Computational study of rovibrational spectrum of CO-CO$_2$

by

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Abstract

The Lanczos algorithm was used to determine $J=0$ and $J=1$ ro-vibrational energy levels for CO-CO$_2$. The fundamental transition energies have good agreement with previous experiments for both the C-bound and O-bound isomers. Likewise, we observed and confirmed a previously unlabeled in-plane state, now labeled a geared state. Other states were labeled and confirmed, such as the CO-libration state. Rotational constants obtained from $J=1$ energy levels also have good agreement with previous experiments.

There is strong coupling between the bends and torsion, which makes the in-plane Potential Energy Surface (PES) cuts different from the out-of-plane cuts. There is an out-of-plane path, however its barrier is still higher than its geared counterpart. When close to equilibrium, a T-shape, a vibration on the torsional coordinate does not significantly change the geometry of the molecule, making vibration along this coordinate very floppy.
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## Contents

Abstract

Acknowledgments

Contents

List of Tables

List of Figures

Chapter 1: Introduction
  1.1 Purpose ........................................... 1
  1.2 Organization of Thesis ............................ 2

Chapter 2: Theory
  2.1 The Nuclear Motion Hamiltonian ............... 3
    2.1.1 Born-Oppenheimer approximation .......... 4
    2.1.2 Kinetic Energy Operator .................. 5
    2.1.3 Rotational constants ....................... 8
  2.2 Variational Principle .......................... 9
  2.3 Coordinate System ................................ 11
  2.4 Basis functions ................................. 11
    2.4.1 Stretch Basis functions ................... 11
      2.4.1.1 Discrete Variable Representation .... 12
        2.4.1.1.1 Sine DVR .......................... 14
        2.4.1.1.2 Potential Optimized DVR (PODVR) .... 15
        2.4.1.1.3 Tridiagonal Morse DVR ............... 15
      2.4.1.2 Angular basis functions ................. 17
  2.5 Lanczos Algorithm .............................. 20
    2.5.1 Matrix-Vector Products .................... 22

Chapter 3: Potential Energy Surface .......................... 25
List of Tables

3.1 Energies for the minima and transition states of CO-CO$_2$ ............ 30

5.1 Energy levels for the C-bound and O-bound isomers with respect to the ZPE of the C-bound isomer. ................................. 37

5.2 Comparison for fundamental frequencies calculated in this work, in previous works and found experimentally. ......................... 42

5.3 Rotational energy levels and rotational constants for J=1 for the C-bound isomer, for the fundamental vibrational states. ............ 44

5.4 Rotational energy levels and rotational constants for J=1 for the O-bound isomer, for the fundamental vibrational states. ............ 45

5.5 Comparison for the rotational constants obtained in this work, previous experiments and previously calculated for the C-bound isomer. .... 45

5.6 Comparison for the rotational constants obtained in this work, previous experiments and previously calculated for the O-bound isomer. .... 45
List of Figures

2.1 Coordinates used to describe CO-CO$_2$ .................................................. 6

3.1 Potential Energy Surface (PES) plot of CO-CO$_2$ using extended co-
ordinates. ............................................................... 26
3.2 Definition of the extended angles $\tilde{\theta}_1$ and $\tilde{\theta}_2$. ................................. 27
3.3 PES plots which show the out-of-plane path for CO-CO$_2$. ......................... 29
3.4 $r_0$ cuts through the PES for several relevant configurations. .................... 31

5.1 Probability Density (PD) and Wave Function (WF) plots for the first
geared state. ................................................................. 40
5.2 PD and WF plots for the first anti-geared state of the C-bound isomer. 40
5.3 WF cuts for the ground state and the first 3 geared states for the
C-bound isomer. ................................................................. 41
5.4 PD plots for the ground state and the first three out-of-plane states. 43
Chapter 1

Introduction

1.1 Purpose

Vibrational spectroscopy is a large area of research in Chemistry, that can help in the understanding of several different properties of molecules.[1] Because of this, having good theoretical calculations is important, as it can help to locate new transitions and interpret and understand experimental spectra better.[2] However, one of the biggest challenges in theoretical spectroscopy is the size of the problem to solve as the molecules get bigger; for an N-atom molecule there are 3N-6 internal degrees of freedom, and the size of the problem increases exponentially with the number of degrees of freedom. This calls for an increased efficiency in the methods used in the area, otherwise the problems quickly become intractable.

Van der Waals molecules are especially interesting and challenging due to their multiple stable structures and their large amplitude motion.[2, 3] This large amplitude motion makes it necessary to have a good Potential Energy Surface (PES) and calls for improved methods to calculate their spectra. The CO-CO$_2$ molecule studied in this research is a Van der Waals dimer, which is formed by CO and CO$_2$ and has two stable
isomers. Due to the great abundance of both individual isomers in the atmosphere, product of the burning of fossil fuels, the interaction of both isomers is of interest for atmospheric modeling,[4]. It is also of chemical and astrophysical interest. Also, due to its similarities with other Van der Waals dimers, the methodologies used here, as well as some of the results can apply to other similar molecules.

There have been some harmonic studies of this dimer[5, 6, 7] which have good agreement with experimental observations for the frequencies of the lower energy isomer, however there is poor agreement for the second, higher laying isomer. Likewise some states have been observed experimentally, but are still not properly labeled. The main aim of this work is to get a better agreement with experimental levels, even for the second, higher laying isomer, and label previously unlabeled states.

1.2 Organization of Thesis

Chapter 2 outlines the basic theory used in ro-vibrational spectroscopy and gives details on the specific tools used in this research. Chapter 3 goes over the procedure used to get obtain the PES. Chapter 4 goes over the choice of parameters used, as well as some other details on the calculation. Chapter 5 goes over the results and discusses them. Finally, chapter 6 gives an overview of the whole document, as well as an outline of some possible future work.
Chapter 2

Theory

2.1 The Nuclear Motion Hamiltonian

The general spin-free, non-relativistic nuclear Hamiltonian can be written as:

\[ H \Psi = \left( -\sum_{i=1}^{N} \frac{1}{2m_i} \nabla^2 + V \right) \Psi = E \Psi, \]  

(2.1)

where \( H \) is the Hamiltonian, \( N \) is the number of particles, \( m_i \) is the mass of the \( i^{th} \) particle, \( \nabla^2 \) is the Laplace operator and \( V \) is the PES. The first term in this Hamiltonian is the Kinetic Energy term, while \( V \) is the potential energy. This Hamiltonian is used in a Cartesian, space fixed coordinate system.

A set of coordinates with the origin at the center of mass of the nuclei can be defined, so that the internal degrees of freedom of the molecule can be separated from the general movement of the molecule. After doing this transformation the Hamiltonian can be rewritten as:

\[ H = T_{CM} + T + V \]  

(2.2)
where $T_{CM}$ is the kinetic energy of the center of mass and $T$ is the kinetic energy for all electronic and vibrational degrees of freedom of the molecule, and $V$ is the electrostatic potential energy.[8]

Then, ignoring the $T_{CM}$ term to focus only in the internal dynamics of the molecule, the spin-free rovibronic Hamiltonian $H_{rve}$ can be written as:

$$H_{rve} = T + V,$$  \hspace{1cm} (2.3)

which is generally difficult to solve without approximations.[8]

### 2.1.1 Born-Oppenheimer approximation

The most important approximation used in order to solve the rovibronic Schrödinger equation is the Born-Oppenheimer approximation. This approximation assumes that the rovibronic Schrödinger’s equation can be solved in two steps. In the first step the electronic Schrödinger’s equation is solved assuming that the nuclei are fixed in their positions, then this procedure is repeated for several different nuclear configurations; then the electronic energies obtained from the previous step are used to generate a Potential Energy Surface (PES). In the second step, the rotational-vibrational Schrödinger’s equation is solved using the PES generated in the first step.[9] This approximation can be used due to the big difference in mass between the electrons and nuclei.

As a result of the Born-Oppenheimer approximation, the rovibronic Schrödinger equation is reduced from a $(3l-3)$-dimensional problem to a $3n$-dimensional electronic Schrödinger equation and a $(3N-3)$-dimensional rotation-vibration (ro-vibration) Schrödinger equation, where $l$ is the number of particles (nuclei and electrons), $n$ is the number
2.1. THE NUCLEAR MOTION HAMILTONIAN

of electrons and \( N \) is the number of nuclei. Then, the ro-vibrational Schrödinger equation takes the following form:

\[
(T_N + V_N)\Psi_{rv} = E_{rv}\Psi_{rv},
\]

(2.4)

where \( T_N \) is the nuclear kinetic energy term, the sum of \( T^0 \) and \( T' \) from equation 2.3, and \( V_N \) is an intermolecular PES built from the solution of the electronic Schrödinger equation for several different nuclear configurations.[8]

2.1.2 Kinetic Energy Operator

One coordinate system used to represent the Kinetic Energy Operator (KEO) is the polyspherical coordinates, which consist of 3 Euler angles for the rotation of a body-fixed frame, 3 Cartesian coordinates for the movement of the center of mass of the molecule, and \( 3N-6 \) internal coordinates: \( N-1 \) magnitudes of orthogonal vectors \( \vec{r}_0, \vec{r}_1, \ldots, \vec{r}_{N-1} \), \( N-2 \) planar angles \( \theta_i \) between of \( \vec{r}_0 \) and \( \vec{r}_i \) and \( N-3 \) dihedral angles between the plane normal to \( \vec{r}_0 \times \vec{r}_1 \) and the plane normal to \( \vec{r}_0 \times \vec{r}_i \), where \( N \) is the number of nuclei. Chapuisat and Iung developed a KEO for this coordinate system[10]. An example of a coordinate system of this kind is shown in Figure 2.1, where it is used to describe CO-CO\(_2\), the molecule which will be studied in this thesis. The vectors are labeled depending on the system to minimize coupling and facilitate a physical interpretation of the coordinates. For example for CO-CO\(_2\) the vectors are chosen in such a way that the \( \theta_1 \) and \( \theta_2 \) bends represent a bend of one monomer with respect to the other, also \( r_1 \) and \( r_2 \) are chosen to represent each monomer for the same reason.

