructed in the previous question, interpret the physical origin of the lines observed at 20, 18.5, and 21.6 THz. Does the order of magnitude of the amplitude of the latter two lines seem consistent with the theoretical model?

2.9 Propose a hypothesis to qualitatively explain the physical origin of the lines observed at 16.3 and 23.7 THz.
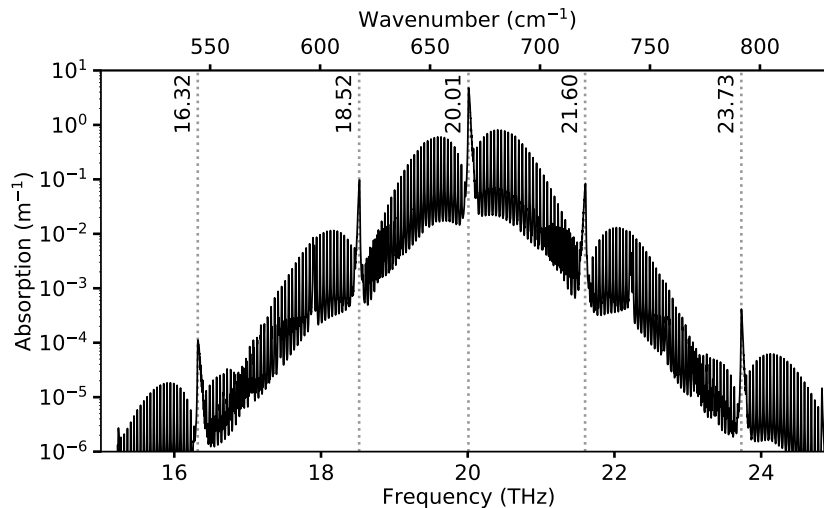

FIGURE 3 – Semi-logarithmic plot of the absorption spectrum of CO_2 in the vicinity of frequency ω_1.

Exercice 3
Ro-vibrational spectrum of CO_2

The purpose of this exercise is to take into account the rotational motion of the CO_2 molecule, in order to achieve a complete description of its infrared spectrum.

1. Rigid rotor model

We first consider the rigid rotor model, which disregards the vibrations of the molecule. The only remaining degrees of freedom are then associated with the orientation of the molecule in space, described using spherical coordinates θ and φ as shown in Fig. 4. The axis of the molecule is thus represented by the unit vector $\vec{u}$, defined by the usual expression :

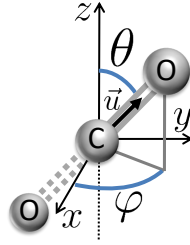$$\vec{u} = \begin{vmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{vmatrix} \tag{5}$$

FIGURE 4 – Representation of the CO_2 molecule, assumed to be a rigid rotor whose orientation is determined by the colatitude $\theta \in [0, \pi]$ and the longitude $\varphi \in [0, 2\pi[$.

We consider the Hilbert space $\mathcal{E}_{\text{rot}}$, where the state of the system is entirely determined by a ket $|Y\rangle \in \mathcal{E}_{\text{rot}}$ associated with the angular wavefunction $Y(\theta, \varphi)$. The inner product reads

$$\langle Y_1 | Y_2 \rangle = \int_0^\pi \int_0^{2\pi} Y_1^*(\theta, \varphi) Y_2(\theta, \varphi) \sin\theta \ d\theta d\varphi. \tag{6}$$

The Hamiltonian associated with the rotational motion of the molecule is written as

$$\hat{H}_{\text{rot}} = \frac{\hat{L}^2}{2I} = \hbar B \frac{\hat{L}^2}{\hbar^2}, \tag{7}$$

where $\hat{\vec{L}}$ is the angular momentum operator and I is the moment of inertia of the molecule. The quantity $B = \hbar/(2I)$ is called the rotational constant of the molecule.

