The Potential Energy Surface of CO_2 from an algebraic approach

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Abstract

The potential energy surface for the ground state of the $^{12}C\ ^{16}O_2$ molecule is estimated through an algebraic approach based on unitary groups. It is shown that a purely algebraic approach may lead to a unphysical surface even when the fit turns out to be of a remarkable high quality. The vibrational description is obtained in the framework of the $U(2) \times U(3) \times U(2)$ model, where the $U(2)$ algebras are associated with the CO bond stretching and the $U(3)$ algebra with the OCO bending. The algebraic representation of the Hamiltonian is obtained through the connection between the coordinates and momenta and the generators of the dynamical algebra. It is shown that through this connection is possible to choose the appropriate set of spectroscopic parameters leading to the right Potential Energy Surface (PES). The fit from which the PES is estimated involves 101 energy levels with an standard deviation of $rms = 0.53$ cm^{-1}.

Keywords:CO_2, force constants, algebraic approach.

1. Introduction

Algebraic approaches to vibrational excitations of molecules have been a common alternative in recognition pattern techniques applied to spectroscopy [1, 2, 3]. They are particularly useful when the generation of the spectrum using integro-differential techniques to solve the Schrödinger equation implies a massive computing task [4]. These approaches, however, are often restricted to considering harmonic oscillator bases associated with vibrational normal modes. This type of basis has the disadvantage that a strong admixture of states are observed when the analysis is extended towards higher excited energy regions. However it possesses the clear advantage of keeping the connection with coordinates and momenta, providing the possibility of calculating the force constants.

An alternative approach, also within the harmonic oscillator basis, consists in considering a change to a local basis [5, 6, 7, 8]. This basis turns out to be more useful for two reasons. On the one hand it allows the results provided by the normal basis to be recovered when local harmonic oscillators are considered. On the other hand this choice opens the possibility of considering alternative bases, like Morse and/or Pöschl-Teller functions, which reflect more accurately the main physical properties of a pure local bond.

In any case, it may happen that several fits have the same accuracy level in the description of the vibrational spectrum. In such case there are two ways of evaluating the physical content of the parameters: by testing the wave functions through the description of the transition intensities or through the calculation of the molecular potential energy surface (PES) in order to compare with the result of other approaches, e.g. *ab initio* calculations. When the algebraic approach is based on a harmonic oscillator basis, both alternatives of parameter testing are potentially avaliable, but this may not be the case for other algebraic approaches where the connection with the configuration space is not given.

At the beginning of the eighties, a novel approach based on unitary algebras was proposed to describe the rovibrational spectra of molecules [9, 10]. This model was applied to triatomic and tetratomic molecules, with a particular success to linear molecules [11, 12, 13, 14]. From the original $U(4)$ vibron model for diatomic molecules, stems two other models, the one dimensional (1D) limit- $U(2)$ model- which turns out to be equivalent to the algebraic treatment of a 1D Morse or Pöschl-Teller oscillators [15, 16, 17], and the two dimensional (2D) limit- $U(3)$ model- which is particularly relevant for the description of bending modes of linear molecules [18]. Also the $U(3)$ model was demonstrated appropiate for molecular systems having a behavior between the rigidly linear and rigidly bent limits, in particular quasilinear and quasirigid molecular species [19, 20, 21, 22, 23]. The basic idea behind the use of models based on unitary algebras to describe physical systems with ν degrees of freedom consists in adding an extra boson to the ν physical bosons in such a way that the total number of bosons is kept constant. Thus, the total space is appropriately cut off, allowing the description of the system in terms of an irreducible representation of the dynamical algebra $U(\nu + 1)$. In this approach molecules are treated as a set of collective bosonic excitations, called vibrons [24].

In the different limits of the vibron model the introduction of the scalar boson hinders the connection with traditional approaches in phase space. Consequently, the vibron model is usually used as a phenomenological approach. The Hamiltonian is expanded in terms of the generators of the dynamical algebra, where Fermi and Darling-Dennison-like interactions have to be identified. In the framework of this phenomenological description, however, it could happen that more than one fit provide the same level of accuracy for the description of the vibrational spectrum. In such a case only the study of transition intensities can lead to the right physical spectroscopic parameters. However, when the feedback provided by infrared or Raman spectra is not available, the spectroscopic parameters could correspond to a local minimum, far from their true physical values. Hence, the connection of the algebraic approach with the space of coordinates and momenta becomes crucial to elucidate the physical values of the parameters. In the last ten years successful efforts to connect the molecular algebraic approaches based on unitary groups with their corresponding description in configuration space have been made by our group. Firstly the exact connection of the $U(2)$ model with the Morse and Pöschl-Teller potentials was established [15, 16, 17], allowing PESs to be estimated [25, 26, 27, 28, 29, 30]. Later on a connection was established between the $U(\nu+1)$ model of ν equivalent oscillators proposed by *Michelot and Moret-Bailly* [31] and the space of coordinates and momenta [32, 33, 34, 35]. More recently, an explicit connection between the $U(3)$ algebraic model, used to describe the bending degrees of freedom of linear triatomic molecules, and the configuration space was established [36, 37]. A summary of these efforts can be found in a recently published review [38].

Based on the explicit connection of the $U(3)$ algebraic model with the approaches expressed in terms of coordinates and momenta, it has been possible to calculate the PES from a fit to experimental data. In particular, results for the vibrational excitations of $^{12}CO_2$ in its electronic ground state have been presented [36]. A novel contribution of that work was that a local-mode model preserving the polyad was used to describe a molecule with a strong normal-mode behavior, taking advantage of the profits of the anharmonization approach that considers the anharmonicities from the outset [39]. In Ref. [36] a set of 101 experimental energies were fitted with a root mean square deviation of 0.53 cm^{-1}. This highly accurate description can be considered useful for the standards of high resolution molecular spectroscopy. From the spectroscopic parameters the PES was estimated. Because of the importance of this molecule, there are plenty of references in the literature where the $^{12}CO_2$ force constants have been computed, making possible their comparison between different approaches. Although in general the PES obtained was reasonable, the Fermi force constant value was far from the previous calculation of Chedin [40]. In this work we analyze this discrepancy, which has led to the search of another local minimum. In fact, two sets of spectroscopic parameter, having different values of the Fermi interaction similar in magnitude but with opposite signs, give rise to energy fits of the same quality. In this work we select between these two options by comparing force constants obtained using a different approach [40], focusing in particular **on** the Fermi force constant. The success of this analysis shows the importance of having access to the connection of the algebraic approach with the configuration space.

The outline of the present paper is the following. In Section §2 we briefly present the Hamiltonian in configuration space for a linear triatomic molecule. We then transform the Hamiltonian into a second quantization representation in terms of harmonic creation and annihilation operators defined from local or internal coordinates. The basic ingredients of the connection of the $U(2)\times U(3)\times U(2)$ model with configuration space together with the corresponding algebraic Hamiltonian are given in Section §3. Section §4 is devoted to the new analysis of the vibrational spectroscopic description of the CO_2 in its ground state. Finally, a summary and conclusions are presented in Section §5.