The coordinate system is then "orthogonal".[12] Orthogonal here means that there is an orthogonal transformation between the new set of mass-weighted nuclear position
2.1. THE NUCLEAR MOTION HAMILTONIAN

Figure 2.1: Coordinates used to describe CO-CO$_2$. $r_0$ is the center of mass separation, the length of the vector $\vec{r}_0$; $\theta_1$ is the angle between $\vec{r}_0$ and $\vec{r}_1$, $\theta_2$ is the angle between $\vec{r}_0$ and $\vec{r}_2$, and $\phi_2$ is the torsional angle: the angle between the plane formed by $\vec{r}_0$ and $\vec{r}_1$, and the plane formed by $\vec{r}_0$ and $\vec{r}_2$. Red circles represent oxygen atoms, while gray circles represent carbon atoms. The bond lengths for both CO and CO$_2$ are fixed at equilibrium, while CO$_2$ is assumed to be planar. Reprinted from [11], with the permission of AIP Publishing.

vectors and the original internal mass-weighted Cartesian vectors.[13] The orthogonal vectors have the advantage that the matrix elements over the angles is analytical, and therefore only the matrix elements for the radial coordinates have to be numerically calculated.[12] After simplifying the notation[14] the KEO becomes:

$$T = T_s + T_{br,diag} + T_{br,off} + T_{cor}, \quad (2.5)$$

where

$$T_s = -\sum_{k=0}^{N-2} \frac{1}{2\mu_k} \frac{\partial^2}{\partial r_k^2}, \quad (2.6)$$
\[ T_{br,\text{diag}} = [B_0(r_0) + B_r(r_1)] \left[ -\frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \sin \Theta_1 \frac{\partial}{\partial \theta_1} + \frac{1}{\sin^2 \theta_1} (J_z - L_z)^2 \right] \\
+ \sum_{k=2}^{N-2} [B_0(r_0) + B_k(r_k)] \frac{l_k^2}{2} \\
+ B_0(r_0) \left[ J^2 - 2(J_z - L_z)^2 - 2J_z(L_z) + 2 \sum_{k \neq k' = 1}^{N-1} l_k l_{k'} \right], \tag{2.7} \]

\[ T_{br,\text{off}} = B_0(r_0) \left[ (L_+) a_+ - (L_-) a_- + \sum_{k \neq k' = 3}^{N-1} (l_k + l_{k'} - l_k l_{k'}) \right], \tag{2.8} \]

\[ T_{\text{cor}} = -B_0(r_1)[J_- (a_+ + L_+) + J_+ (a_- + L_-)], \tag{2.9} \]

where

\[ B_i(r_i) = \frac{1}{2\mu_i r_i^2}, \tag{2.10} \]

\[ L_z = \sum_{k=3}^{N-1} l_{kz}, \tag{2.11} \]

\[ L_\pm = \sum_{k=3}^{N-1} l_{k\pm}, \tag{2.12} \]

\[ l_\pm = l_{i\pm} \pm i l_{iy} \quad (i = 2, \ldots, N - 2), \tag{2.13} \]

\[ J_\pm = J_x \pm iJ_y, \tag{2.14} \]

\[ a_\pm^2 = \pm \frac{\partial}{\partial \theta_2} - \cot \theta_2 (J_z - L_z), \tag{2.15} \]

where \( J_\pm, J_z, l_{kx}, l_{ky}, l_{kz} \) and \( l_k^2 \) are the angular momentum operators, and \( \mu_i \) are reduced masses, which depend on the specific coordinate vector used and have been previously described by Bramley and Carrington.\[13\]

This description is more suitable for bound systems, weakly bound or dissociative
systems. However, it’s not always the best for collisional systems due to the fact that the reference vectors are chosen a priori, and therefore in the case of dissociation in two fragments it is only suitable if one reference vector points in the right direction from the beginning, which is not always the case. In the case of a collisional system, there can be some significant coupling between coordinates even after dissociation if the vectors are not chosen carefully, which is not possible to know a priori; however CO-CO$^2$ is a weakly bound system, and therefore an appropriate set of coordinates can be chosen a priori.

### 2.1.3 Rotational constants

As a part of this coordinate system, another problem has to be separately solved. The separation of the coordinate system into internal coordinates and a set of external coordinates, the problem is separated into the rotation of the whole body-fixed axis of the molecule, and all the vibration of the molecule in the intra-molecular coordinates.

So, after the separation, the rigid rotor Hamiltonian is:

$$H_{rot} = \hbar^{-2}(A_e J_a^2 + B_e J_b^2 + C_e J_c^2),$$  \hspace{1cm} (2.16)

where the rotational constants are defined as

$$A_e = \hbar^2 \{[I^e]^{-1}\}^2_{aa}/(2hc),$$ \hspace{1cm} (2.17)

and likewise for $B_e$ and $C_e$. $\{[I^e]\}_{\alpha\beta}$ is an element of the momentum of the inertia matrix in its equilibrium configuration. The rotation axes of the molecule are ordered so that $A > B > C$. Now, using the $|J, k\rangle$ basis, for $J=1$ one can solve a 3x3
matrix with the matrix elements corresponding to the functions $|1, 1\rangle$, $|1, -1\rangle$ and $|1, 0\rangle$. After diagonalizing the rotational Hamiltonian in this basis, one ends up with the following matrix:

$$
\begin{bmatrix}
A+B & 0 & 0 \\
0 & A+C & 0 \\
0 & 0 & B+C
\end{bmatrix},
$$

(2.18)

where each element in the diagonal would correspond to a different $J=1$ energy level. Then, using the fact that $A > B > C$ the $J=1$ energy levels obtained in this work can be used to obtain the three rotational constants by solving for a 3x3 system of equations using the relations above.

### 2.2 Variational Principle

One popular tool used to calculate the energy levels for similar problems is the variational principle. In its most primitive form, the variational principle states that when using any test state $|\psi\rangle$, the expectation value of $H$ using said general $|\psi\rangle$ will be equal to or larger than the energy of the ground state of the system[15]:

$$
E_g \leq \langle \psi | H | \psi \rangle.
$$

(2.19)

Therefore, the state $|\psi\rangle$ can be expanded in any basis

$$
|\psi\rangle = \sum_i c_i |\phi_i\rangle,
$$

(2.20)

and the ground state energy can be approximated by changing the coefficients $c_i$ in the expansion until convergence is reached. So, using this expansion and a basis state
2.2. VARIATIONAL PRINCIPLE

on the left one obtains:

\[ \sum_{j+1}^{N} c_j \langle \phi_i | (H - E) | \phi_j \rangle = 0, \quad (2.21) \]

or using matrix elements:

\[ \sum_{j=1}^{N} c_j (H_{ij} - ES_{ij}) = 0 \quad i=1,2,\ldots,N, \quad (2.22) \]

where \( H_{ij} = \langle \phi_i | H | \phi_j \rangle \) are the matrix elements of the Hamiltonian in that basis and \( S_{ij} = \langle \phi_i | \phi_j \rangle \) are elements of the overlap matrix in that basis. When using an orthogonal basis, the matrix S becomes the identity matrix.

This principle was generalized for excited states and proved independently by MacDonald[16] and Hylleraas and Undheim[17], who showed that when using a full variational basis and even when obtaining multiple eigenvalues, all the eigenvalues obtained will be upper bounds for the real eigenvalues, including excited states. So, for all eigenstates, the problem can be represented by the generalized eigenvalue problem:

\[ HU = SUE, \quad (2.23) \]

where U is a matrix of coefficients, where each column is equal to the coefficients \( c_j \) of the expansion and E is a diagonal matrix where each element in the diagonal corresponds to the energy of a specific state. In this thesis, only orthogonal basis functions were used, and the problem is reduced to a regular eigenvalue problem.
2.3 Coordinate System

The coordinate system used in this thesis for both the 4-D intermolecular potential and to calculate the spectrum of CO-CO$_2$ are shown in figure 2.1. The $\vec{r}_1$ vector is aligned with the CO monomer and points from the C atom to the O atom, $\vec{r}_2$ is aligned with the CO$_2$ monomer, while $\vec{r}_0$ is a vector pointing from the center of mass of CO to the center of mass of CO$_2$. $r_0$ is the length of the $\vec{r}_0$ vector. $\theta_1$ and $\theta_2$ are the angles between $\vec{r}_0$ and the vectors $\vec{r}_1$ and $\vec{r}_2$ respectively. The last coordinate is the dihedral (out-of-plane) torsional angle, $\phi_2$ which is the angle between the vectors $\vec{r}_0 \times \vec{r}_1$ and $\vec{r}_0 \times \vec{r}_2$.

2.4 Basis functions

The basis functions used in this thesis are

$$f_{a_0}(r_0)u_{l_1l_2m_2K}^{JMP}(\theta_1, \theta_2, \phi_2; \alpha, \beta, \gamma),$$

where $f_{a_0}$ is a discrete variable representation (DVR) function [18], $u_{l_1l_2m_2K}^{JMP}$ is a parity-adapted rovibrational function.[19, 14]

The next subsection will describe the choice for the stretch basis functions, while the following one will describe the angular basis functions of choice in this thesis.

2.4.1 Stretch Basis functions

The main tool used for the stretch basis functions is the DVR, which can be constructed using several different basis functions. This subsection will first describe a general DVR, and then outline the different options available and their role in this
2.4. BASIS FUNCTIONS

thesis.