1.1 In the following, we will use the eigenbasis $\{|\ell, m\rangle\}$ of $\hat{L}^2$ and $\hat{L}_z$, consisting of the spherical harmonics $Y_{\ell,m}(\theta, \varphi)$, with $\ell \in \mathbb{N}$. Recall the eigenvalues of $\hat{L}^2$ as well as the possible values of m.

1.2 Using the rotational constant B, express the energy values E_ℓ of the system, and the associated degeneracies.

1.3 Show in two different ways that the oxygen nuclei considered here are bosons.

1.4 Exchanging the two nuclei is equivalent to performing a central symmetry with respect to the origin, which is described by the parity operator $\hat{\Pi}$. Knowing that $\hat{\Pi}|\ell, m\rangle = (-1)^\ell |\ell, m\rangle$, what can we deduce about the allowed values of ℓ when taking into account the indistinguishable nature of the oxygen nuclei ?

1.5 In the context of the rigid rotor model, do you think the CO_2 molecule can absorb electromagnetic radiation ?

2. Ro-vibrational spectrum associated with the antisymmetric stretching mode

We now combine rotational and vibrational motions. For sake of simplicity, we will consider just one mode of vibration, namely the antisymmetric stretching mode with frequency ω_3. We are therefore in the state space $\mathcal{E}_3 \otimes \mathcal{E}_{\text{rot}}$, where $\mathcal{E}_3 = \mathcal{L}^2(\mathbb{R})$. The vibrational mode considered is that shown in Fig. 1(e), except that the molecule is now aligned according to the vector $\vec{u}$ introduced above. Consequently, eq. 4 expressing the dipole operator must be replaced by

$$\hat{\vec{\mu}} = \mu_3 (\hat{a}_3 + \hat{a}_3^\dagger) \hat{\vec{u}}, \tag{8}$$

where $\hat{a}_3$ acts in $\mathcal{E}_3$ while $\hat{\vec{u}}$ is now an observable acting in $\mathcal{E}_{\text{rot}}$. The Hamiltonian of the system is written $\hat{H} = \hat{H}_3 + \hat{H}_{\text{rot}}$, where $\hat{H}_3$ is defined by eq. 3 and $\hat{H}_{\text{rot}}$ is defined by eq. 7.

2.1 Write the energy value $E_{n,\ell}$ associated with eigenstate $|n\rangle \otimes |\ell, m\rangle$.

2.2 Recall without calculation the parity of the eigenfunctions of the one-dimensional harmonic oscillator, then deduce the action of the operator exchanging the two oxygen nuclei on state $|n\rangle \otimes |\ell, m\rangle$.

2.3 Deduce the permitted values for ℓ depending on the values taken by n.

2.4 It is assumed that at room temperature the system can be randomly in one of the states $|0\rangle \otimes |\ell, m\rangle$, where ℓ satisfies the condition obtained in the previous question. Calculate the matrix element $\langle n'| \otimes \langle \ell', m'| \hat{\vec{\mu}} \cdot \vec{\mathcal{E}}_0 |0\rangle \otimes |\ell, m\rangle$, where it will be assumed that the electric field $\vec{\mathcal{E}}_0$ is aligned along the z axis, then identify the $|n'\rangle \otimes |\ell', m'\rangle$ states accessible following interaction with infrared radiation.

You will need to use the relation

$$Y_{\ell,m}(\theta) \cos\theta = \alpha_{\ell,m} Y_{\ell+1,m}(\theta) + \beta_{\ell,m} Y_{\ell-1,m}(\theta), \tag{9}$$

where $\alpha_{\ell,m}$ and $\beta_{\ell,m}$ are known real coefficients whose explicit expression as a function of ℓ and m will not be necessary. We obviously have $\beta_{\ell,\ell} = 0$.

2.5 Express as a function of ω_3 and B the corresponding energy differences, $E_{n',\ell'} - E_{0,\ell}$, according to the allowed values of $\Delta\ell = \ell' - \ell$.