2. Hamiltonian for the CO_2 molecule

The approach to describe the vibrational excitations of the carbon dioxide usually consists in expanding the kinetic energy as well as the potential energy in terms of the symmetry coordinates

$$Q_{\Sigma_g} = \frac{1}{\sqrt{2}}\left(q_1+q_2\right), \qquad Q_{\Sigma_u} = \frac{1}{\sqrt{2}}\left(q_1-q_2\right) \quad , \tag{1a}$$

$$Q_{+} = -\frac{1}{\sqrt{2}}\left(q_a+iq_b\right), \quad Q_{-} = \frac{1}{\sqrt{2}}\left(q_a-iq_b\right) \quad , \tag{1b}$$

where the bond length displacements are denoted as $q_i = \Delta r_i = r_i - r_e$ where r_i is the i-th bond length and r_e is the equilibrium bond length for $i=1,2$. For the bends [41]

$$q_a = r_e\ \mathbf{e}_Y\cdot\frac{\mathbf{r_1}\times\mathbf{r_2}}{r_1 r_2} \quad , \quad q_b = -r_e\ \mathbf{e}_X\cdot\frac{\mathbf{r_1}\times\mathbf{r_2}}{r_1 r_2} \quad , \tag{2}$$

where $\mathbf{r_1}$ and $\mathbf{r_2}$ are vectors from the C-atom to each one of the O-atoms. The unit vectors $\mathbf{e}_X$ and $\mathbf{e}_Y$ lie on the direction of the X and Y-axis of the axis system, with its origin in the molecule's center of mass. This set of coordinates for the bending mode is not unique, but Eq. (2) is the appropriate choice to carry out the connection to the $U(3)$ algebraic approach [36]. Symmetry coordinates have the advantage of leading **the**

Hamiltonian to a block diagonal **matrix**, whose eigenvectors carry quantum numbers (irreducible representations) associated with the **symmetry group of the molecule**. In matrix form

$$\tilde{\mathcal{Q}} = \tilde{\mathbf{q}} S \quad , \tag{3}$$

where

$$\tilde{\mathcal{Q}} = \Big(\mathcal{Q}_{\Sigma_u}, \mathcal{Q}_{\Sigma_g}, \mathcal{Q}_{-}, \mathcal{Q}_{+} \Big) \quad , \tag{4}$$

and

$$S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & -i & -i \end{pmatrix} \quad . \tag{5}$$

In terms of the symmetry coordinates and the corresponding conjugate momenta

$$\tilde{\mathbf{P}} = \Big(P_{\Sigma_u}, P_{\Sigma_g}, P_{-}, P_{+} \Big) \quad , \tag{6}$$

given by

$$\hat{P}_{\Sigma_u} = -i\hbar \frac{\partial}{\partial Q_{\Sigma_u}}; \qquad \hat{P}_{\Sigma_g} = -i\hbar \frac{\partial}{\partial Q_{\Sigma_g}}, \tag{7a}$$

$$\hat{P}_{+} = -\frac{1}{\sqrt{2}} \left(\hat{p}_a - i \hat{p}_b \right), \quad \hat{P}_{-} = \frac{1}{\sqrt{2}} \left(\hat{p}_a + i \hat{p}_b \right) \quad , \tag{7b}$$

the Hamiltonian takes the form

$$\hat{H} = \frac{1}{2} \tilde{\mathcal{P}} \; \mathcal{G} \; \mathcal{P} + V(\mathcal{Q}) \quad , \tag{8}$$

where

$$\mathcal{G} = \tilde{\mathbf{S}} \; \mathbf{G} \; \mathbf{S} \quad . \tag{9}$$

The transformed Wilson matrix $\mathcal{G}$ is block diagonal, as expected. The expansion of the $\mathcal{G}$ matrix and the potential in terms of the symmetry coordinates leads to a Hamiltonian of the form [36]

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb} \quad . \tag{10}$$

The first term, $\hat{H}_s$, is the pure stretching contribution

$$
\begin{aligned}
\hat{H}_s = \frac{1}{2} g^0_{\Sigma_g\Sigma_g} \hat{P}^2_{\Sigma_g} + \frac{1}{2} g^0_{\Sigma_u\Sigma_u} \hat{P}^2_{\Sigma_u} + \frac{1}{2} f_{\Sigma_g\Sigma_g} \hat{Q}^2_{\Sigma_g} + \frac{1}{2} f_{\Sigma_u\Sigma_u} \hat{Q}^2_{\Sigma_u} \\
+ \frac{1}{4!} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} \hat{Q}^4_{\Sigma_g} + \frac{1}{4!} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \hat{Q}^4_{\Sigma_u} + \frac{6}{4!} f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} \hat{Q}^2_{\Sigma_g} \hat{Q}^2_{\Sigma_u} \quad . \qquad (11)
\end{aligned}
$$

The second term, $\hat{H}_b$, corresponds to the part of the Hamiltonian depending solely on bending coordinates and momenta

$$
\begin{aligned}
\hat{H}_b = g^0_{+-} \hat{P}_+ \hat{P}_- + f_{+-} \hat{Q}_+ \hat{Q}_- + \left(\frac{\partial^2 g_{+-}}{\partial Q_+ \partial Q_-} \right)_0 \hat{P}_+ \hat{Q}_+ \hat{Q}_- \hat{P}_- \\
+ \frac{1}{2!} \frac{1}{2} \left(\frac{\partial^2 g_{++}}{\partial Q^2_+} \right)_0 (\hat{P}_+ Q_+ Q_+ P_+ + P_- Q_- Q_- P_-) + \frac{6}{4!} f_{++--} \hat{Q}^2_+ \hat{Q}^2_- \quad . \qquad (12)
\end{aligned}
$$

The third term, $\hat{H}_{sb}$, embodies the stretch-bend interaction terms

$$
\begin{aligned}
\hat{H}_{sb} = \left(\frac{\partial g_{+-}}{\partial Q_{\Sigma_g}} \right)_0 Q_{\Sigma_g} \hat{P}_+ \hat{P}_- + \left(\frac{\partial g_{\Sigma_g +}}{\partial Q_+} \right)_0 \hat{P}_{\Sigma_g} \left(\hat{Q}_+ \hat{P}_+ + \hat{P}_- \hat{Q}_- \right) \\
+ \frac{6}{3!} f_{\Sigma_g +-} \hat{Q}_{\Sigma_g} \hat{Q}_+ \hat{Q}_- + \frac{1}{2} \left(\frac{\partial^2 g_{+-}}{\partial Q^2_{\Sigma_g}} \right)_0 \hat{Q}^2_{\Sigma_g} \hat{P}_+ \hat{P}_- + \frac{1}{2} \left(\frac{\partial^2 g_{+-}}{\partial Q^2_{\Sigma_u}} \right)_0 \hat{Q}^2_{\Sigma_u} \hat{P}_+ \hat{P}_- \\
+ \frac{1}{2} \left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial Q_+ \partial Q_-} \right)_0 \hat{P}^2_{\Sigma_g} \hat{Q}_+ \hat{Q}_- + \frac{1}{2} \left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial Q_+ \partial Q_-} \right)_0 \hat{P}^2_{\Sigma_u} \hat{Q}_+ \hat{Q}_- \qquad (13) \\
+ \frac{12}{4!} f_{\Sigma_g\Sigma_g+-} \hat{Q}^2_{\Sigma_g} \hat{Q}_+ \hat{Q}_- + \frac{12}{4!} f_{\Sigma_u\Sigma_u+-} \hat{Q}^2_{\Sigma_u} \hat{Q}_+ \hat{Q}_- \quad .
\end{aligned}
$$

Here $\mathcal{G}$ is the symmetry adapted Wilson kinetic matrix [42], with elements $||\mathcal{G}|| = g_{\alpha\beta}$.