2.4.1.1 Discrete Variable Representation

The DVR is a convenient representation for the stretch coordinates due to its ease of use.\[18\] The DVR can easily be obtained if one first expands functions in a set of basis functions that can be used for a Gaussian quadrature. Those basis functions can be defined as:

$$\phi_n(x) = \sqrt{\omega(x)}C_n(x), \quad (2.25)$$

where \(C_n(x)\) is the orthogonal polynomial, with its normalization constant included, and \(\omega(x)\) is the weight function. Therefore the orthonormality relations can be written as:

$$\delta_{ln} = \int_{x=a}^{x=b} \phi_l^*(x)\phi_n(x)dx, \quad (2.26)$$

$$\delta_{ln} = \sum_{\alpha=1}^{N} \frac{\omega_\alpha}{\omega(x_\alpha)}\phi_l^*(x_\alpha)\phi_n(x_\alpha), \quad (2.27)$$

where \(a\) and \(b\) are the lower and upper limits of the domain of integration for the quadrature, respectively, and \(N\) is the size of the basis. Likewise, the matrix elements for a coordinate \(x\) are:

$$X_{ln} = \int_{x=a}^{x=b} \phi_l^*(x)x\phi_n(x)dx, \quad (2.28)$$

$$X_{ln} = \sum_{\alpha=1}^{N} \frac{\omega_\alpha}{\omega(x_\alpha)}\phi_l^*(x_\alpha)\phi_n(x_\alpha)x_\alpha, \quad (2.29)$$
Then both equations can be written in matrix form, using the transformation matrix $T$, with matrix elements:

$$
T_{\alpha j}^T = \sqrt{\frac{\omega_\alpha}{\omega(x_\alpha)}} \phi_j(x_\alpha).
$$

(2.30)

Therefore equation (2.27) can be written as:

$$
I = TI^{DVR}T^T,
$$

(2.31)

and likewise matrix elements for coordinate $x$ can be obtained from:

$$
X = TX^{DVR}T^T,
$$

(2.32)

where $T$ is a square matrix, $T^T$ is its transpose, $I^{DVR}$ is a unit matrix labeled by the quadrature points and $X^{DVR}$ is a diagonal matrix of values $x$ at the quadrature points, which are the DVR points.

Therefore the orthonormality relations take the following form:

$$
T^\dagger T = TT^\dagger = I.
$$

(2.33)

Equation (2.32) can then be transformed using the last identity:

$$
T^T XT = X^{DVR}.
$$

(2.34)

The most important part of this transformation is that after it, the matrix representation of the $x$ coordinate is diagonal. In the case of a Gaussian quadrature, the diagonalization of $X$ generates Gaussian quadrature points as eigenvalues.
2.4. BASIS FUNCTIONS

Even when not using quadrature, a DVR basis can be generated from any representation as long as the Hamiltonian is known in that representation, and a transformation to diagonalize said representation is known. This is achieved by representing the coordinate in any basis of interest, and then diagonalizing it using equation (2.34). The following subsections describe some different DVR basis that can be used and their role in this thesis. A Sine DVR was used as a benchmark to test other DVRs, while a PODVR was discarded due to a poor efficiency and ultimately a Tridiagonal Morse DVR was used in this thesis.

2.4.1.1.1 Sine DVR

The Sine DVR is a general and flexible DVR basis with that only has one parameter besides its size, the range of the method. Because of this, it was initially used as a benchmark. It was ultimately not used as the stretch basis due to its big size.

The sine DVR uses the particle-in-a-box eigenfunctions as a basis:

\[ \phi_j(x) = \begin{cases} \sqrt{2/L} \sin\left(j\pi\left(x - x_0\right)/L\right) & \text{for } x_0 \leq x \leq x_{N+1}, \\ 0 & \text{else.} \end{cases} \]  

(2.35)

where \( L = x_{N+1} - x_0 \), and \( x_0 \) and \( x_{N+1} \) are the boundaries of the box.[20] As mentioned before, the biggest advantage of this basis is the reduced amount of parameters, as the only parameter that needs to be tuned is the range of the box; this makes it easy to use in a wide array of situations.
2.4. BASIS FUNCTIONS

2.4.1.1.2 Potential Optimized DVR (PODVR)

The Potential Optimized DVR (PODVR), which uses a model potential to create the basis was the second basis tested and compared to the sine DVR basis. The PODVR has the main advantage that it does not have any adjustable parameters, as it is generated by using the potential; however this basis was discarded at the end because its size was comparable to the benchmark Sine DVR basis used, most likely due to coupling with other coordinates.

An N point PODVR basis is obtained by approximating a good model potential along the coordinate being analyzed (often a cut along that coordinate, fixing all other values at equilibrium), and solving Schrödinger’s equation to get slightly more than N eigenfunctions for that coordinate; then the matrix representation of that coordinate for those eigenfunctions is diagonalized and only the first N eigenfunctions.[18, 21] This, however is not a Gaussian quadrature, and therefore is an approximation. However it has been found to be quite useful for multidimensional problems, as the PODVR points are concentrated in regions where the wavefunction has a significant amplitude. However PODVRs have shown poor results when coupling between coordinates is big because the model potential being solved only involves one coordinate and therefore it doesn’t take the coupling into account.[18]

2.4.1.1.3 Tridiagonal Morse DVR

The Tridiagonal Morse (TDM) DVR is the basis used through this thesis. It was chosen at the end due to its size when compared to the benchmark sine DVR basis, which is almost an order of magnitude bigger. However, this basis is harder to implement as it has 3 different adjustable parameters besides its size, but when properly
2.4. BASIS FUNCTIONS

adjusted the size reduction is noticeable.

This TDM DVR is generated using a orthogonal set of functions which tridiagonalizes the Morse oscillator Hamiltonian:

\[ \chi_n(z) = \left[ \frac{\alpha n!}{\Gamma(2\gamma + n + 1)} \right]^{1/2} z^{\gamma+1/2} \exp(-z/2) L_n^{2\gamma}(z), \]  

(2.36)

where

\[ z = \frac{2}{\alpha \hbar} (2\mu D)^{1/2} \exp[-\alpha (r - r_e)], \]  

(2.37)

and \( \mu \) is the reduced mass, \( r_e \) is the equilibrium bond length, \( \alpha \) and \( D \) are the Morse potential parameters and \( L_n^{2\gamma}(z) \) is an associated Laguerre polynomial, with \( \gamma > -1/2 \), but arbitrary.[21] This TDM DVR has several advantages, even when compared to another, more intuitive basis: the basis generated from the Morse oscillator eigenfunctions. The eigenfunctions of the Morse oscillator have proven to be very efficient, however the eigenvalues of this representation are not Gaussian quadrature points, and due to truncation, eigenfunctions in the continuum are not included, which leads to poor results for high-lying energy levels. On the other side, the tridiagonal Morse basis functions have the same weight function, and therefore they can be used for a Gaussian quadrature, while keeping the efficiency of the Morse oscillator eigenfunctions. The tri-diagonal Morse basis functions have also been shown to have good results when used as a basis for the stretch of a molecule.[21] Because of this, only a TDM DVR was used in this thesis. This representation also has simple matrix elements for \( Q \) (the coordinate being used) and \( P_q \) (the momentum operator).[21] Because of this, only the TDM DVR will be used in this research. The discrete variable
representation of the TDM basis is:

\[ \text{TDMDVR} H_{TDM} = T_{TDM}^t M T_{TDM}, \quad (2.38) \]

where

\[
M_{nn'}/\hbar c = \left\{ \begin{array}{c}
-\frac{\beta^2 \omega}{2} \left[ n + \left( \gamma + \frac{1}{2} \right)^2 + \left( \frac{1}{\beta^2} - \gamma - n - 1 \right) (2n + 2\gamma + 1) \right] + \frac{\omega}{2\beta^2} \delta_{nn'} \\
+ \frac{\beta^2 \omega}{2} \left\{ \left( \frac{1}{\beta^2} - \gamma - n \right) \times [n(n + 2\gamma)]^{1/2} \right\} \delta_{n,n'+1} \\
+ \frac{\beta^2 \omega}{2} \left[ \left( \frac{1}{\beta^2} - \gamma - n - 1 \right) [(n+1)(n+1 + 2\gamma)]^{1/2} \right] \delta_{n,n'-1}, \quad (2.39)
\end{array} \right.
\]

\( T_{TDM} \) is the transformation matrix that diagonalizes \( Q \), \( \beta = (-2x/\omega)^{-1/2}, x = -\frac{\alpha^2 h^2}{2\hbar \mu} \) and \( \omega \hbar c = \hbar \left( \frac{2\alpha^2 D}{\mu} \right)^{1/2} \). Which is to say, the T matrices can be obtained from diagonalizing \( Q \) in this basis.

In summary a sine DVR basis was generated, however it was only used as a benchmark due to its size. Then a PODVR was generated as an attempt to reduce the size of the stretch basis, however the efficiency increase was negligible. Finally a TDM DVR was fit for the stretch, and significant size reduction was achieved.

2.4.1.2 Angular basis functions

The functions used as a basis for the rotation and bends in this thesis are the parity-adapted basis functions. These basis functions are constructed as a linear combination of products of spherical-harmonic type functions and Wigner functions, and therefore share their properties; however this linear combination also makes it possible to calculate energy levels with even and odd parities separately. This subsection will
2.4. BASIS FUNCTIONS

first outline the original functions used to construct the parity adapted basis, then
the effect of the parity operator $E^*$ on this function will be described, and finally the
parity-adapted basis will be outlined.

