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Determination of the elastic constants in the classical vibrational model of the CO_2 molecule

Determinación de las constantes elásticas en el modelo vibracional clásico de la molécula CO_2

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In this article, we report an experimental method to calculate the values of the elastic constants that correspond to longitudinal and transverse vibrations in the classical model of the CO2 molecule. In classical molecular physics, the CO2 is treated as a linear array of three point-particles that interact by a harmonic coupling. The experimental wavenumbers of the normal modes of vibrations of CO2 were obtained from IR spectroscopy on an atmospheric air sample, and they were applied the calculation of the respective normal mode elastic constants. This article does not provide new research in molecular physics, but it is rather made for teaching purposes.

En este artículo, reportamos un método experimental para calcular los valores de las constantes elásticas que corresponden a las vibraciones longitudinal y transversal en el modelo clásico de la molécula CO_2. En física molecular clásica, El CO_2 es tratado como un arreglo lineal de tres partículas puntuales que interactúan a través de un acoplamiento harmónico. El número de onda experimental de los modos normales de vibración de CO_2 fueron obtenidos desde una espectroscopía IR en una muestra de aire atmosférico, y fueron aplicados a los cálculos de las respectivos modos normales de las constantes elásticas. Este artículo no proporciona nueva investigación en física molecular sino que sus propósitos son para educación.

KEYWORDS

CO_2 molecular vibration, IR espectroscopy, Lagrangian models, linear triatomic molecules, normal modes.

PALABRAS CLAVES

Vibración molecular de CO_2, Espectroscopía IR, Modelos Lagrangianos, Moléculas triátomicas lineales, modos normales.

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I | INTRODUCCIÓN

THE experiment consisted on performing infrared (IR) spectroscopy on an air sample and from it deduce the elastic constants for the normal vibrational modes of the classical harmonic modeling of CO_2 molecule. This document is intended to be used as a reference for teaching in undergraduate courses on classical mechanics as it does not provide new results but rather a didactic proposal for an experimental demonstration on molecular vibrations. We shall make a review of the physical principles behind the experiment in this section.

Air is commonly a background compound whose spectrum is subtracted before performing spectrometry of a material of interest (however in this project, the CO_2 in air is the molecule of interest). Infrared spectrometers have detectors that measure the transmitted radiation through a sample. As time passes, air changes its vapor concentration and temperature which makes it necessary to change the background that must be subtracted before taking measurements. However only the intensity of the spectrum changes (assuming no other chemical species are added to air) since the molecular concentrations do not alter the characteristic absorption lines of each molecule.

The CO_2 is a triatomic molecule (displayed schematically in Figure 1) in which the oxygen and carbon atoms are joined by covalent bonds, which in this article are modeled by a classical harmonic interaction.

The vibrations of a molecule are given by its normal modes. Each absorption line in a IR molecular spectrum corresponds to a normal mode. The four normal modes of carbon dioxide (shown in Figure 2) are the symmetric stretch, the asymmetric stretch and two transverse bending modes. The two bending modes have the same energy and differ only in the direction of the bending motion. Modes that have the same energy are called degenerate. In the classical treatment of molecular vibrations, each normal mode is treated as a simple harmonic oscillator.

In general linear molecules have $3N-5$ normal modes, where N is the number of atoms (Schrader, 1995). The five remaining degrees of freedom for a linear molecule are three coordinates for the motion of the center of mass and two rotational angles. Also, normal modes are independent, which means that normal modes do not exchange energy. For example, if the symmetric stretch is excited, the energy stays in the symmetric stretch (Banwell y McCash, 1994). In the case of CO_2, it has 4 vibrational modes, 2 longitudinal (symmetric and asymmetric) and a transverse mode which is $2-fold$ degenerate.

Normal node analysis in the classical harmonic approximation of molecules can be set up from Newton's equations or with a Lagrangian treatment (which we shall adopt). Let the longitudinal displacements of the oxygen atoms be x_1 and x_3, and for the carbon atom be x_2.The Lagrangian of the longitudinal motion becomes:

$$\mathcal{L}_L = \frac{1}{2}m_0\left(\dot{x_1}^2+\dot{x_3}^2\right)+\frac{1}{2}m_C\dot{x_2}^2-\frac{1}{2}k_1\left[(x_1-x_2)^2+(x_3-x_1)^2\right], \qquad (1)$$

where $M_O = 15.9994$ uma is the oxygen mass, $M_C = 12.011$ uma is the carbon mass (Wapstra, Audi, y Hoekstra, 1988), k_1 is the elasticity constant in the longitudinal movement.