An algebraic representation of the Hamiltonian (10) is obtained through the introduction of bosonic creation and annihilation operators [36]

$$
a^\dagger_\Gamma = \alpha^\Gamma \hat{Q}_\Gamma - \frac{i}{2\hbar\alpha^\Gamma} \hat{P}_\Gamma \ , \quad a_\Gamma = \alpha^\Gamma \hat{Q}_\Gamma + \frac{i}{2\hbar\alpha^\Gamma} \hat{P}_\Gamma \quad ; \Gamma = \Sigma_g, \Sigma_u \qquad (14a)
$$

$$
a^\dagger_\pm = \alpha^\pm \hat{Q}_\pm + \frac{i}{2\hbar\alpha^\pm} \hat{P}_\mp \ , \quad a_\pm = -\alpha^\pm Q_\mp + \frac{i}{2\hbar\alpha^\pm} \hat{P}_\pm \quad . \qquad (14b)
$$

with the definitions

$$
\left(\alpha^{\Sigma_g} \right)^2 = \frac{1}{2\hbar} \omega_{\Sigma_g} \mu_{\Sigma_g} \quad ; \quad \left(\alpha^{\Sigma_u} \right)^2 = \frac{1}{2\hbar} \omega_{\Sigma_u} \mu_{\Sigma_u} \quad , \qquad (15a)
$$

$$
\left(\alpha^+ \right)^2 = \left(\alpha^- \right)^2 = (\alpha)^2 = \frac{1}{2\hbar} \sqrt{\frac{f_{+-}}{g^0_{+-}}} = \frac{1}{2\hbar} \sqrt{\frac{f_{q_a q_a}}{g^0_{q_a q_a}}} \quad . \qquad (15b)
$$

where $\Gamma = \Sigma_g, \Sigma_u$, $\mu_\Gamma = 1/g^0_{\Gamma\Gamma}$ is the reduced mass of the stretching vibrational modes, and $g^0_{\Gamma\Gamma}$ is the diagonal $\mathcal{G}$ matrix element given for the symmetry coordinates in the equilibrium.

The Hamiltonian obtained through the substitution of (14) into (10) may be diagonalized in the basis of the direct product of harmonic oscillator functions associated with each symmetry coordinate. It is possible, however, to carry out the diagonalization in a local basis, although not in a straightforward way. The CO_2 molecule presents a strong normal-mode behavior and consequently starting from a local mode scheme in configuration space does not provide us the correct description. It has been shown that a suitable approach to deal with this problem consists in introducing the following canonical transformation that preserves the polyad [36, 38, 43, 44]

$$a^\dagger_{\Sigma_g} = \frac{1}{\sqrt{2}}(c^\dagger_1 + c^\dagger_2) \ \ , \ \ a^\dagger_{\Sigma_u} = \frac{1}{\sqrt{2}}(c^\dagger_1 - c^\dagger_2) \ \ , \tag{16}$$

where $c^\dagger_i(c_i)$ are also bosonic operators associated with the i-th oscillator. The local operators $c^\dagger_i(c_i)$ do not correspond to the physical local bosonic operators $a^\dagger_i(a_i)$, but their action on an isomorphic local basis may be chosen to be the same. In fact we establish the isomorphism

$$c^\dagger_i(c_i) \leftrightarrow a^\dagger_i(a_i). \tag{17}$$

Applying the transformation (16) together with the isomorphism (17), the following algebraic Hamiltonian in the local harmonic representation is obtained

$$\begin{aligned}\hat{H} = {} & \tilde{\omega}_s \sum_{k=1}^{2} \left(a^\dagger_k a_k + a_k a^\dagger_k \right) + \lambda_s \sum_{k\neq j=1}^{2} a^\dagger_k a_j + \alpha^s_1 \left(\hat{n}^2_1 + \hat{n}^2_2 \right) \\ & + \alpha^s_2 \left(a^{\dagger 2}_1 a^2_2 + a^{\dagger 2}_2 a^2_1 + 4\hat{n}_1\hat{n}_2 \right) + \alpha^s_3 \left(\hat{n}_1 a^\dagger_2 a_1 + \hat{n}_2 a^\dagger_1 a_2 + H.c. \right) \\ & + \tilde{\omega}_b \hat{n} + \alpha^b_1 \hat{n}^2 + \alpha^b_2 \hat{\ell}^2 + \alpha^{sb}_1 \left\{ \left(a^\dagger_1 + a^\dagger_2 \right) a_+ a_- + H.c. \right\} \\ & + \alpha^{sb}_2 \left(\hat{n}_1 + \hat{n}_2 \right) \hat{n} + \alpha^{sb}_3 \left(a^\dagger_1 a_2 + a^\dagger_2 a_1 \right) \hat{n} \ \ , \end{aligned} \tag{18}$$

with the definitions

$$\begin{aligned} \hat{n}_k &= a^\dagger_k a_k \ ; \quad k = 1, 2 \ \ , \\ \hat{\ell} &= a^\dagger_+ a_+ - a^\dagger_- a_- = \hat{n}_+ - \hat{n}_- \ \ , \\ \hat{n} &= a^\dagger_+ a_+ + a^\dagger_- a_- = \hat{n}_+ + \hat{n}_- \ \ , \end{aligned} \tag{19}$$

where $\hat{n}_k$ is the number of quanta for the k-th stretching oscillator, $\hat{n}$ is the total number of bending quanta, and $\hat{\ell}$ is the vibrational angular momentum. In Eq. (18) we have restricted the interactions to preserve the polyad number $P = 2(n_{\Sigma_g}+n_{\Sigma_u})+(n_+ + n_-)$. The expressions for the spectroscopic parameters in terms of the structure and force constants are detailed in Appendix A. The diagonalization of Eq. (18) can be carried out in a local basis given in terms of the direct product of harmonic local oscillators. Because of the canonical character of the transformation (16), the diagonalization in this bosonic local basis gives rise to the same results that the Hamiltonian in terms of the original operators (14). However, a significant improvement can be obtained proposing a local mode approach for the stretches in terms of Morse oscillators, instead of harmonic oscillators, together with the incorporation of anharmonic effects for the bending degrees of freedom, as we show in the next section.

3. Algebraic approach based on unitary groups

A remarkable improvement to the previous description can be achieved with the introduction of the anharmonization procedure [36, 44]

$$a_i^\dagger \to b_i^\dagger, \qquad a_i \to b_i, \tag{20}$$

for the local stretching oscillators. These new operators $\hat{b}_i^\dagger(\hat{b}_i)$ should be interpreted as ladder operators of the Morse eigenstates $|\psi^j_{v_i}\rangle$ with the matrix elements [26]

$$\hat{b}^\dagger|\Psi^j_v\rangle = \sqrt{(v+1)(1-(v+1)/\kappa)}\;|\Psi^j_{v+1}\rangle, \tag{21a}$$

$$\hat{b}\;|\Psi^j_v\rangle = \sqrt{v(1-v/\kappa)}\;|\Psi^j_{v-1}\rangle, \tag{21b}$$

where $\kappa = 2j+1$ is related with the depth of the potential.

For the bends we have

$$a_\pm^\dagger \to b_\pm^\dagger, \qquad a_\pm \to b_\pm, \tag{22}$$

with matrix elements [36]

$$b_\pm^\dagger|[N];n^\ell\rangle = \sqrt{\left(\frac{n\pm\ell}{2}+1\right)\left(1-\frac{n}{N}\right)}\;|[N];(n+1)^{\ell\pm1}\rangle \;\;, \tag{23a}$$

$$b_{\pm}|[N];n^{\ell}\rangle = \sqrt{\left(\frac{n\pm\ell}{2}\right)\left(1-\frac{n-1}{N}\right)}\,|[N];(n-1)^{\ell\mp1}\rangle \quad , \tag{23b}$$

where the kets $|[N];n^{\ell}\rangle$ correspond to the $U(3) \supset U(2) \supset O(2)$ chain [45]. The operators $b_{\pm}^{\dagger}(b_{\pm})$ appear from their connection with the local coordinates, $\hat{Q}_{\pm}$, and momenta, $\hat{P}_{\pm}$, in the framework of the $U(3)$ model [36]

$$\hat{Q}_{\pm} \simeq \sqrt{\frac{\hbar}{2\omega\mu}}(b_{\pm}^{\dagger} - b_{\mp}) \quad , \quad \hat{P}_{\pm} \simeq -\frac{i}{2}\sqrt{2\hbar\omega\mu}(b_{\mp}^{\dagger} + b_{\pm}) \quad , \tag{24}$$

except in the large N limit, when $b_{\pm}^{\dagger}(b_{\pm})$ operators are replaced by $a_{\pm}^{\dagger}(a_{\pm})$ as in Eq. (14). The parameters ω and μ are $\omega = \sqrt{f_{+-}g_{+-}^{0}} = \sqrt{f_{q_a q_a}g_{q_a q_a}^{0}}$ and $\mu = 1/g_{q_a q_a}^{0}$.