2.6 Using the previous results, discuss the infrared spectrum shown in Fig. 5. You can
- explain qualitatively the general shape of the absorption spectrum,
- deduce from the spectrum the numerical values of B and the length of the CO bond,
- explain the growth and decay of the spectrum envelope away from the central frequency (assuming for sake of simplicity that $\alpha_{\ell,m}$ and $\beta_{\ell,m}$ are independent of ℓ and m),
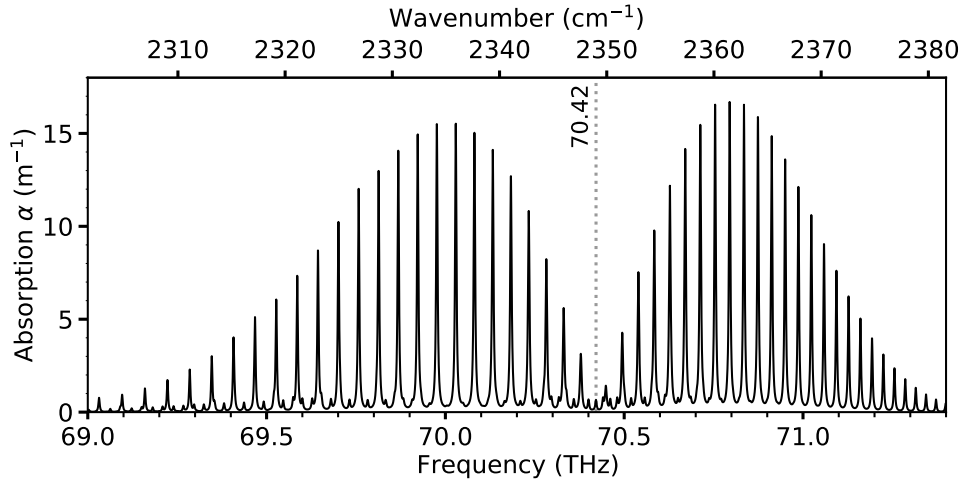- discuss features not predicted by the simplified theoretical model developed in this exercise.

FIGURE 5 – Infrared absorption spectrum of CO_2 near the frequency ω_3.

3. Ro-vibrational spectrum associated with bending modes

This final section uses some of the results demonstrated in Exercise 2.

We now combine the rotational motion with the two bending modes of frequency ω_1 (this time neglecting the stretching modes). The theoretical treatment is considerably more complicated, since both rotational and bending motions contribute to the total angular momentum $\hat{\vec{L}}$ of the molecule. We assume that $\hat{\vec{L}}$ commutes with its projection $\hat{K} = \hat{\vec{L}} \cdot \hat{\vec{u}} = \hat{\vec{u}} \cdot \hat{\vec{L}}$ along the $\vec{u}$ axis of the molecule. We also admit that this projection corresponds to the angular momentum $\hat{K}$ already studied in exercise 2. The projection of the angular momentum in the plane perpendicular to the axis of the molecule is called $\hat{\vec{L}}_\perp = \hat{\vec{L}} - \hat{K}\hat{\vec{u}}$. The Hamiltonian is now written

$$\hat{H} = \hat{H}_1 + \hbar B \frac{\hat{L}_\perp^2}{\hbar^2}, \qquad (10)$$

where B is the rotational constant introduced above. The observables $\hat{H}_1$, $\hat{K}$, $\hat{L}^2$ and $\hat{L}_z$ commute with each other and can be diagonalized in the common eigenbasis $\{|n, k; \ell, m\rangle\}$, with the same eigenvalues as those obtained in part 1 of exercise 2 and part 1 of this exercise. However, given the more complex motion of the molecule, the corresponding wave functions are no longer proportional to the spherical harmonics $Y_{\ell,m}(\theta, \varphi)$, so the selection rules established in 2.4 are modified. We admit that infrared transitions are now possible for $\Delta\ell = -1, 0,$ or $+1$.