Each term in this basis is the product of a basis function for the bends and another
basis function for the rotation:

$$|l_1l_2m_2; JMK⟩ = |l_1l_2m_2⟩ |JMK⟩ , \quad (2.40)$$

where $|l_1l_2m_2⟩$ are spherical-harmonic type functions and $|JMK⟩$ are symmetric top
functions:

$$⟨θ_1θ_2φ_2|l_1l_2m_2⟩ = Θ_l_1 l_2^{m_1}(θ_1)Y_m_2^{m_2}(θ_2, φ_2), \quad (2.41)$$

$$⟨αβγ|JMK⟩ = \sqrt{\frac{2J+1}{8π^2}}D_{MK}^{J}(α, β, γ), \quad (2.42)$$

$$⟨αβγ|JMK⟩ = \sqrt{\frac{2J+1}{8π^2}}e^{i(Mα+Kγ)}d_{MK}^{J}(β), \quad (2.43)$$

and

$$Y_l_i^{m_1}(θ_i, φ_i) = \frac{1}{\sqrt{2π}}Θ_l_i^{m_1}(θ_i)e^{im_iφ_i}, \quad (i = 2, 3). \quad (2.44)$$

$D_{MK}^{J}$ are Wigner functions, $α, β, γ$ are Euler angles and $P = 0, 1$ correspond to even
and odd parities. $Θ_l_i^{m_1}(θ)$ are normalized associated Legendre functions with the $(-1)^m$
Condon-Shortley phase factor already included. $M$ and $K$ are quantum numbers
for the projection of the total angular momentum on the space-fixed $Z$ axis and the
body-fixed $z$ axis respectively. $m_1$ is not associated with any coordinate and instead
follows the next equation:

$$m_1 ≡ K - m_2. \quad (2.45)$$
Now in order to get a parity-adapted basis function from the product basis introduced in equation 2.40 first the effect of $E^*$, the parity operator, on an arbitrary function of the rovibrational coordinates has to be known. It can be found that:

$$E^* f(\theta_1, \theta_2, \phi_2; \alpha, \beta \gamma) = f(\theta_1, \theta_2, -\phi_2; \alpha + \pi, \pi - \beta, \pi - \gamma).$$  \hspace{1cm} (2.46)$$

Now, from this general expression, the effect of the parity operator on the basis functions described in equation (2.40) is:

$$E^* |l_1 l_2 m_2; JMK\rangle = (-1)^J |l_1 l_2 \bar{m}_2; JM \bar{K}\rangle,$$

where $\bar{m}_2 \equiv -m_2$ and $\bar{K} \equiv -K$. So, knowing the effect of parity on the basis functions, a final parity adapted basis can be found as a linear combination of the original functions in equation (2.40):

$$u^{JMP}_{l_1 l_2 m_2 K} = N_{m_2, K} \frac{1}{\sqrt{2}} \left[ |l_1 l_2 m_2; JMK\rangle + (-1)^{J+P} |l_1 l_2 \bar{m}_2; JM \bar{K}\rangle \right],$$  \hspace{1cm} (2.48)

where

$$N_{m_2, K} = \frac{1}{\sqrt{1 + \delta_{m_2,0} \delta_{K,0}}}.$$  \hspace{1cm} (2.49)$$

where $P = 0, 1$, corresponding to even and odd parity respectively. The number of functions from Eq. 2.40 must be the same as the number of parity-adapted basis functions, which means there must be some restrictions on the ranges of the quantum numbers for the parity-adapted basis. The restrictions are as follows:

$$K \in [0, J],$$  \hspace{1cm} (2.50)
2.5. LANCZOS ALGORITHM

\[ m_2 \in [0, m_{\text{max}}] \quad (K = 0), \quad (2.51) \]
\[ m_2 \in [-m_{\text{max}}, m_{\text{max}}] \quad (K \neq 0), \quad (2.52) \]

while also excluding the combination \((-1)^{J+P} = -1\) and \(m_2 = K = 0\), where \(m_{\text{max}}\) is the maximum value of \(m_2\).

2.5 Lanczos Algorithm

After defining the representation that is going to be used for the Schrödinger equation, a solution needs to be found for the equation. In small systems the Hamiltonian matrix can be directly diagonalized, but for bigger systems the storage and processing power needed for a direct method might be too large and therefore those methods are unpractical. Because of this, iterative methods like the Lanczos method[22] are used due to the fact that they don’t need to store the full matrix.[23]

The algorithm has been slightly modified since its inception in order to stabilize it and for a matrix \(A\) it is defined as[24]:

**Initialization**

Choose an arbitrary vector \(v_1\) so that \(|v_1| = 1\).
- \(\beta_1 = 0, \quad v_0 = 0\)
- for \(j = 1, \ldots, m\)
  - \(w_j = Av_j - \beta_j v_{j-1}\)
  - \(\alpha_j = w_j^T v_j\)
  - \(w_j = w_j - \alpha_j v_j\)
  - \(\beta_{j+1} = |w_j|\)
  - \(v_{j+1} = \frac{w_j}{\beta_{j+1}}\)
end for

A $m \times m$ tri-diagonal matrix $T$ is obtained as a result of this procedure, the elements of the main diagonal are $\alpha_j$, while the elements of the first subdiagonal and first super diagonal are $\beta_j$. Then the transformation matrix $V$ would be the matrix with columns $v_j$, such that $T = V^*AV$. Once this transformation is done, one can obtain the eigenvalues from this new tri-diagonal matrix.

For large but sparse matrices the Lanczos method offers two advantages. First, the matrix that is to be tri-diagonalized only enters the algorithm through its product with the vectors $v_i$, therefore only a routine that calculates the product of the matrix $A$ with a vector $\vec{x}$ is needed, as opposed to the storage of the complete matrix. The other main advantage is that a basic Lanczos recursion only needs the two most recently generated Lanczos vectors which can save even more storage space.[23]

The algorithm has some other features, for instance it approximates eigenvalues in both extremes of the spectrum better than the values in the middle.[25] One of the biggest problems with the Lanczos algorithm is that although convergence of the algorithm has been proved in exact arithmetic[26] the algorithm presents some losses of orthogonality in the Lanczos vectors when using non-exact arithmetic[23], these losses make the exact arithmetic proof invalid for numerical calculations. However, in his PhD thesis Paige[27] explained the losses in orthogonality and eventually some alternatives were developed.[28, 29, 30, 31, 23] Still, in this thesis the basic Lanczos procedure is used as it is sufficient for this approach.

Those losses of orthogonality in a numerical implementation of the Lanczos algorithm introduce some extra eigenvalues are introduced, often called "spurious". These eigenvalues can either replicate the real eigenvalues or they might move to completely
2.5. LANCZOS ALGORITHM

Different parts of the spectrum once the matrix is enlarged.\cite{30} In order to identify spurious eigenvalues one can reduce the rank of the tri-diagonal matrix by removing its first column and row, and then obtaining the eigenvalues for this new trimmed matrix. Finally, the new eigenvalues can be compared to those of the original matrix; every eigenvalue of the trimmed matrix that is also an eigenvalue of the original matrix is labeled spurious and discarded.\cite{30}

There are various ways to exploit symmetry, for example constructing symmetry adapted basis functions.\cite{32} In most cases this is not convenient due to the fact that the matrix vector products are more efficient if the basis is a product basis\cite{33,34} and this is not often the case\cite{32}, however in this work the basis used is a pure product basis and therefore a direct approach can be used.

2.5.1 Matrix-Vector Products

The Matrix-Vector products are then a crucial part of what makes the Lanczos algorithm a more efficient scheme to obtain eigenvalues than the traditional, direct approaches. This products are usually the most expensive part of the algorithm, however if the basis used is a product basis:

\[
B(x_1, x_2, \ldots, x_f) = \prod_{k=1}^{f} b_k(x_k),
\]

(2.53)

where \(b_i(x_i)\) is a basis function in one dimension, and the Hamiltonian can be written in a sum of products form:

\[
\hat{H} = \sum_{l=1}^{g} \prod_{k=1}^{f} \hat{h}^{(k,l)}(x_k),
\]

(2.54)
where $\hat{h}(k,l)$ are functions of one coordinate, then the products can be performed more efficiently. So, the Hamiltonian is a sum of $g$ terms which in turn are products of $f$ single variable functions. The KEO discussed previously in section 2.1.2 that was used in this work has this kind of factorizability, therefore the full matrix elements of the KEO are never calculated and only the one-dimensional matrix elements of the KEO are needed.

Using equations (2.54) and (2.53), a matrix vector product of the Hamiltonian $\hat{H}$ and a vector $u$ can be performed as a sum over all coordinates as:

$$\hat{H}u_{i_1,i_2,...,i_f} = \sum_{l=1}^{g} \sum_{i_1}^{n_1} \sum_{i_2}^{n_2} \cdots \sum_{i_N}^{n_N} h_{i_1,l}^{(1,l)} h_{i_2,l}^{(2,l)} \cdots h_{i_f,l}^{(f,l)} u_{i_1,i_2,...,i_f} = u'_{i_1,i_2,...,i_f},$$  \hspace{1cm} (2.55)

which can then be reordered into:

$$\sum_{l=1}^{g} \sum_{i_1}^{n_1} h_{i_1,l}^{(1,l)} \sum_{i_2}^{n_2} h_{i_2,l}^{(2,l)} \cdots \sum_{i_f}^{n_N} h_{i_f,l}^{(f,l)} u_{i_1,i_2,...,i_f} = u'_{i_1,i_2,...,i_f}. \hspace{1cm} (2.56)$$

When using this approach, one performs the sums sequentially, starting from right to left, and storing the result to use it in the next sum. This reordered version has a much more favorable scaling than the original, direct approach. Assuming each coordinate has the same amount of basis functions $n_N = n$, this method has a scaling of $n^{f+1}$, compared to the usual $n^{2f}$ scaling.[13]