We thus proceed to apply the anharmonization procedures (20) and (22), leading to the following Hamiltonian

$$\begin{aligned}\hat{H} = {} & \tilde{\omega}_s \sum_{i=1}^{2}\left(b_i^{\dagger}b_i + b_i b_i^{\dagger}\right) + \lambda_s \sum_{i\neq j=1}^{2} b_i^{\dagger}b_j + \alpha_1^{s}\left(\hat{n}_{s,1}^{2} + \hat{n}_{s,2}^{2}\right) \\ & + \alpha_2^{s}\left(b_1^{\dagger 2}b_2^{2} + b_2^{\dagger 2}b_1^{2} + 4\hat{n}_{s,1}\hat{n}_{s,2}\right) + \alpha_3^{s}\left(\hat{n}_{s,1}b_2^{\dagger}b_1 + \hat{n}_{s,2}b_1^{\dagger}b_2 + H.c.\right) \\ & + \tilde{\omega}_b\hat{n} + \alpha_1^{b}\hat{n}^{2} + \alpha_2^{b}\hat{\ell}^{2} + \alpha_1^{sb}\left\{\left(b_1^{\dagger} + b_2^{\dagger}\right)\hat{b}_{+}\hat{b}_{-} + H.c.\right\} \\ & + \alpha_2^{sb}\left(\hat{n}_{s,1} + \hat{n}_{s,2}\right)\hat{n} + \alpha_3^{sb}\left(b_1^{\dagger}b_2 + b_2^{\dagger}b_1\right)\hat{n} \quad ,\end{aligned} \tag{25}$$

with the definition

$$\hat{n}_{s,i} = b_i^{\dagger}b_i \quad , \quad i = 1,2 \quad , \tag{26}$$

where the connection between spectroscopic parameters and force constants is assumed to be identical to the connection previously obtained making use of the harmonic basis. The first term in Eq. (25) is equivalent to two independent Morse oscillators. Hence this Hamiltonian may be interpreted as modeling three interacting oscillators: a 2D oscillator (bending degrees of freedom) and two 1D Morse oscillators (stretching degrees of freedom). In order to carry out the necessary calculations, we select the $U(2) \times U(3) \times U(2)$ basis

$$|[N_s],[N];v_1 v_2;n^{\ell}\rangle = |\psi_{v_1}^{j}\rangle \otimes |\psi_{v_2}^{j}\rangle \otimes |N;n^{\ell}\rangle \quad , \tag{27}$$

which corresponds to the $U(3) \supset U(2) \supset SO(2)$ dynamical symmetry of the 2D vibron model. The diagonalization of the Hamiltonian (25) gives rise to a set of eigenvectors

$$|P;\nu_1,\nu_2,\nu_3;\Gamma,\gamma\rangle = \sum_{v_1,v_2,n} C^{P;\nu_1,\nu_2,\nu_3;\Gamma,\gamma}_{v_1,v_2,n} \; |\psi^j_{v_1}\rangle \otimes |\psi^j_{v_2}\rangle \otimes |N;n^\ell\rangle, \tag{28}$$

where P is the polyad, Γ and γ label the irreducible representations and their components, while the set $\{\nu_1,\nu_2,\nu_3\}$ corresponds to the normal-mode labeling. It should be clear that the latter are approximate quantum numbers, which can be extracted because of the approach followed in the symmetrization of the states [46, 47]. Here it is equivalent to label the states either by ℓ or Γ,γ. This labeling scheme is good enough for our purposes because the molecule is highly normal. The eigenstates (28) have the novel feature that they are obtained from an anharmonized procedure [36, 38, 43, 44]. We now proceed to analyze the CO_2 molecule.

4. $^{12}CO_2$ Potential Energy Surface

In its ground state the molecule ^{12} CO_2 is linear with a experimental bond length $r_e = 1.1615$ Å[48, 49]. Thus, its point symmetry group is $\mathcal{D}_{\infty h}$, with four vibrational degrees of freedom: two stretching modes ($\Sigma_g^+ \oplus \Sigma_u^+$) and a doubly degenerate bending mode ($\Pi_u^\pm$).

The Hamiltonian (25) has 11 spectroscopic parameters. However, since the parameters α_1^b and α_2^b depend on the same force constant f_{++--}, we expect two different estimates when the Hamiltonian is expanded up to 4th order, as we did in present work. The diagonalization of the Hamiltonian (25) is carried out in a symmetry adapted basis which is obtained projecting the basis functions (27) [46, 47]. The spectroscopic parameters are optimized with an iterative non-linear least square method. The quality of the fit is expressed in terms of the *rms* deviation

$$rms = \left[\sum_{i=1}^{N_{exp}} (E^i_{exp} - E^i_{cal})^2/(N_{exp}-N_{par})\right]^{1/2} \quad , \tag{29}$$

where N_{exp} is the total number of experimental energies and N_{par} the number of parameters optimized in the fit. All the experimental data included were evenly weighted.

We assign statistical uncertainties to the obtained parameters. For each parameter x_i, two types of uncertainty estimates are considered: the delta-error (δx_i) and the epsilon-error (ϵx_i). A detailed discussion on these two error estimates can be found in Ref. [33, 50, 51].

In Ref. [36] is reported a fit to 101 vibrational levels, obtaining a deviation of rms= 0.53 cm^{-1}. The fit encompasses all the experimental term energies up to polyad $P = 9$. The values for the boson numbers N_s and N were found to be $N_s = 160$ and $N = 150$, which were obtained by minimization using the criterion of minimum deviation. The question which arises concerns the physical character of the description. It is widely recognized that the resulting wave functions are a very sensitive indicator and its behavior can determine whether the determined force constants are similar to the physical ones. Hence, the testing of the obtained wave functions through the estimation of transition intensities is a very exigent check of the validity of the model. In fact, this type of analysis can provide a conclusive test about the goodness of the energy fit. This alternative will be presented elsewhere by studying the Raman spectrum [52].

In this work we shall pay attention to the quality of the predicted force constants in order to evaluate the fit quality and closeness to physical spectroscopic parameters. Since in this molecule the Fermi interaction is crucial to obtain a fit of spectroscopic quality, a reasonable value for the corresponding force constant is expected to be obtained. In Ref. [36] the parameter obtained was $\alpha_1^{sb} = 34.1$ cm^{-1}, with the corresponding estimated force constant $f_{q_1 q_a q_a} = -5.40$ aJÅ^{-3}. This value is pretty far from the force constant obtained by *Chedin* given by $f_{q_1 q_a q_a} = -0.8841$ aJÅ^{-3} [40]. This large difference suggests that the optimization of the spectroscopic parameters has fallen into a local minimum different from the physical minimum. Indeed, we have found another minimum with the same values for the number of bosons and similar values for the spectroscopic parameters, with the exception of the one corresponding to the Fermi interaction. We have considered the same 101 vibrational levels, obtaining again the deviation of rms= 0.53 cm^{-1}. In addition to the experimental and calculated energies, Table 1 includes state labels, both normal-mode and local-mode, as well as the square of the maximum component in each basis. The simultaneous assignment of the states in both (approximate) normal-mode and local-mode schemes is useful because in general in the same spectrum may coexist states with a local-mode character and others with a normal-mode character. The spectroscopic parameters as well as their corresponding uncertainty estimates associated with the fit in Table 1 are given in Table 2. The epsilon and delta error magnitudes indicate that the parameters are well determined. In addition to this, the correlation matrix has been computed, obtaining matrix elements not greater than 0.96, which further supports that parameters are well determined.