The normal coordinates for this Lagrangian (without normalization) are $Q_a = x_1 + x_3$ and $Q_s = x_1 - x_3$. The condition to eliminate translation of the center of mass is given by $m_O(x_1 + x_3) + m_C x_2 = 0$, which yields to the longitudinal Lagrangian expressed in normal modes as

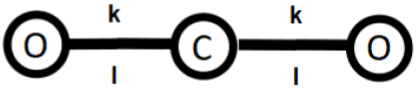

Figura 1: Simplied scheme of the CO_2molecule; l represents the length of separation in mechanical equilibrium (with value of 116.3 pm (Chedin, 1979)) and k represents the elastic constant (having different values for the longitudinal or transverse motion) used in the harmonic approximation of the interatomic coupling.

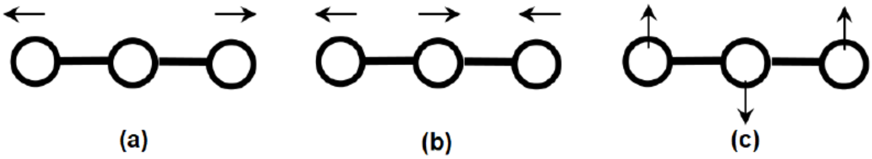

Figura 2: Normal modes of vibration for the linear triatomic molecule. Figure (a) represents a symmetrical movement where the oxygen atoms move in opposite directions while the carbon atom is stationary; (b) represents an asymmetrical movement in which oxygen atoms move in the same direction while the carbon atom oscillates respect to the oxygen atoms; and (c) represents the transverse movement (which is 2-fold degenerate) respect to the axis of molecule.

$$\mathcal{L}_L = \frac{\mu m_O}{4m_C}\dot{Q}_a^{\,2} + \frac{m_O}{4}\dot{Q}_s^{\,2} - \frac{k_1\mu^2}{4m_C^2}Q_a^2 - \frac{k_1}{4}Q_s^2, \tag{2}$$

where $m = 2m_O + m_C$. A more extensive disscussion on normal modes of linear triatomic molecules can be found in several texts (e.g. (Landau y Lifshitz, 1969), (Goldstein, Poole, y Safko, 2014)). For the transverse movement, we can similarly set up coordinates y_1, y_3 for the oxigen atoms, y_2 for the carbon atom. The condition $m_O(y_1 + y_3) + m_C y_2 = 0$ eliminates translation and $y_1 = y_3$ eliminates the rotation of the molecule. The Lagrangian for transverse motion becomes (Landau y Lifshitz (1969)):

$$\mathcal{L}_T = \frac{1}{2}m_0\left(\dot{y_1}^2 + \dot{y_3}^2\right) + \frac{1}{2}m_C\dot{y_2}^2 - \frac{1}{2}k_2 l^2\delta^2 = \frac{m_C m_O}{4\mu}l^2\delta^2 - \frac{k_2}{2}l^2\delta^2, \tag{3}$$

where δ is the normal coordinate for transverse vibrations, given by:

$$\delta = \frac{(y_1 - y_2) + (y3 - y2)}{l} \tag{4}$$

From the Lagrangians expressed in normal coordinates 2 and 3, it is easy to find the expression for the longitudinal and transverse angular frequencies of vibration, given as

$$\omega_S = \sqrt{\frac{k_1}{m_O}}, \qquad \omega_A = \sqrt{\frac{\mu k_1}{m_C m_O}}, \qquad \omega_T = \sqrt{\frac{2\mu k_1}{m_C m_O}} \tag{5}$$

where ω_S, ω_A and ω_T are the angular frequencies for the symmetric, asymmetric longitudinal and transverse normal nodes, respectively. In general, $k_1 \neq k_2$, due to the difference in the type of movement. From 5, we can calculate the elastic constants once the frequencies are known. In IR spectroscopy, we