The KEO terms usually have this structure and therefore this scheme can be used, however, the potential doesn’t usually have this sum of products form. So, the potential matrix elements are defined using quadrature:
\[ \langle u_{l_1,l_2,m_2}^{JMP} | V | u_{l_1,l_2,m_2}^{JMP} \rangle = \sum_{\alpha_1,\alpha_2} T_{l_1,\alpha_1}^{(m_1')} T_{l_2,\alpha_2}^{(m_2')} f_{\alpha_1,\alpha_2}^{m_1,m_2} I_{l_1,\alpha_1}^{m_1} T_{l_2,\alpha_2}^{(m_2)} , \]  

(2.57)

where \( V \) is the potential, \( I \) is the integral of the potential over \( \phi_2 \) and the \( T \) matrices are defined as:

\[ T_{l_\alpha}^{(m)} = \sqrt{w_\alpha} \Phi_{l}^{m}(z_\alpha), \]

(2.58)

using Gauss-Legendre quadrature points, with weights \( (z_\alpha, w_\alpha) \) and basis function numbers \( l_\alpha \). Finally, the matrix-vector product is:

\[ Vx = x_{l_1,l_2,m_2}' = \sum_{\alpha_1} T_{l_1,\alpha_1}^{(m_1')} \sum_{\alpha_2} T_{l_2,\alpha_2}^{(m_2')} \sum_{m_2} f_{\alpha_1,\alpha_2}^{m_1,m_2} \sum_{l_1} T_{l_1,\alpha_1}^{(m_1)} \sum_{l_2} T_{l_2,\alpha_2}^{(m_2)} x_{l_1,l_2,m_2}. \]

(2.59)

This product is performed sequentially in a similar way to the KEO matrix-vector product. The integrals \( f_{\alpha_1,\alpha_2}^{m_1,m_2} \) can be performed using a Fast Fourier Transform (FFT). \cite{35}
Chapter 3

Potential Energy Surface

In this thesis a 4-D \textit{ab initio} Potential Energy Surface (PES) for CO-CO\textsubscript{2} on the same coordinates described in section 2.4 was used. This PES was generated by Richard Dawes and Ernesto Quintas-Sánchez from Missouri University of Science and Technology\cite{11} using an automated interpolating moving least squares method recently released as a software package under the name AUTOSURF.\cite{36, 37}

In order to generate this surface, the bond lengths for CO and CO\textsubscript{2} were held rigid, as well as the bond angle for CO\textsubscript{2}. The bond length $r_1$ for CO is 1.1282 Å as in previous works\cite{38, 39} which corresponds to a rotational constant of $B = 1.9317$ cm\textsuperscript{-1}.\cite{38, 40} Meanwhile, CO\textsubscript{2} is a linear monomer, and both bonds have the same distance $r_{CO} = 1.162086$ Å, which corresponds to the rotational constant 0.39021894 cm\textsuperscript{-1}.\cite{41, 42} The mass for $^{16}$O was 15.9949146221 u while the mass for $^{12}$C was 12 u.

A plot of the PES can be found in figure 3.1. This plot only shows planar configurations, when $\phi_2 = 0^\circ$ or $180^\circ$, by using extended coordinates $(\tilde{\theta}_1, \tilde{\theta}_2)$. This plot optimizes the intermolecular distance, $r_0$ to minimize the energy. These extended coordinates are similar to ones used previously,\cite{39} however in this previous work they
Figure 3.1: Potential Energy Surface (PES) plot of CO-CO$_2$ using extended angles $\tilde{\theta}_1$ and $\tilde{\theta}_2$, with $r_0$ optimized to get the lowest energy. The two minima, "TC" (T-shaped, C-atom in) and "TO" (T-shaped, O-atom in) are highlighted in the plot, and a visual representation of both configurations are highlighted and shown. The saddle points TS (the saddle point for the geared path) and TS$^*$ (the saddle point for the anti-geared path) are highlighted and shown as well. The geared path for the molecule is highlighted with a dashed curve, this path takes the molecule through TC, TS$^c$, TO$^c$, TO and TS to go back to TC. Reprinted from [11], with the permission of AIP Publishing.

had a range from $-180^\circ$ to $180^\circ$, while a range from $0^\circ$ to $360^\circ$ shows the wavefunctions more clearly. This modified extended coordinates are defined in Figure 2.1.

As it can be seen in Figure 3.1, the extended coordinates can show the full planar cyclical motion that CO-CO$_2$ goes through. There it can be seen that CO-CO$_2$ goes through the global minimum (TC), TS$^c$, the secondary minimum (TO$^c$), TO and TS
Figure 3.2: Definition of the extended angles \( \tilde{\theta}_1 \) and \( \tilde{\theta}_2 \), which are modified from a previously defined and similar set of extended angles.\[39\] The previously defined angles were defined in a range from \(-\pi\) to \(\pi\), while this modified extended angles are defined from 0 to \(2\pi\). The new quadrants \( \Pi' \), \( \Pi'' \), \( \Pi''' \) can be obtained from the previously defined quadrants \( \Pi \), \( \Pi' \), \( \Pi'' \) of a previous work\[39\] In each quadrant a wavefunction \( \Psi(\theta_1, \theta_2, \phi_2, \gamma) \) is shown, where \( \theta_1 \), \( \theta_2 \) and \( \phi_2 \) are the angles defined in Figure 2.1 and \( \gamma \) is an Euler angle. From this figure, one can obtain the extended angles by equating the first or second arguments of the wavefunction to the extended angles. For example, for the top right quadrant, \( \tilde{\theta}_1 = 2\pi - \theta_1 \) and \( \tilde{\theta}_2 = 2\pi - \theta_2 \). Reprinted from [11], with the permission of AIP Publishing.

before returning to TC. This path can be easily followed in extended coordinates, although one must exit the plot and re-enter it two times, using the usual 0° to 180° would split the minima and increase the number of times the plot must be exited and re-entered in order to show the full cycle. However, using extended coordinates makes every point appear twice in the plot in Figure 3.1.

It should also be noted that due to CO\(_2\)'s symmetry, the top half of the plot is equivalent to the bottom half, while the right half is equivalent to the left half.
due to the definition of the extended coordinates. This path is mostly along the geared coordinate \( Q_g = \theta_1 + \theta_2 \), and as it will be seen later, this coordinate is very relevant in CO-CO\(^2\)'s motion. Likewise, there is a secondary path along the anti-g geared coordinate \( Q_a = \theta_1 - \theta_2 \), however it is less relevant due to its steepness and higher energy barrier. This geared and anti-g geared paths are common in Van der Waals dimers.[43, 44, 45, 46] However in those cases the minima was slipped parallel, as opposed to the T-shaped minima of CO-CO\(^2\).

Figure 3.3 shows two other PES plots in which an out-of-plan path between TC and TO can be observed. Figure 3.3 a shows a \( \theta_1, \phi_2 \) plot, with \( \theta_2 \) fixed at its equilibrium value and \( r_0 \) optimized to reduce the potential, with the restriction that \( r_0 \) should be between its equilibrium values at TC and TO. This restriction is placed in order to show a clear path between both isomers. Figure 3.3 b shows a \( \theta_1, \theta_2 \) plot with \( \phi_2 \) fixed at 90\(^\circ\) and \( r_0 \) optimized under the same restriction as Figure 3.3 a. Both figures show the same path from TC to TO, in which \( \phi_2 \) is fixed at 90, \( \theta_2 \) is fixed at equilibrium and \( \theta_1 \) changes from 180\(^\circ\) to 0\(^\circ\), going from TC, to an "X-shaped" configuration labeled X, and into TC.

It can be seen that in planar configurations, when \( \phi_2 = 0^\circ \) or 180\(^\circ\), \( \theta_1 \) and \( \theta_2 \) are coupled in the geared or anti-g geared coordinate. However, when the molecule is not restricted to in-plane shapes, when \( \phi = 90^\circ \), \( \theta_1 \) and \( \theta_2 \) completely de-couple. This in-plane coupling could be due to each monomer "pushing" each other when they are in the same plane, while when out-of-plane each monomer would not obstruct each other. This kind of out-of-plane path might be present in some other T-shaped Van der Waals molecules.

Table 5.2 shows all relevant minima, TC and TO, as well as all relevant saddle
Figure 3.3: PES plots which show the out-of-plane path for CO-CO$_2$. a) A PES as a function of $\theta_1$ and $\phi_2$, with the fixed value $\theta_2 = 90^\circ$ and $r_0$ optimized to minimize energy while restricted to be between the equilibrium values at TC and TO. P is a configuration in which both isomers are parallel to each other and in the same plane, with $\theta_1 = \theta_2 = 90^\circ$, while X labels an out-of-plane configuration where both monomers are in a "cross" shape. $\phi_2$ is only shown in a range from 0$^\circ$ to 180$^\circ$ due to symmetry in CO-CO$_2$, therefore only the symmetrically unique part of the PES is shown. $\phi_2$ is undefined at TC and TO, however when a small perturbation to $\theta_1$ is introduced so that $\theta_1 = 180^\circ - \epsilon$ or $0 + \epsilon$, the shape is close to TC and TO respectively, and any change in $\phi_2$ only produces a small change in configuration, which makes the potential flat at both the left and right sides of the plot. b) PES as a function of $\theta_1$ and $\theta_2$, with $\phi_2$ fixed at 90$^\circ$, and $r_0$ optimized to minimize the energy while restricted to be between the equilibrium values at TC and TO. Reprinted from [11], with the permission of AIP Publishing.

points: TS (the geared path’s saddle point), TS* (the anti-geared path’s saddle point) and X (the out-of-plane path’s saddle point). As it can be seen there, the geared path has the lowest barrier, followed by the out-of-plane path, while the anti-geared path has the highest energy barrier.