From Table 2 we have the $\alpha_1^{sb} = -36.002$ cm^{-1}, whose absolute value is similar to the previous one but opposite in sign. In Table 3 we present the force constants obtained from the spectroscopic parameters of Table 2 and their relations with the force constants given in Appendix A. The new fit provides the force constant $f_{q_1 q_a q_a} = -0.9592$ aJÅ^{-3}, which is now comparable to *Chedin*' s constant. Although the new set of spectroscopic parameters does not improve the energy description, a large change appears in the wave functions, as we next discuss. We shall study a two dimensional subspace in order to understand the effect over the wave functions associated with a change of sign in the Fermi interaction. Let us consider in the notation of Eq. (28), the states $|2; 100; \Sigma_g\rangle$ and $|2; 020; \Sigma_g\rangle$ with the diagonal contributions E_1 and E_2 interacting with the Fermi interaction with strength w. This situation is analyzed in Ref.[53], here we recall the relevant details. The matrix representation $||\hat{H}||$ of this situation yield the following eigenvalues

$$E_+ = \frac{1}{2}\{(E_1 + E_2) + d\}, \tag{30}$$

$$E_- = \frac{1}{2}\{(E_1 + E_2) - d\}, \tag{31}$$

with $d = \sqrt{(E_1 - E_2)^2 + 4w^2}$ and corresponding eigenvectors

$$|\psi_+\rangle = N_+ \left\{ \frac{(E_1 - E_2) + d}{2w} |2; 100; \Sigma_g\rangle + |2; 020; \Sigma_g\rangle \right\}, \tag{32}$$

$$|\psi_-\rangle = N_- \left\{ \frac{(E_1 - E_2) - d}{2w} |2; 100; \Sigma_g\rangle + |2; 020; \Sigma_g\rangle \right\}, \tag{33}$$

where $N_\pm$ are normalization constants. First we note that the eigenvalues do not depend on the sign of the strength w. This explains that the spectrum is basically invariant when the sign of the Fermi parameter is changed. The situation for the eigenstates is quite different since they depend on the sign of w. Indeed, the weights of the basis change with the sign. It becomes obvious in the situation $E_1 - E_2 = 0$. In this case the states $|\psi_\pm\rangle$ undergo the transformation

$$|\psi_\pm\rangle = \frac{1}{2}\{|2;100;\Sigma_g\rangle \pm |2;020;\Sigma_g\rangle\} \rightarrow |\psi_\mp\rangle = \frac{1}{2}\{|2;100;\Sigma_g\rangle \mp |2;020;\Sigma_g\rangle\} \qquad (34)$$

with the change $w \rightarrow -w$. This is a crucial transformation when dealing with transition intensities. In a future work we shall show that indeed, the new fit provides the correct wave functions to describe the Raman spectrum [52].

In this work we have thus determined a different PES of $^{12}CO_2$ molecule to that calculated in a former work [36] with similar energy fitting. By comparing the force constants with those in Ref. [40], we have assessed that the PES obtained in the present work is very close to the physical one. We should stress that this is possible because of the connection between the algebraic approach and the space of coordinates and momenta. In an algebraic description without this connection, only when studying the transition intensities it is possible to determine whether the parameters are physical.

5. Conclusions

In this work we have shown a criterion to obtain the right PES of a molecule, when more than one set of spectroscopic parameters are obtained with similar quality for the vibrational spectrum. In particular we have presented the case of the $^{12}CO_2$ molecule in its ground state. This molecule is an example where a good fit to the vibrational spectrum does not assure a good quality of the eigenstates, and consequently a full spectroscopic description.

A remarkable feature of our model is that a local description is used for a molecule with a strong normal behavior, giving rise to reasonable values for the energies as well as for the force constants. Our approach starts working out the Hamiltonian in configuration space. Its algebraic representation is obtained by introducing the bosonic creation and annihilation operators associated to the normal modes. The local description is introduced through a canonical transformation, which after an anharmonization procedure gives rise to the $U(2) \times U(3) \times U(2)$ model.

A highly accurate description of the vibrational excitations $^{12}CO_2$ is presented, with a *rms* deviation of 0.53 cm^{-1}. Compared to the deviation obtained in the harmonic limit of the Hamiltonian, $rms = 1.0$ cm^{-1}, it implies an improvement close to 50%. The transformation from the fitted algebraic spectroscopic parameters to the force constants has allowed us to test which potential energy surface should be chosen as the physical one by comparing them with previous results, i.e. from Chedin [40]. The fits of present work and from Ref. [36] correspond to two fitting minima. Through the analysis of the Fermi resonances, we were able to discriminate between both results. We have thus shown that consistency of PES with previous results may help to determine the set of physical spectroscopic parameters. Although the obvious approach would consist in testing the wave functions, when it is not possible, this approach turns out to be crucial.

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Appendix A. Relation between algebraic spectroscopic parameters and force constants

In this appendix we present the relation of the spectroscopic parameters associated with the Hamiltonian (18) and (25) with the molecular structure and force constants. All terms consistent with the polyad preservation are included. We should stress that these relations are not completely equal to the ones presented in Ref.[36] because of two reasons: in Ref.[36] the third **term** of the bending Hamiltonian (12) was not included, and there was a misprint in the **expressions of the** spectroscopic parameters α_2^{sb} and α_3^{sb}.

For the stretching parameters we have

$$\begin{aligned}\tilde{\omega}_s = {} & \frac{1}{2}\hbar\omega_{\Sigma_g} + \frac{1}{2}\hbar\omega_{\Sigma_u} + \frac{9}{2}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} + \frac{9}{2}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \\ & + \frac{1}{2}\frac{6}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2(2\alpha^{\Sigma_u})^2} f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} + \alpha_2^{sb},\end{aligned} \tag{35}$$

$$\begin{aligned}\lambda_s = {} & \frac{1}{2}\hbar\omega_{\Sigma_g} - \frac{1}{2}\hbar\omega_{\Sigma_u} + 6\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} - 6\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \\ & + \alpha_3^{sb}\end{aligned} \tag{36}$$

$$\begin{aligned}\alpha_1^s = {} & \frac{6}{4}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} + \frac{6}{4}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \\ & + \frac{3}{2}\frac{6}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2(2\alpha^{\Sigma_u})^2} f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} \quad ,\end{aligned} \tag{37}$$

$$\begin{aligned}\alpha_2^s = {} & \frac{6}{4}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} + \frac{6}{4}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \\ & - \frac{1}{2}\frac{6}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2(2\alpha^{\Sigma_u})^2} f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} \quad ,\end{aligned} \tag{38}$$

$$\alpha_3^s = 3\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} - 3\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \quad . \tag{39}$$