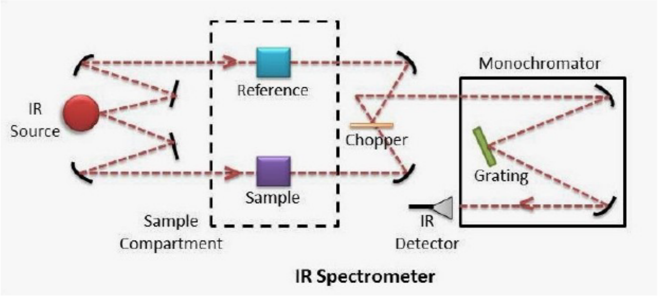

Figura 3: A simplified scheme of a two-beam absorption spectrometer (Schrader, 1995). A beam of infrared light is produced, passed through an interferometer, and then split into two separate beams. One is passed through the sample, the other passed through a reference. The beams are both reflected back towards a detector, however first they passed through an optical chopper, which quickly alternated the beams that enter the monochromator and finally passed to the detector. The two signals are then compared and a printout is obtained. The reference sample is an indicative and comparative for samples to measure.

measure the wavenumbers (conventionally given as $1/\lambda$, where λ is the wavelength) for which normal mode vibrations occurs; and thus we can relate it with the frequencies of normal mode oscillations via the relation $\omega = 2\pi c/\lambda$, where c is the speed of light in vacuum.

It should be clarified that only the asymmetric longitudinal and transverse wavenumbers ($1/\lambda_A$ and $1/\lambda_T$, respectively) can be measured in IR spectroscopy. The reason for this, lies in the physical principles for the detection of the normal modes vibrations, which will be explained at the end of this section. Thus the relevant expressions for the calculation of the elastic constants become:

$$k_1 = \frac{m_C m_O}{m_C + 2m_O}\left(\frac{2\pi c}{\lambda_A}\right)^2 \tag{6}$$

$$k_2 = \frac{1}{2}\frac{m_C m_O}{m_C + 2m_O}\left(\frac{2\pi c}{\lambda_S}\right)^2, \tag{7}$$

The physical principle of the infrared spectrometer lies on the absorbance of electromagnetic wave by the molecules. In the Figure 3 we show a basic scheme of an common IR spectrometer.
The infrared radiation send by the source of the spectrometer, interacts with the molecules, causing polarization, which in turn results in a fluctuation of the electric dipole moment of the molecule, then this induces an electric field that interacts with the electric field associated with the infrared radiation. If the frequency of the electromagnetic wave is the same of the molecule, absorption occurs (Scherer, 1978). By this process, the normal modes of a molecule can be detected on the spectrum by matching the absorption lines.

A symmetric stretch does not result in a change of the electric dipole moment (initially zero for the CO_2 molecule), so it is IR-inactive (and thus it could not be detected in the experiment), while the asymmetric stretch and transverse motion do result in a change in dipole moment so they both are IR-active.

Figura 4: Experimental apparatus, a Nicolet iS5 FT-IR spectrometer and the iD1 transmission chamber.

Respect to the computation of the spectrum, Fourier transform (FT) IR spectroscopy (which the technique applied in the experiment) takes advantage of the interferometer arrangement shown in Figure 3. As one of its mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, due to wave interference. Different wavelengths are modulated at different rates, so that at each moment the beam coming out of the interferometer has a different spectrum (Schrader, 1995). Afterward, a Fourier transformation algorithm takes all this data and works backward to infer what the absorption is at each wavelength.

II | METHODOLOGY

The experimental apparatus mainly consisted of a *Nicolet iS5 FT-IR* (Fourier transform infrared) spectrometer, shown in figure 4. The wavenumber interval that the spectrometer measured was between $4000cm^{-1} - 400cm^{-1}$. The sample was air at room temperature and atmospheric pressure, which contains a $0.04\,\%$ of CO_2 at these conditions (Schrader, 1995). The absorption lines of other molecules, specially H2O have important contributions on the spectrum of air (Scherer, 1978). Although the percentage of CO_2 in the sample is low, it is still noticeable in the spectrum (as it is seen in the results) since, as remarked before, the molecular concentration does not change the wavenumber domain of absorption lines, it only changes the transmittance intensity.

An $iD1$ transmission chamber was placed on the spectrometer. The chamber only has the purpose of insulating the sample and protecting the instrument from contamination and spillage. A desiccant of silica was introduced in order to reduce the concentration of H_2O, since it is a strong absorbent of infrared radiation (its absorption lines are still present as it is confirmed in the results). The sample of atmospheric air entered the chamber and measurements were finally performed in 16 sweeps to collect the average spectrum, which was displayed in the OMNIC IR data software.