Figure 3.4 shows $r_0$ PES cuts through the stationary points shown in Figure 3.1. This plot shows the anisotropy of the interactions, because of this anisotropy the
Table 3.1: Energies for the minima and transition states shown in Figures 3.1 and 3.3. $E_{abs}$ are relative to the dissociation energy, while $E_{rel}$ are relative to TC, the minima. $\theta_1$, $\theta_2$, and $\phi_2$ are in degrees and $r_0$ is in Angström. Due to the definition of the coordinate system in Figure 2.1, when the molecule is in certain T-shaped configurations ($\theta_1 = 0^\circ$ or $180^\circ$ and $\theta_2 = 90^\circ$ or $270^\circ$), $\phi_2$ is undefined. Reprinted from [11], with the permission of AIP Publishing.

<table>
<thead>
<tr>
<th>Stat. Pt.</th>
<th>$\theta_1$, $\theta_2$, $\phi_2$, $r_0$</th>
<th>Ab initio $\theta_1$, $\theta_2$, $\phi_2$, $r_0$[5]</th>
<th>$E_{abs}$ (cm$^{-1}$)</th>
<th>$E_{rel}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>(180, 90, -, 3.868)</td>
<td>(180, 90, -, 3.957)</td>
<td>-398.3</td>
<td>0</td>
</tr>
<tr>
<td>TO</td>
<td>(0, 90, -, 3.534)</td>
<td>(0, 90, -, 3.610)</td>
<td>-297.8</td>
<td>100.43</td>
</tr>
<tr>
<td>TS</td>
<td>(90, 180, 0, 4.434)</td>
<td></td>
<td>-180.0</td>
<td>218.3</td>
</tr>
<tr>
<td>X</td>
<td>(90, 90, 90, 3.529)</td>
<td></td>
<td>-150.1</td>
<td>248.2</td>
</tr>
<tr>
<td>TS*</td>
<td>(92, 76, 0, 6.951)</td>
<td></td>
<td>-97.5</td>
<td>300.8</td>
</tr>
</tbody>
</table>

The potential had to be symmetrized to be numerically exact on the permutation of two O-atoms in CO$_2$. When symmetrizing, the largest difference in the quadrature grid between points that should be exact due to this symmetry was 0.0076904 cm$^{-1}$. 
Figure 3.4: $r_0$ cuts through the PES for relevant configurations, shown in Figures 3.1, 3.3 and Table 3.1. Reprinted from [11], with the permission of AIP Publishing.
Chapter 4

Ro-Vibrational Calculations

4.1 Computational details

The previously discussed Lanczos method is used with parity-adapted rovibrational functions and DVR functions in order to solve Schrödinger’s equation for CO-CO₂, following the example of previous works.[47, 48, 49, 50, 45, 51, 35, 52, 53] The rotational constant for CO is 1.9225125 cm⁻¹[54] and the rotational constant for CO₂ is 0.39021894 cm⁻¹.[44]

4.1.1 Parameter choice

The choice of parameters can be split in two parts, the stretch basis and the angular basis. First the process used to obtain the stretch basis will be described and afterwards the same will be done for the angular basis.

As it was mentioned in section 2.4.1, several different DVR basis were used for the stretch in this thesis. A sine DVR basis was first produced as a benchmark, then a PODVR basis was generated and discarded due to its size, and finally a TDM DVR basis was used for all calculations in this thesis.
The large sine DVR basis used as a benchmark for the stretch basis was built so that the change in energy for all energy levels below 140 cm\(^{-1}\) above the zero point energy (ZPE) when increasing the basis size was below .0001 cm\(^{-1}\). This error size was chosen so that it was the same as the errors for the rotational constants obtained experimentally.[55, 56] The final size of the benchmark sine DVR basis was 150 and its range was defined in the range (5.0 Bohr, 38.0 Bohr).

After the benchmark was produced, two different DVRs were generated in an attempt to reduce the basis size. Those two basis were compared to the sine DVR benchmark and only accepted if all levels below below 140 cm\(^{-1}\) above the zero point energy (ZPE) had a maximum error of .0001 cm\(^{-1}\) with respect to the benchmark. The first basis tested was a PODVR, however this basis didn’t converge with respect to the benchmark until its size was close to the benchmark, and so it was discarded. As it was mentioned in section 4 , this could be due to a strong coupling between the stretch and other coordinates.

The final basis used for the stretch was a TDM DVR basis, which has three parameters: \(D_e\), \(\omega\), and \(r_e\). The initial values for \(D_e\), \(\omega\) and \(r_e\) were obtained from an \(r_0\) cut with the rest of the coordinates fixed at equilibrium. After those initial values were obtained, \(\omega\) and \(r_e\) were manually optimized until the error for all energy levels below 140 cm\(^{-1}\) above the ZPE with respect to the benchmark was smaller than .0001 cm\(^{-1}\). After optimization, the final TDM DVR basis has 20 functions with \(D_e = 398\) cm\(^{-1}\), \(\omega = 54.5\) cm\(^{-1}\) and \(r_e = 6.85\) Bohr and uses \(\alpha = A - 2[A/2] = 0.606\), with \(A = 4D_e/\omega_e\) so that all the bound states of the Morse Hamiltonian are exactly reproduced by the TDM basis.[21]
For the angular basis $u_{l_1 l_2 m_2 K}^{IMP}$ that was described in section 2.4.1.2 a similar procedure to the one used for the sine DVR basis was followed. The size of the basis was slowly increased until the change in energy for all energy levels below 140 cm$^{-1}$ above the zero point energy (ZPE) when increasing the basis size was below .0001 cm$^{-1}$. The final parameters of the angular basis were $l_{max} = m_{max} = 45$ and the size of the J=0 A+ basis is about 329,000 functions.

$N_{\theta_1} = N_{\theta_2} = 46$ Gauss-Legendre quadrature points were used to compute the integrals in the potential, explained in section 2.5.1. Also, a potential ceiling of $V_{ceil} = 2098.4$ cm$^{-1}$ was used in order to accelerate Lanczos convergence and to reduce the spectral range of the Hamiltonian matrix.

### 4.1.2 Other details

The calculations were performed using the Lanczos algorithm, which was discussed in section 2.5, using the RV4 Code.[50]

The full permutation-inversion group[8] of CO-CO$_2$ is $G_4$, which has four irreducible representations labeled A+, A-, B+ and B-. A and B label states that are symmetric or anti-symmetric under permutation of the two O atoms in CO$_2$ respectively, while + and - label even or odd parity levels respectively.

Due to this symmetry, the basis in equation 2.24 can be A/B symmetry adapted by restricting $l_2$ to be even or odd, respectively. The matrix-vector products used as a part of Lanczos algorithm are performed sequentially, as was explained in section 2.5.1.

All calculations were performed using a computer with an AMD Opteron(tm) Processor 6386 SE CPU. The computation of the J=0, A+ levels took 4.36 hours of
4.1. COMPUTATIONAL DETAILS

CPU time and a maximum of .64 GB of memory during the computations.
Chapter 5

Results

5.1 Historical context

As it was seen in figure 3.1, this isomer has two relevant configurations, both of which are T-shaped and have been studied in the past. Legon and Suckley[4] were the first ones to study the C-bound isomer and were later followed by others.[57, 6] The higher-laying O-bound isomer was experimentally confirmed[56] after \textit{ab initio} calculations initially predicted its existence.[5] There are two experimentally observed inter-monomer transition frequencies, an in-plane transition and an out-of-plane state,[56, 55]

There is an in-plane state for both isomers that has been observed and its frequency measured, however it has only been labeled as "CO-rock/geared bend". In addition to this state, there are experimental measurements for the frequency of an out-of-plane state. The previous \textit{ab initio} results and experimental results have decent agreement, however for the higher lying O-bound isomer the agreement is poor.
Table 5.1: Energy levels for the C-bound and O-bound isomers with respect to the ZPE of the C-bound isomer. All levels that are localized in the O-bound well shown in figure 3.1 have their energies with respect to the O-bound isomer's ZPE in parentheses; likewise, their quantum numbers are preceded by a 2 to indicate that they correspond to this isomer. The number in front of the symmetry label is a cardinal number. The quantum numbers used are $v_g$ for the geared states, $v_a$ for the anti-geared states, $v_t$ for the CO libration states and $v_s$ for the stretch states. Reprinted from [11], with the permission of AIP Publishing.