On the other hand, for the purely bending parameters

$$\begin{aligned}\tilde{\omega}_b = {} & \hbar\omega + \frac{\hbar^2}{4}\left(\frac{\partial^2 g_{+-}}{\partial Q_+ \partial Q_-}\right)_0 + \frac{1}{2}\frac{\hbar^2}{4}\left(\frac{\partial^2 g_{++}}{\partial Q_+^2}\right)_0 + 3\frac{6}{4!}\frac{1}{(2\alpha)^4} f_{++--} \\ & + \alpha_2^{sb},\end{aligned} \tag{40}$$

$$\alpha_1^b = \frac{\hbar^2}{8}\left(\frac{\partial^2 g_{+-}}{\partial Q_+ \partial Q_-}\right)_0 + \frac{\hbar^2}{16}\left(\frac{\partial^2 g_{++}}{\partial Q_+^2}\right)_0 + \frac{3}{2}\frac{6}{4!}\frac{1}{(2\alpha)^4} f_{++--} \ , \tag{41}$$

$$\alpha_2^b = \frac{\hbar^2}{8}\left(\frac{\partial^2 g_{+-}}{\partial Q_+ \partial Q_-}\right)_0 - 3\frac{\hbar^2}{16}\left(\frac{\partial^2 g_{++}}{\partial Q_+^2}\right)_0 - \frac{1}{2}\frac{6}{4!}\frac{1}{(2\alpha)^4} f_{++--} \ , \tag{42}$$

while for the stretching-bending interaction parameters

$$\begin{aligned}\alpha_1^{sb} = {} & -\frac{1}{\sqrt{2}}\left(\frac{\partial g_{+-}}{\partial Q_{\Sigma_g}}\right)_0 \frac{\hbar^2\alpha^2}{2\alpha^{\Sigma_g}} - \frac{1}{\sqrt{2}}\left(\frac{\partial g_{+\Sigma_g}}{\partial Q_+}\right)_0 \hbar^2\alpha^{\Sigma_g} + \frac{1}{\sqrt{2}}\frac{6}{3!}\frac{1}{2\alpha^{\Sigma_g}(2\alpha)^2} f_{\Sigma_g+-} \\ \alpha_2^{sb} = {} & -\frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial Q_{\Sigma_g}^2}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_g})^2} - \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial Q_{\Sigma_u}^2}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_u})^2}\end{aligned}$$

$$
\begin{aligned}
&- \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial Q_+ \partial Q_-}\right)_0 \frac{\hbar^2 \left(\alpha^{\Sigma_g}\right)^2}{(2\alpha)^2} - \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial Q_+ \partial Q_-}\right)_0 \frac{\hbar^2 \left(\alpha^{\Sigma_u}\right)^2}{(2\alpha)^2} \\
&- \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2 (2\alpha)^2} f_{\Sigma_g\Sigma_g+-} - \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_u})^2 (2\alpha)^2} f_{\Sigma_u\Sigma_u+-} , \\
\alpha_3^{sb} = &-\frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial Q_{\Sigma_g}^2}\right)_0 \frac{\hbar^2 \alpha^2}{(2\alpha^{\Sigma_g})^2} + \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial Q_{\Sigma_u}^2}\right)_0 \frac{\hbar^2 \alpha^2}{(2\alpha^{\Sigma_u})^2} \\
&- \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial Q_+ \partial Q_-}\right)_0 \frac{\hbar^2 \left(\alpha^{\Sigma_g}\right)^2}{(2\alpha)^2} + \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial Q_+ \partial Q_-}\right)_0 \frac{\hbar^2 \left(\alpha^{\Sigma_u}\right)^2}{(2\alpha)^2} \\
&- \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2 (2\alpha)^2} f_{\Sigma_g\Sigma_g+-} + \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_u})^2 (2\alpha)^2} f_{\Sigma_u\Sigma_u+-} .
\end{aligned}
$$

The force constants in terms of the normal coordinates are also related with the force constants in the local-mode scheme. This relation is given by

$$
\begin{aligned}
f_{\Sigma_g\Sigma_g} &= f_{q_1q_1} + f_{q_1q_2} \ , \\
f_{\Sigma_u\Sigma_u} &= f_{q_1q_1} - f_{q_1q_2} \ , \\
f_{+-} &= -f_{q_aq_a} \ , \\
f_{\Sigma_g+-} &= -\sqrt{2} f_{q_1q_aq_a} \ , \\
f_{++--} &= \frac{2}{3} f_{q_aq_aq_aq_a} \ , \\
f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} &= \frac{1}{2} f_{q_1q_1q_1q_1} + 2 f_{q_1q_1q_1q_2} + \frac{3}{2} f_{q_1q_1q_2q_2} \ , \\
f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} &= \frac{1}{2} f_{q_1q_1q_1q_1} - 2 f_{q_1q_1q_1q_2} + \frac{3}{2} f_{q_1q_1q_2q_2} \ , \\
f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} &= \frac{1}{2} f_{q_1q_1q_1q_1} - \frac{1}{2} f_{q_1q_1q_2q_2} \ , \\
f_{\Sigma_g\Sigma_g+-} &= -f_{q_1q_1q_aq_a} - f_{q_1q_2q_aq_a} \ , \\
f_{\Sigma_u\Sigma_u+-} &= -f_{q_1q_1q_aq_a} + f_{q_1q_2q_aq_a} \ .
\end{aligned} \tag{43}
$$

Appendix B. Derivatives of the Wilson matrix

In this appendix we present **the non-vanishing** Wilson matrix elements in the symmetry **coordinates** as well as their derivatives at equilibrium. **For** a linear molecule **it is not** possible to obtain a closed analytical expression of the Wilson matrix **elements** when the coordinates $\{q_a, q_b\}$ are used. It is possible, however, to establish an approach to calculate the derivatives evaluated at equilibrium, as **was** explained in Ref.[37].

$$g^0_{q_1q_1} = \frac{1}{m_C} + \frac{1}{m_O} \tag{44}$$

$$g^0_{q_1q_2} = -\frac{1}{m_C} \tag{45}$$

$$g^0_{+-} = -g^0_{q_aq_a} = -g^0_{q_bq_b} \tag{46}$$

$$g^0_{q_aq_a} = g^0_{q_bq_b} = \frac{4}{m_C} + \frac{2}{m_O} \tag{47}$$

$$\left(\frac{\partial g_{+-}}{\partial Q_{\Sigma_g}}\right)_0 = \frac{2\sqrt{2}}{r_e}\left(\frac{1}{m_O} + \frac{2}{m_C}\right) \tag{48}$$

$$\left(\frac{\partial g_{\Sigma_g+}}{\partial Q_+}\right)_0 = \frac{\sqrt{2}}{m_C r_e} \tag{49}$$

$$\left(\frac{\partial^2 g_{+-}}{\partial Q_+ \partial Q_-}\right)_0 = -\frac{1}{r_e^2}\left(\frac{6}{m_C} + \frac{5}{2m_O}\right) \tag{50}$$

$$\left(\frac{\partial^2 g_{++}}{\partial Q_+^2}\right)_0 = -\frac{1}{r_e^2}\left(\frac{4}{m_C} + \frac{3}{2m_O}\right) \tag{51}$$

$$\left(\frac{\partial^2 g_{+-}}{\partial Q_{\Sigma_g}^2}\right)_0 = -\frac{6}{r_e^2}\left(\frac{2}{m_C} + \frac{1}{m_O}\right) \tag{52}$$

$$\left(\frac{\partial^2 g_{+-}}{\partial Q_{\Sigma_u}^2}\right)_0 = -\frac{2}{r_e^2}\left(\frac{4}{m_C} + \frac{3}{m_O}\right) \tag{53}$$

$$\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial Q_+ \partial Q_-}\right)_0 = -\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial Q_+ \partial Q_-}\right)_0 = -\frac{1}{m_C r_e^2} \tag{54}$$

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Table 1. Energies (in cm^{-1}) of $^{12}CO_2$ provided by the fit using the Hamiltonian (25). The rms deviation obtained is 0.53 cm^{-1}.