3.1 Knowing that $\hat{L}^2 = \hat{L}_\perp^2 + \hat{K}^2$, show that $|n, k; \ell, m\rangle$ is an eigenvector of $\hat{L}_\perp^2$ for an eigenvalue to be determined, then deduce the expression of the energy $E_{n,k,\ell}$ associated with $\hat{H}$.

3.2 The electric field associated with the infrared radiation is assumed to be polarized along the z axis. Explain why $\hat{\mu}_z$ commutes with $\hat{L}_z$, then deduce that an infrared transition must respect the selection rule $\Delta m = 0$.

3.3 Consider a transition from state $|0, 0; \ell, m\rangle$ to state $|1, k; \ell + \Delta\ell, m\rangle$. Recall the possible values of k, then deduce the transition frequencies in the three cases $\Delta\ell = -1, 0$ or 1. Based on these results, interpret the part of the spectrum shown in Fig. 3 located between 19 and 21 THz.

3.4 Using the results obtained in the previous exercise, explain the general shape of the spectrum shown in Fig. 3.

3.5 Figure 6 represents the infrared spectrum emitted by the Earth into space (also called spectral emittance), calculated using a simplified radiative transfer model [1]. The emission spectra, repre-

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1. D. Louapre, github.com/scienceetonnante/RadiativeForcing (2023).

sented near ω_1, are based on three models of CO_2 absorption spectra : the first (a) only considers the vibration at ω_1, the second (b) includes molecular rotations but does not account for Fermi resonance, while the third (c) uses the spectrum shown in Figure 3, which also includes the Fermi resonance studied in Exercise 2. The additional absorbed power (called radiative forcing) due to a doubling of the CO_2 concentration according to these three models is respectively (a) 0.1, (b) 1.8, and (c) 4.1 W/m^2. Comment on these results using Figures 3 and 6 and then conclude.
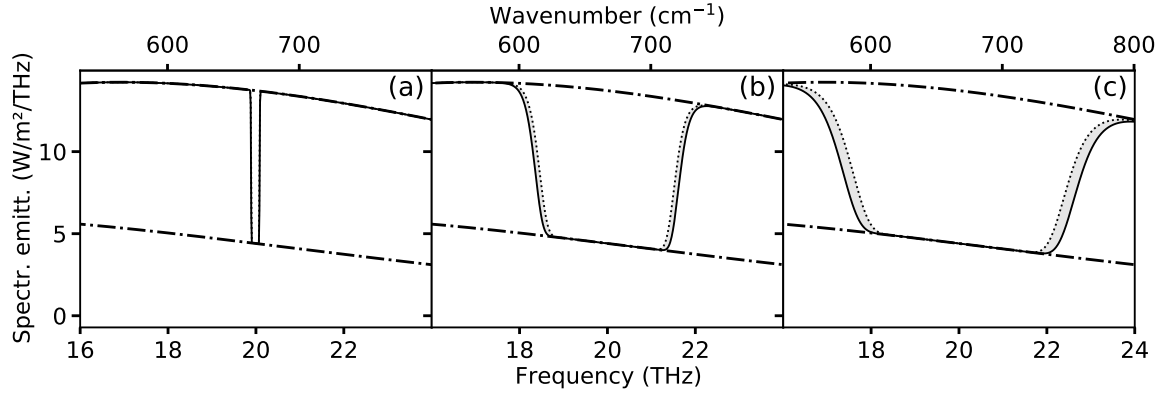

FIGURE 6 – Representation of the Earth's spectral emittance near ω_1 for a CO_2 concentration of 280 ppm (dotted line) and 560 ppm (solid line). The theoretical model considers only the vibration at ω_1 (a), vibrations and rotations without (b) or with (c) Fermi resonance. The dashed lines represent the blackbody emission spectrum for temperatures of 288 K (upper curve) and 216 K (lower curve). The latter value corresponds to the temperature at the top of the atmosphere.