<table>
<thead>
<tr>
<th>$E (E_{O-bound})$ [cm$^{-1}$]</th>
<th>n-sym</th>
<th>$(v_g,v_a,v_t,v_s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000</td>
<td>1A+</td>
<td>(0,0,0,0)</td>
</tr>
<tr>
<td>24.4546</td>
<td>1B+</td>
<td>(1,0,0,0)</td>
</tr>
<tr>
<td>44.5664</td>
<td>1B-</td>
<td>(0,0,1,0)</td>
</tr>
<tr>
<td>47.3698</td>
<td>2A+</td>
<td>(2,0,0,0)</td>
</tr>
<tr>
<td>50.2140</td>
<td>3A+</td>
<td>(0,0,0,1)</td>
</tr>
<tr>
<td>64.4973 (0.0000)</td>
<td>4A+</td>
<td>2(0,0,0,0)</td>
</tr>
<tr>
<td>68.2473</td>
<td>1A-</td>
<td>(1,0,1,0)</td>
</tr>
<tr>
<td>68.8211</td>
<td>2B+</td>
<td>(3,0,0,0)</td>
</tr>
<tr>
<td>70.0601</td>
<td>3B+</td>
<td>(1,0,0,1)</td>
</tr>
<tr>
<td>79.1763 (14.6790)</td>
<td>4B+</td>
<td>2(1,0,0,0)</td>
</tr>
<tr>
<td>86.0042</td>
<td>5A+</td>
<td>(0,0,2,0)</td>
</tr>
<tr>
<td>87.9203</td>
<td>6A+</td>
<td>(4,0,0,0)</td>
</tr>
<tr>
<td>88.6163 (24.12)</td>
<td>2B-</td>
<td>2(0,0,1,0)</td>
</tr>
<tr>
<td>89.5665</td>
<td>5B+</td>
<td>(0,1,0,0)</td>
</tr>
<tr>
<td>90.2245</td>
<td>3B-</td>
<td>(2,0,1,0)</td>
</tr>
<tr>
<td>90.7751</td>
<td>7A+</td>
<td>(2,0,0,1)</td>
</tr>
<tr>
<td>92.3644</td>
<td>4B-</td>
<td>(0,0,1,1)</td>
</tr>
<tr>
<td>94.1768 (29.6795)</td>
<td>8A+</td>
<td>2(2,0,0,0)</td>
</tr>
<tr>
<td>96.2892</td>
<td>9A+</td>
<td>(0,0,0,2)</td>
</tr>
<tr>
<td>104.5450 (40.0477)</td>
<td>2A-</td>
<td>2(1,0,1,0)</td>
</tr>
<tr>
<td>104.9504</td>
<td>6B+</td>
<td>(5,0,0,0)</td>
</tr>
<tr>
<td>107.7748 (43.2775)</td>
<td>10A+</td>
<td>2(0,0,0,1)</td>
</tr>
<tr>
<td>107.9768</td>
<td>7B+</td>
<td></td>
</tr>
<tr>
<td>109.7627</td>
<td>3A-</td>
<td>(3,0,1,0)</td>
</tr>
<tr>
<td>110.1747 (45.6774)</td>
<td>8B+</td>
<td>2(3,0,0,0)</td>
</tr>
<tr>
<td>110.6554</td>
<td>9B+</td>
<td></td>
</tr>
<tr>
<td>111.7702</td>
<td>4A-</td>
<td></td>
</tr>
<tr>
<td>112.9367</td>
<td>10B+</td>
<td>(1,0,0,2)</td>
</tr>
<tr>
<td>113.3010 (48.8039)</td>
<td>11B+</td>
<td>2(0,1,0,0)</td>
</tr>
<tr>
<td>114.0523 (49.5550)</td>
<td>11A+</td>
<td>2(0,0,2,0)</td>
</tr>
<tr>
<td>114.2612</td>
<td>12A+</td>
<td></td>
</tr>
<tr>
<td>119.8673</td>
<td>13A+</td>
<td></td>
</tr>
<tr>
<td>120.6303 (56.1330)</td>
<td>5B-</td>
<td></td>
</tr>
<tr>
<td>123.3091</td>
<td>6B-</td>
<td>(0,0,3,0)</td>
</tr>
</tbody>
</table>
5.2 Vibrational levels

Table 5.1 shows the energy levels obtained for both isomers, as well as their symmetries and their quantum numbers. The energies of the states localized in the O-bound well with respect to the ZPE of that isomer are shown in parentheses. This energies in parentheses can be directly compared with experimental results for the transition frequencies of the O-bound isomer. The ZPE of the C-bound isomer is -286.90 cm$^{-1}$, which is 111.383 cm$^{-1}$ higher than the global minima, shown in Figure 3.1 and Table 3.1.

All assignments were made using 1D and 2D probability distribution (PD) and wavefunction (WF) plots. The PD plots were produced by integrating over the remaining 2 or 3 coordinates for the 2D and 1D PD plots, respectively. The plots were examined, and its nodal structure was used to produce the labels. Likewise, the energies of the fundamentals were used to label states. For example, once the first geared state was found to have an energy of 45.4546 cm$^{-1}$, the second state was looked for at around twice that value, 90.9092 cm$^{-1}$. Finally, symmetry was also used to confirm assignments, by using the product rules for the $C_{2v}$ group so that, for example, a state labeled $\nu_g + \nu_t$ would have a symmetry that is the product of the symmetries of both states, B+ and B-, therefore the symmetry for this state would be A-.

In general, WF plots were examined before the PD plots because the integration over the other coordinates might hide some crucial features of the state. This can be seen in Figure 5.1, were the state could be labeled as a CO$_2$ bend if only the PD plot is taken into account, due to the node at $\theta_2 = 90$, however the WF cuts reveal the real nature of this state. In the extended WF cut, which shows planar configurations, it can be seen that $\theta_1$ and $\theta_2$ are coupled in a geared bend, while the $\phi_2 = 90$ WF
cut shows that when constrained to this values this state does behave like a $\theta_2$ bend. This shows that $\theta_1$, $\theta_2$ and $\phi_2$ are strongly coupled, and this nuanced behavior is not shown in the PD, which could lead to some mis-labeling. However, it should be noted that the uncoupled CO$_2$-rock is smaller, specially for higher energy states, this is not clearly shown in the WF cuts due to the contour interval used to highlight the nodal structure for this states.

As it can be seen in Figure 3.1 and Table 3.1, the O-bound well is 100.5 cm$^{-1}$ higher than the global C-bound well. However, the ground state of the O-bound isomer is only 64.4973 cm$^{-1}$ higher than the O-bound ground state. This happens because the ZPE of the C-bound isomer is higher than its O-bound counterpart.

Another important observation from Table 5.1 is that the first geared state has an energy 65.1119 cm$^{-1}$ lower than the first anti-geared state. This can be explained by looking at Figure 3.1, where it can be seen that both wells are steeper in the anti-geared direction than in the geared direction. However, the first CO-libration also has a lower energy than the first anti-geared state, but still higher than the first geared state. This is also due to the steepness of the wells in the anti-geared direction.

As it was mentioned before, only the WF cuts show the true nature of the geared states, as shown in figure 5.1. This same phenomenum can be observed for the anti-geared states, shown in Figure 5.2. The PD plot does not have any nodes, however the extended WF cut shows the anti-geared nature of the state in planar configurations. And just like in the geared-state, at $\phi_2 = 90$ the bends becomes uncoupled and turns into a pure CO$_2$ bend at $\phi_2 = 90^\circ$. These geared states are very common in Van der Waals dimers (for example [58]), however the uncoupling of the bends as $\phi_2$ changes from planar configurations ($\phi_2 = 0, 180$) to out-of-plane configurations ($\phi_2 = 90$)
Figure 5.1: Probability Density (PD) and Wave Function (WF) plots for the first geared state of the C-bound isomer, with an energy of 24.4546 cm\(^{-1}\). a) PD plot for \(\theta_1\) and \(\theta_2\). b) WF cut using extended coordinates, and \(\vec{r}_0\) fixed at equilibrium. c) WF cut for \(\theta_1\) and \(\theta_2\) with \(\vec{r}_0\) fixed at equilibrium and \(\phi_2 = 90^\circ\). Reprinted from [11], with the permission of AIP Publishing.

Figure 5.2: PD and WF plots for the first anti-geared state of the C-bound isomer, with an energy of 89.5665 cm\(^{-1}\). a) PD plot for \(\theta_1\) and \(\theta_2\). b) WF cut using extended coordinates and \(\vec{r}_0\) fixed at equilibrium. c) WF cut for \(\theta_1\) and \(\theta_2\) with \(\vec{r}_0\) fixed at equilibrium and \(\phi_2\) fixed at 90°. Reprinted from [11], with the permission of AIP Publishing.

hadn’t been observed before.

Figure 5.3 shows extended WF cuts and \(\phi_2 = 90\) WF cuts for the ground state and the first 3 geared states. There the evolution of the nodal structure can be clearly appreciated, as the states become higher more nodes along the geared coordinate appear in the extended WF cuts, while more nodes along \(\theta_2\) appear in the \(\phi_2 = 90\) cut.

PD plots for CO-libration states can be found in Figure 5.4, which correspond to the \(\theta_1, \phi_2\) PES cut in figure 3.3. As shown there, there is an out-of-plane between
5.2. VIBRATIONAL LEVELS

Figure 5.3: WF cuts for the ground state [a) and b)] and the first 3 geared states [c) and d); e) and f); g) and h)] for the C-bound isomer. This states are ordered by their energies 0.0000, 24.4546, 47.3698 and 68.8211 cm$^{-1}$. All WF cuts on the left [a), c), e) and g)] are in extended coordinates to show the in-plane behavior of CO-CO$_2$, while the plots on the right use the normal $\theta_1$ and $\theta_2$ defined in Figure 2.1, with $\phi_2$ fixed at 90°, in order to show the out-of-plane behavior. All WF cuts on the right [b), d), f) and h)] use the normal $\theta_1$ and $\theta_2$ coordinates defined in Figure 2.1. $r_0$ is fixed at its equilibrium value, at TC. In order to clearly show the nodal progression in the out-of-plane WF cuts, the contour interval used for those plots is around half of the interval used for the extended coordinate WF cuts. Reprinted from [11], with the permission of AIP Publishing.
Table 5.2: Comparison for fundamental frequencies calculated in this work, in previous works[5] and found experimentally[55]. All energies are in cm$^{-1}$. Reprinted from [11], with the permission of AIP Publishing.

<table>
<thead>
<tr>
<th>Sym.</th>
<th>State</th>
<th>C-bound isomer</th>
<th>O-bound isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>B+</td>
<td>$v_g$</td>
<td>24.4546</td>
<td>24.30</td>
</tr>
<tr>
<td></td>
<td>$v_a$</td>
<td>89.5665</td>
<td>90.79</td>
</tr>
<tr>
<td>B-</td>
<td>$v_t$</td>
<td>44.5664</td>
<td>42.81</td>
</tr>
<tr>
<td>A+</td>
<td>$v_s$</td>
<td>50.2140</td>
<td>56.39</td>
</tr>
</tbody>
</table>

both wells along $\theta_1$ when $\phi_2 = 90$. As it can be seen in the PD plots, the amplitude of the states is the largest at $\phi_2 = 90$, and as the states become higher, the oscillation along $\theta_1$ become bigger and more focused on $\phi_2 = 90$. A similar behavior can be observed for isomer 2.