State[a]	Polyad[a]	State[b]	Contribution[b]	State[c]	Contribution[c]	Energies		
		(normal)	(normal)	(local)	(local)	Exp.[d]	Theor.	$\Delta\ E$
Symmetry	Σ_g^+							
1	2	1 0 0	0.512	0 0 1 1	0.488	1285.41[e]	1286.15	-0.74
2	2	0 2 0	0.512	0 0 1 1	0.512	1388.19[e]	1387.67	0.52
1	4	1 2 0	0.515	0 0 2 2	0.289	2548.37	2549.32	-0.96
2	4	2 0 0	0.660	0 0 2 2	0.335	2671.14	2671.16	-0.02
3	4	1 2 0	0.480	0 0 2 2	0.377	2797.14	2796.18	0.96
4	4	0 0 2	1.000	1 1 0 0	0.503	4673.33[e]	4673.19	0.13
1	6	1 4 0	0.434	1 0 2 2	0.434	3792.70	3793.08	-0.38
2	6	3 0 0	0.515	0 0 3 3	0.247	3942.49	3942.33	0.16
3	6	3 0 0	0.386	0 0 3 3	0.310	4064.28	4064.17	0.10
4	6	1 4 0	0.458	0 0 3 3	0.281	4225.10	4224.12	0.98
5	6	0 2 2	0.546	1 1 1 1	0.275	5915.21	5915.31	-0.10
6	6	1 0 2	0.546	1 1 1 1	0.228	6016.69	6016.60	0.09
2	8	3 2 0	0.336	0 0 4 4	0.184	5197.25	5196.23	1.02
4	8	3 2 0	0.372	0 0 4 4	0.303	5475.57	5476.08	-0.52
6	8	1 2 2	0.509	3 0 1 1	0.379	7133.82	7133.45	0.37
7	8	2 0 2	0.661	4 0 0 0	0.495	7259.74	7259.71	0.03
8	8	1 2 2	0.491	3 0 1 1	0.366	7377.68	7378.11	-0.44
Symmetry	Σ_u^+							
1	2	0 0 1	1.000	1 0 0 0	1.000	2349.14[e]	2349.07	0.07
1	4	0 2 1	0.517	1 0 1 1	0.517	3612.84[e]	3613.25	-0.41
2	4	1 0 1	0.517	2 0 0 0	0.517	3714.78[e]	3714.48	0.30
1	6	1 2 1	0.513	2 0 1 1	0.513	4853.62[e]	4853.91	-0.28
2	6	2 0 1	0.662	3 0 0 0	0.500	4977.83[e]	4977.84	0.00
3	6	1 2 1	0.487	2 0 1 1	0.487	5099.66[e]	5099.41	0.25
4	6	0 0 3	1.000	2 1 0 0	0.754	6972.58[e]	6972.48	0.10
1	8	1 4 1	0.444	2 0 2 2	0.444	6075.98[e]	6075.28	0.70
2	8	3 0 1	0.487	1 0 3 3	0.262	6227.92[e]	6227.47	0.45
3	8	3 0 1	0.418	1 0 3 3	0.299	6347.85[e]	6348.19	-0.34
4	8	1 4 1	0.455	2 0 2 2	0.455	6503.08[e]	6503.52	-0.44
5	8	0 2 3	0.575	2 1 1 1	0.434	8192.55[e]	8192.44	0.11
6	8	1 0 3	0.575	2 1 1 1	0.321	8293.95[e]	8294.13	-0.18

[a] The column labeled State indicates the state position from lower to higher energy inside the polyad for a given symmetry. The second column, labeled Polyad, indicates the polyad to which the state belongs.

[b] The third and fourth columns, with headings State and Contribution, assign normal-mode labels ($\nu_1\ \nu_2\ \nu_3$) to the state according to the square value of the largest contribution in this basis.

[c] The fifth and sixth columns, with headings State and Contribution, assign local-mode labels ($v_1\ v_2\ n_+\ n_-$) to the state and its squared maximum component in the local basis is shown.

[d] Experimental vibrational energies are taken from Ref. [54], otherwise is indicated.

[e] Experimental energies were taken from Ref. [55].

Table 1. Continuation.

State[a]	Polyad[a]	State[b] (normal)	Contribution[b] (normal)	State[c] (local)	Contribution[c] (local)	Energies Exp.[d]	Energies Theor.	Δ E
Symmetry Π_g								
1	3	0 1 1	1.000	1 0 1 0	1.000	3004.01[e]	3004.05	-0.04
1	5	1 1 1	0.509	2 0 1 0	0.509	4247.71	4248.18	-0.47
2	5	0 3 1	0.509	1 0 2 1	0.509	4390.63	4390.32	0.31
1	7	1 3 1	0.510	2 0 2 1	0.510	5475.07[e]	5475.10	-0.02
2	7	2 1 1	0.594	3 0 1 0	0.448	5632.77[e]	5632.89	-0.13
3	7	1 3 1	0.487	2 0 2 1	0.487	5790.58[e]	5790.52	0.06
4	7	0 1 3	1.00	2 1 1 0	0.754	7602.52[e]	7602.52	0.00
1	9	1 5 1	0.407	2 0 3 2	0.407	6688.18[e]	6686.73	1.44
2	9	3 1 1	0.470	1 0 4 3	0.283	6863.56[e]	6863.13	0.43
3	9	3 1 1	0.385	1 0 4 3	0.338	7023.68[e]	7024.46	-0.78
4	9	1 5 1	0.442	2 0 3 2	0.442	7203.82[e]	7204.89	-1.06
5	9	0 3 3	0.533	2 1 2 1	0.402	8803.27	8803.01	0.26
6	9	1 1 3	0.533	2 1 2 1	0.353	8944.15	8944.54	-0.39
Symmetry Π_u								
1	1	0 1 0	1.000	0 0 1 0	1.000	667.38[e]	667.51	-0.13
1	3	1 1 0	0.530	0 0 2 1	0.470	1932.47	1933.39	-0.92
2	3	0 3 0	0.530	0 0 2 1	0.530	2076.86[e]	2076.21	0.65
1	5	1 3 0	0.509	1 0 2 1	0.509	3181.46	3182.34	-0.88
2	5	2 1 0	0.591	0 0 3 2	0.400	3339.36	3339.47	-0.11
3	5	1 3 0	0.482	0 0 3 2	0.354	3500.67	3499.65	1.02
4	5	0 1 2	1.00	1 1 1 0	0.503	5315.71[e]	5315.68	0.03
1	7	1 5 0	0.395	1 0 3 2	0.395	4416.15	4416.03	0.12
2	7	3 1 0	0.487	0 0 4 3	0.271	4591.12	4591.02	0.10
3	7	3 1 0	0.364	0 0 4 3	0.345	4753.45	4753.59	-0.14
4	7	1 5 0	0.446	0 0 4 3	0.254	4938.39	4937.65	0.74
5	7	0 3 2	0.512	1 1 2 1	0.257	6537.96	6538.02	-0.06
6	7	1 1 2	0.512	1 1 2 1	0.246	6679.71	6679.73	-0.02
4	9	3 3 0	0.360	0 0 5 4	0.307	6179.01	6180.19	-1.18
5	9	1 7 0	0.397	1 0 4 3	0.397	6388.09	6388.56	-0.48
6	9	1 3 2	0.509	3 0 2 1	0.380	7743.70	7742.89	0.81
7	9	2 1 2	0.595	4 0 1 0	0.446	7901.48	7901.56	-0.08
8	9	1 3 2	0.490	3 0 2 1	0.365	8056.02	8056.85	-0.82

Table 1. Continuation.