III | RESULTS

The collected spectrum is shown in Figure 5. The wave numbers $\left(\lambda^{-1}\right)$ of the normal vibrational modes of CO_2 molecule were identified as:

$$\lambda_A^{-1} = 2339cm^{-1}, \qquad \lambda_T^{-1} = 668cm^{-1}, \tag{8}$$

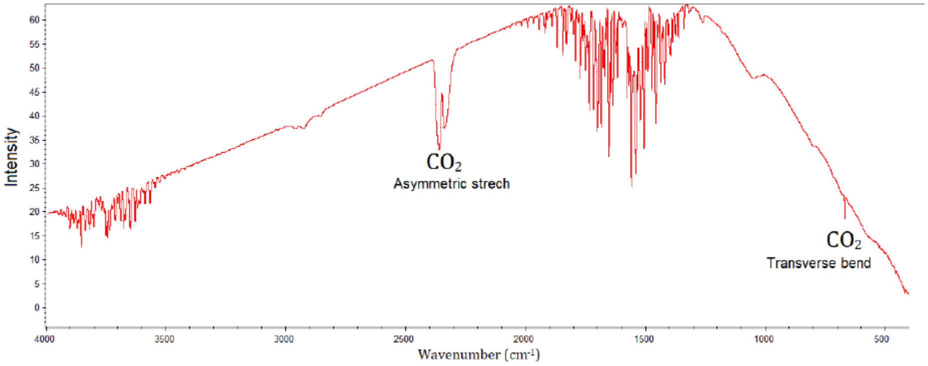

Figura 5: Spectrum of air given in a wavenumber domain in the range of $4000cm^{-1}$ *to* $400cm^{-1}$*. The* CO_2 *asymmetric stretch and transverse bend regions are marked.*

were the subscript A denotes the asymmetric longitudinal oscillation, and T denotes the transverse oscillation. Comparing the eigen-wavenumbers with more accurate experimental measures ($\lambda_A^{-1} = 2349cm^{-1}$ and $\lambda_T^{-1} = 667cm^{-1}$ (Workman, 2000)) we find a percentage error:

$$\Delta\lambda_A^{-1} = 0.43\,\%, \qquad \Delta\lambda_T^{-1} = 0.15\,\%, \tag{9}$$

The experimental wavenumbers were applied in the expression for the elastic constants 6 and 7, which resulted in the values:

$$k_1 = 1407.16N/m \qquad k_2 = 57.37N/m \tag{10}$$

IV | DISCUSSION AND CONCLUSSION

When we analyze the IR spectrum of air (shown in figure 5), it is noticeable the lack of CO_2 content as its absorption lines do not appear to be deep for either normal mode, and it indicates that the transversal normal mode generates less absorption than the asymmetric longitudinal normal mode. On the other hand, the experimental error percentage for either normal mode wavenumbers is bellow the 0.5 %, which indicates that the experimental variation of the wavenumber is small but still perceptible. This difference in the experimental value is likely generated due to the calibration of the spectrometer, since the presence of others chemical compounds do not affect the normal mode frequency.

The resulting elastic constant values allow us to complete the classical harmonic approximation model for CO_2 molecule by coupling the atoms with classical harmonic potentials instead of the actual quantum electrodynamic interactions. This classical model does not predict values that could be tested with experiments, but rather gives a simplified physical explanation of the motion that the molecule is undergoing to produce the experimental spectrum. Thus the classical model can provide an easier physical intuition of the molecule, but more rigorous molecular model is needed when if we want to predict the frequencies for the vibrations of a molecule of interest.

Several methods for making molecular orbital calculations can be found in the literature (such as

Schrader (1995) and Wathelet, Champagne, Mosley, Perpéte, y André (1998)) in which the coupling forces are calculated in terms of the quantum state of the system. It should also be noticed that for much higher temperatures the harmonic potential model could be rendered as a bad approximation to describe the interactions between atoms (since the interatomic displacements would increase with temperature) and thus other models must be used, such as the Morse potential for the case of diatomic molecules (Girifalco y Weizer, 1959).

We must also remark that the investigation could not identify the symmetric longitudinal mode of CO_2 (which is at a wavenumber of $1333cm^{-1}$ (Workman, 2000)) since its electric dipole moment does not change (because of the symmetry of motion between atoms) with the transmission of IR radiation and thus does not cause an absorption line. The other vibrational modes do yield a change in the electric dipole moment when they interact with the radiation of the same frequency and thus produce perceptible absorption lines.

As a recommendation for performing this experiment, the calibration of the spectrometer must verified before making measurements, and the spectrum of air samples should be taken at different times of the day to confirm that only the transmission intensity is altered, since the changes vapor concentration and temperature do not directly affect the characteristic absorption lines of each molecule.

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