5.3 Results comparison

Table 5.2 shows the intermolecular frequencies obtained in this thesis, previous harmonic \textit{ab initio} results by Ford and co-workers[5] and experimental observations[55, 56] for different states for both isomers. As it can be seen there, there is good agreement between our calculations, previous harmonic calculations and experimental results for the C-bound isomer. However, the agreement between the previous theoretical results and experimental observations is poor for the O-bound isomer. Our results have good agreement even for this isomer. This could be due to anharmonicity in the higher laying O-bound well.

The experimental studies refer to the $v_g$ state as an in-plane rock[56, 55], indicating that the state could either be a coupled or de-coupled bend. As it was shown before, this state is geared at $\phi_2 = 0^\circ$ or $180^\circ$ but a CO$_2$ rock at $\phi_2 = 90^\circ$. 
Figure 5.4: PD plots for the ground state [a) and b)] and the first three out-of-plane states [c) and d); e) and f); g) and h)], with energies 0.0000, 44.5664, 86.0042 and 123.3091 cm$^{-1}$. All plots on the left [a), c), e) and g)] show PD plots as a function of $\theta_1$ and $\phi_2$, while all plots on the right [b), d), f) and h)] show PD plots as a function of $\theta_1$ and $\theta_2$. Like Figure 3.3, the range for $\phi_2$ has been limited to be between 0$^\circ$ and 180$^\circ$ due to the symmetry of CO$_2$. Reprinted from [11], with the permission of AIP Publishing.
5.4. Ro-vibrational levels

Table 5.3: Rotational energy levels and rotational constants for \( J=1 \) for the C-bound isomer, for the fundamental vibrational states \( v_g, v_a, v_t, v_s \). All energies are in cm\(^{-1}\) and are relative to the ZPE of the C-bound isomer. Reprinted from [11], with the permission of AIP Publishing.

<table>
<thead>
<tr>
<th>( J=0 ) level ((v_g, v_a, v_t, v_s))</th>
<th>( l_{01} ) (sym)</th>
<th>( l_{11} ) (sym)</th>
<th>( l_{10} ) (sym)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000 (0,0,0,0)(A+)</td>
<td>0.1165(A-)</td>
<td>0.4495(B-)</td>
<td>0.4584(B+)</td>
<td>0.3957</td>
<td>0.0627</td>
<td>0.0538</td>
</tr>
<tr>
<td>24.4546 (1,0,0,0)(B+)</td>
<td>24.5719(B-)</td>
<td>24.9044(A-)</td>
<td>24.9141(A+)</td>
<td>0.3960</td>
<td>0.0635</td>
<td>0.0538</td>
</tr>
<tr>
<td>44.5663 (0,0,1,0)(B-)</td>
<td>44.6838(B+)</td>
<td>45.0166(A+)</td>
<td>45.0250(A-)</td>
<td>0.3957</td>
<td>0.0630</td>
<td>0.0545</td>
</tr>
<tr>
<td>50.2140 (0,0,0,1)(A+)</td>
<td>50.3267(A-)</td>
<td>50.6631(B-)</td>
<td>50.6717(B+)</td>
<td>0.3971</td>
<td>0.0606</td>
<td>0.0521</td>
</tr>
<tr>
<td>89.5665 (0,1,0,0)(B+)</td>
<td>89.6798(B-)</td>
<td>89.9900(A-)</td>
<td>89.9984(A+)</td>
<td>0.3711</td>
<td>0.0609</td>
<td>0.0525</td>
</tr>
</tbody>
</table>

5.4 Ro-vibrational levels

\( J = 1 \) energy levels have been computed and labeled as shown in Tables 5.3 and 5.6. As it was mentioned before, because there are three close \( J = 1 \) levels that can be associated with each vibrational state. These states were assigned according to the results obtained in section 2.1.3 that apply to a prolate top. Tables 5.3 and 5.4 shows our labels and rotational constants for the C-bound and O-bound isomers respectively.

Then, Tables 5.5 and 5.6 show our rotational constants for the ground state, the first geared state and the first CO-libration states for the C-bound and O-bound isomers respectively, and compares them to previous experimental results[55, 56] and previous \textit{ab initio} results.[5] As it can be seen, our results have an excellent agreement with the experimental rotational constants, specially for the C-bound isomer. It should also be noted that our results are closer to experiment than the previous \textit{ab initio} results obtained by assuming that the molecule is rigid.
5.4. RO-VIBRATIONAL LEVELS

Table 5.4: Rotational energy levels and rotational constants for J=1 for the O-bound isomer, for the fundamental vibrational states \( v_g, v_a, v_t, v_s \). All energies are in \( \text{cm}^{-1} \) and are relative to the ZPE of the O-bound isomer. Reprinted from [11], with the permission of AIP Publishing.

<table>
<thead>
<tr>
<th>((v_g, v_a, v_t, v_s))</th>
<th>( l_{01} ) (sym)</th>
<th>( l_{11} ) (sym)</th>
<th>( l_{10} ) (sym)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000 (0,0,0,0)(A+)</td>
<td>0.1374(A-)</td>
<td>0.4593(B-)</td>
<td>0.4719(B+)</td>
<td>0.3969</td>
<td>0.0750</td>
<td>0.0624</td>
</tr>
<tr>
<td>14.6790 (1,0,0,0)(B+)</td>
<td>14.8185(B-)</td>
<td>15.1059(A-)</td>
<td>15.1197(A+)</td>
<td>0.3640</td>
<td>0.0767</td>
<td>0.0629</td>
</tr>
<tr>
<td>24.1190 (0,0,1,0)(B-)</td>
<td>24.258(B+)</td>
<td>24.6124(A+)</td>
<td>24.6234(A-)</td>
<td>0.4297</td>
<td>0.0753</td>
<td>0.0637</td>
</tr>
<tr>
<td>43.2775 (0,0,0,1)(A+)</td>
<td>43.4130(A-)</td>
<td>43.7998(B-)</td>
<td>43.8117(B+)</td>
<td>0.4605</td>
<td>0.0737</td>
<td>0.0618</td>
</tr>
<tr>
<td>48.8038 (0,1,0,0)(B+)</td>
<td>48.9381(B-)</td>
<td>49.2716(A-)</td>
<td>49.2896(A+)</td>
<td>0.4096</td>
<td>0.0761</td>
<td>0.0581</td>
</tr>
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</table>

Table 5.5: Comparison for rotational constants obtained in this work, previous experiments[55] and previously calculated[5], for the ground state, first geared and CO-libration states of the C-bound isomers. All energies are in \( \text{cm}^{-1} \). Reprinted from [11], with the permission of AIP Publishing.

<table>
<thead>
<tr>
<th>Ground State</th>
<th>( v_g )</th>
<th>( v_t )</th>
<th>Ab initio Equib.[5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.3957</td>
<td>0.3957</td>
<td>0.3957</td>
</tr>
<tr>
<td>B</td>
<td>0.0627</td>
<td>0.0628</td>
<td>0.0635</td>
</tr>
<tr>
<td>C</td>
<td>0.0538</td>
<td>0.0538</td>
<td>0.0538</td>
</tr>
</tbody>
</table>

Table 5.6: Comparison for rotational constants obtained in this work, previous experiments[56] and previously calculated[5], for the ground state, first geared and CO-libration states of the C-bound isomers. All energies are in \( \text{cm}^{-1} \). Reprinted from [11], with the permission of AIP Publishing.

<table>
<thead>
<tr>
<th>Ground State</th>
<th>( v_g )</th>
<th>( v_t )</th>
<th>Ab initio Equib.[5]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.3969</td>
<td>0.3972</td>
<td>0.3640</td>
</tr>
<tr>
<td>B</td>
<td>0.0750</td>
<td>0.0745</td>
<td>0.0767</td>
</tr>
<tr>
<td>C</td>
<td>0.0624</td>
<td>0.0621</td>
<td>0.0629</td>
</tr>
</tbody>
</table>
Chapter 6

Summary and Conclusions

6.1 Summary

Low-lying J=0 and J=1 levels for CO-CO$_2$ have been computed using the Lanczos algorithm with parity-adapted ro-vibrational basis functions and a TDM DVR. Fundamental frequencies for the geared and CO-libration states have good agreement with previous experiments for both the O-bound and C-bound isomers. The rotational constants obtained from the J=1 levels are also in good agreement with experiments.

Three relevant paths were found in the PES: the usual geared and anti-geared paths, but there is also an out-of-plane path for $\theta_1$ when $\phi_2 = 90$. The barrier for this out-of-plane path is still higher than it’s geared counterpart, however it’s lower than the anti-geared energy barrier. This kind of dynamics might be similar for other T-shaped Van der Waals dimers.

A state previously labeled as "CO-rock/geared bend" has now been properly labeled as a geared bend, however it should be noted that this state behaves as a geared bend when in-plane configurations, while it behaves like a pure CO$_2$ rock
when $\phi_2 = 90^\circ$ for both isomers. Likewise the CO-libration state has been confirmed.

6.2 Future Work

J>1 ro-vibrational levels could be computed. The main goal of this work was to provide an \textit{ab initio} spectrum of CO-CO$_2$ for experimental groups.

Likewise, after improving our understanding on how the coordinate system behaves when $\phi_2 = 90$ and $\theta_1 = 0,180$, some work with \textit{ab initio} techniques could be implemented on other molecules that presented the same CO-libration states in Venayagamoorthy and Ford’s work, CO-CS$_2$, CO-OCS and CO-CS$_2$.[5]
Bibliography