State[a]	Polyad[a]	State[b] (normal)	Contribution[b] (normal)	State[c] (local)	Contribution[c] (local)	Energies Exp.[d]	Theor.	Δ E
Symmetry Δ_g								
1	2	0 2 0	1.000	0 0 2 0	1.000	1335.13[e]	1335.35	-0.22
1	4	1 2 0	0.542	0 0 3 1	0.458	2585.02	2585.99	-0.97
2	4	0 4 0	0.542	0 0 3 1	0.542	2760.73	2760.03	0.69
1	6	1 4 0	0.505	1 0 3 1	0.505	3821.98	3822.71	-0.72
2	6	2 2 0	0.561	0 0 4 2	0.427	4007.91	4008.11	-0.20
3	6	1 4 0	0.482	0 0 4 2	0.349	4197.36	4196.41	0.95
4	6	0 2 2	1.000	1 1 2 0	0.503	5958.51	5958.50	0.01
2	8	3 2 0	0.473	0 0 5 3	0.279	5245.47	5245.43	0.04
5	8	1 2 2	0.508	1 1 3 1	0.248	7166.05	7165.93	0.12
6	8	0 4 2	0.508	1 1 3 1	0.255	7338.15	7338.29	-0.14
Symmetry Δ_u								
1	4	0 2 1	1.000	1 0 2 0	1.000	3659.27[e]	3659.36	-0.08
1	6	1 2 1	0.525	2 0 2 0	0.525	4887.99	4888.40	-0.42
2	6	0 4 1	0.525	1 0 3 1	0.525	5061.78	5061.51	0.27
1	8	1 4 1	0.507	2 0 3 1	0.507	6103.68[e]	6103.36	0.32
2	8	2 2 1	0.564	1 0 4 2	0.429	6288.49[e]	6288.72	-0.23
3	8	1 4 1	0.487	2 0 3 1	0.487	6474.53[e]	6474.75	-0.22
4	8	0 2 3	1.000	2 1 2 0	0.755	8232.89	8232.88	0.01
Symmetry Φ_g								
1	5	0 3 1	1.000	1 0 3 0	1.000	4314.92	4314.99	-0.07
1	7	1 3 1	0.537	2 0 3 0	0.537	5531.30	5531.58	-0.27
2	7	0 5 1	0.537	1 0 4 1	0.537	5730.61	5730.40	0.21
1	9	1 5 1	0.504	2 0 4 1	0.504	6736.79	6736.03	0.76
2	9	2 3 1	0.546	1 0 5 2	0.444	6944.87	6945.02	-0.15
3	9	1 5 1	0.486	2 0 4 1	0.486	7154.75	7155.08	-0.33
4	9	0 3 3	1.000	2 1 3 0	0.755	8863.68	8863.57	0.11

Table 1. Continuation.

State[a]	Polyad[a]	State[b] (normal)	Contribution[b] (normal)	State[c] (local)	Contribution[c] (local)	Energies Exp.[d]	Theor.	Δ E
Symmetry Φ_u								
1	3	0 3 0	1.000	0 0 3 0	1.000	2003.25	2003.51	-0.26
1	5	1 3 0	0.552	0 0 4 1	0.448	3240.62	3241.56	-0.94
2	5	0 5 0	0.552	0 0 4 1	0.552	3442.22	3441.54	0.68
3	7	1 5 0	0.482	0 0 5 2	0.349	4890.10	4889.32	0.78
4	7	0 3 2	1.000	1 1 3 0	0.503	6601.72	6601.64	0.07
Symmetry Γ_g								
1	4	0 4 0	1.000	0 0 4 0	1.000	2671.72	2672.00	-0.28
1	6	1 4 0	0.560	0 0 5 1	0.440	3898.33	3899.17	-0.85
2	6	0 6 0	0.560	0 0 5 1	0.560	4122.27	4121.64	0.62
Symmetry Γ_u								
1	6	0 4 1	1.000	1 0 4 0	1.000	4970.93	4970.95	-0.01
1	8	1 4 1	0.547	2 0 4 0	0.547	6176.65	6176.77	-0.12
2	8	0 6 1	0.547	1 0 5 1	0.547	6398.07	6397.91	0.16
Symmetry Hg								
1	7	0 5 1	1.000	1 0 5 0	1.000	5627.25	5627.23	0.03
2	9	0 7 1	0.555	1 0 6 1	0.555	7064.52	7064.53	-0.01
Symmetry Hu								
1	5	0 5 0	1.000	0 0 5 0	1.000	3340.72	3340.81	-0.09
Symmetry Ig								
1	6	0 6 0	1.000	0 0 6 0	1.000	4010.07	4009.95	0.12
Symmetry Iu								
1	8	0 6 1	1.000	1 0 6 0	1.000	6283.98	6283.84	0.14

Table2. Parameters of the Hamiltonian (25) in cm^{-1} obtained in the fit to 101 vibrational energies for ^{12}CO$_2$. The statistical error analysis has been included in the last two columns, where the Epsilon and Delta errors are shown.

		Errors	
Parameter	Fit	Epsilon	Delta
$\tilde{\omega}^s$	1864.2	0.2666	0.0268
λ_s	-508.27	0.2069	0.0404
α_1^s	1.4949	0.0728	0.0117
α_2^s	-0.6086	0.0120	0.0053
α_3^s	3.9071	0.0726	0.0228
$\tilde{\omega}^b$	667.35	0.1175	0.0150
α_1^b	0.6243	0.0420	0.0030
α_2^b	-0.4616	0.0412	0.0056
α_1^{sb}	-36.002	0.0351	0.0154
α_2^{sb}	-7.6236	0.1306	0.0112
α_3^{sb}	4.9463	0.1357	0.0173

Table 3 Force constants for carbon dioxide computed using the expressions given in Appendix A considering that the potential function is written in terms of internal coordinates as in Ref. [3].

Force constant	$^{12}CO_2$ Present work	$^{12}CO_2$ Ref.[40]^a	$^{12}CO_2$ Ref.[36]
$f_{q_1q_1}(aJ\mathring{A}^{-2})$	15.95	15.97	15.98
$f_{q_1q_2}(aJ\mathring{A}^{-2})$	1.2381	1.2495	1.5310
$f_{q_1q_1q_1q_1}(aJ\mathring{A}^{-4})$	190.60	678.39	189.61
$f_{q_1q_1q_1q_2}(aJ\mathring{A}^{-4})$	153.15	12.72	152.73
$f_{q_1q_1q_2q_2}(aJ\mathring{A}^{-4})$	57.92	3.65	59.367
$f_{q_aq_a}(aJ\mathring{A}^{-2})$	0.5835	0.5804	0.5721
$f_{q_aq_aq_aq_a}(aJ\mathring{A}^{-4})$	0.7481^b	0.7469	3.3714
	2.018^c	-	-7.1862
$f_{q_1q_aq_a}(aJ\mathring{A}^{-3})$	-0.9551	-0.8841	-5.4013
$f_{q_1q_1q_aq_a}(aJ\mathring{A}^{-4})$	-17.37	0.7484	-19.549
$f_{q_1q_2q_aq_a}(aJ\mathring{A}^{-4})$	-6.867	2.121	-32.880

(a) **"Algebraized contact transformation" formalism** including the ro-vibrational degrees of freedom, using a harmonic oscillator basis (bosonic operators).

(b) Force constant obtained from α_1^b.

(c) Force constant obtained from α_2^b.