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An algebraic approach applied to the determination of the polarizability in CO_2

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Abstract. A local algebraic approach to describe vibrational excitations of molecules presenting both local and normal mode behaviors is presented. This approach allows the connection with configuration space to be established. The model consists in expanding the kinetic energy as well as the potential in terms of coordinates and momenta. An algebraic representation is obtained by introducing creation and destruction bosonic operators associated with the harmonic oscillators. From the resulting Hamiltonian a local algebraic representation is obtained through a canonical transformation to local bosonic operators. Finally an anharmonization is carried out by changing the local bosonic operators to ladder operators associated with the Morse or Pöschl-Teller functions. Since the model is connected with configuration space, non linear curvilinear coordinates are contemplated. Our model is applied to the vibrational spectroscopic description of the $^{12}C^{16}O_2$ molecule. The eigenstates are tested by calculating the derivatives for the polarizability for this molecule.

1. Introduction

Algebraic methods have been used for a long time as a useful tool to describe the vibrational spectroscopic properties of molecules. Usually these methods are based on harmonic oscillator bases because of their direct correspondence with normal modes [1, 2, 3, 4, 5]. A remarkable advantage of the algebraic representation is that it is easy to recognize the polyads [6], subspaces of the basis that interact among themselves through the most important interactions. Polyad-preserving Hamiltonian are valid as long as the description is confined to the low lying region of the spectrum. As the energy increases the polyad stop being useful. In such situations a suitable strategy may consists in breaking the polyad [2, 7, 8, 9], but an alternative route to follow may consists in choosing a different basis. The appropriate approach will depend on the system under study.

Normal modes involve nuclear collective motions, and consequently a harmonic oscillator basis is reasonable when there are not strong differences in their corresponding masses. When large mass differences are present, local modes are invoked [10, 11, 12, 13, 14, 15]. The basic idea of the local models consists in expressing the Hamiltonian in terms of a zeroth order Hamiltonian corresponding of a set of non interacting oscillators coupled by kinetic and potential energy

terms. Local modes are closely related with anharmonicity, a fact that explains the strong mixture of the normal basis to describe the regularities previously mentioned [16]. When local modes are present the natural space to be used correspond to a local basis identified with Morse or Pöschl-Teller functions [17, 18].

Starting in configuration space with a power expansion of the Hamiltonian in terms of normal coordinates it is possible to obtain an algebraic representation using bosonic operators in such a way that the spectroscopic parameters allow the potential energy surface (PES) to be estimated [1, 2]. However, a different scheme either local or normal may be useful for the different molecular degrees of freedom, like in methane for instance [19].

A relatively high success has been reached in modeling the local oscillators in terms of Morse functions. In particular this can be done in the framework of an $su(2)$ algebra. Algebraic local models using an $SU(2)$ basis have been extensively used in phenomenological way in the spectroscopic description of semirigid molecules [20, 21, 22, 23, 24, 25, 26, 27, 28, 29]. The creation and annihilation operators for the Morse and/or Pöschl-Teller (PT) functions were identified as generators of the $su(2)$ algebra [30, 31, 32]. This connection allowed force constants to be obtained, and consequently the PES became available to predict spectra of isotopic species [33, 34, 35, 36, 37, 38, 39, 40].

The natural way to establish the polyad is the normal model scheme. This means that a translation into the local scheme may not be possible, in particular when a strong normal behavior is present. In recent works it has been proved that it is possible to estimate the PES involving any degree of freedom using a local algebraic approach based on $su(2)$ algebras, still preserving polyads [41, 42, 43]. The basic idea consists in starting with the traditional algebraic description in terms of bosonic operators associated to symmetry adapted coordinates, and then apply a canonical transformation to bosonic operators isomorphic to bosonic local creation (annihilation) operators. Finally an anharmonization is carried out by the substitution of the local bosonic operators by ladder operators associated with the Morse/Pöschl-Teller functions. This last step is done preserving the same connection between the spectroscopic operators with the structure and force constants. This approach is unique because it allows to improve the vibrational spectroscopic description without counterpart in configuration space.

On the other hand, the natural molecular vibration description is given in terms of curvilinear coordinates, which can be expanded in terms of normal coordinates. The first approximation consists in considering only linear terms, which implies to identify the nonlinear symmetry adapted coordinates with the normal coordinates. This approximation has been taken in all the applications of the $su(2)$ algebraic approach to describe molecular vibrational excitations [39]. In this contribution we present a general perspective of the local algebraic approach based on $su(2)$ algebras to describe semi-rigid molecules. Our approach assumes the validity of the Born-Oppenheimer approximation and the convergence of the Hamiltonian expansion in terms of both nonlinear coordinates and normal coordinates. We present the study of the vibrational excitations of the specific molecule of carbon dioxide ($^{12}CO_2$) in its ground electronic state, considering non-linear effects in the expansion of the curvilinear coordinates. This study includes the analysis of transition probabilities associated with the Raman spectrum [44], which represents a relevant test for the eigenstates. The description of this spectrum is used to obtain a suitable expansion of the molecular polarizability tensor as a Taylor series in terms of nonlinear and normal coordinates. Although the analysis of this molecule has already been presented in a letter form [45], this was done strictly in the linear approximation. In this work we present the importance and generalization of our approach from a general perspective remarking the effect of the non-linear contributions.

The outline of the present work is as follows. In Section 2 we present in detail the ingredients involved in our algebraic model to obtain the eigenstates in terms of basis of local states associated with anharmonic oscillators. Section 3 is devoted to the application of our algebraic

approach to the CO_2 molecule. The estimation of the derivatives of the polarizability tensor are given in Section 4. Finally, in Section 5, a summary and conclusions are presented.

2. A general local algebraic approach

We start considering the following approximation for the vibrational Hamiltonian $\hat{H}$ in terms of curvilinear internal displacement coordinates [4, 46, 47]

$$H = \frac{1}{2}\tilde{\mathbf{P}}\mathbf{G}(\mathbf{S})\mathbf{P} + V(\mathbf{S}), \tag{1}$$

where $\mathbf{S}$ and $\mathbf{P}$ are column vectors corresponding to the internal displacement coordinates and their conjugate momenta $\hat{P}_\alpha = -i\hbar\partial/\partial S_\alpha$, respectively, while the $\mathbf{G}(\mathbf{S})$ matrix establishes the connection between the internal and Cartesian coordinates. $V(\mathbf{S})$ is the Born-Oppenheimer potential. Here the kinetic energy term not involving momentum operators has been neglected. The usual approach to obtain a suitable Hamiltonian to deal with consists in expanding both the $\mathbf{G}(\mathbf{S})$ matrix and the potential $V(\mathbf{S})$ as a Taylor series around the equilibrium configuration, truncating the expansion where an adequate convergence is achieved. In this way we have for the $\mathbf{G}(\mathbf{S})$ matrix

$$G_{ij}(\mathbf{S}) = G^o_{ij}(\mathbf{S}) + \sum_\alpha \left(\frac{\partial G_{ij}}{\partial S_\alpha}\right)_o S_\alpha + \ldots, \tag{2}$$

while for the potential

$$V(\mathbf{S}) = \frac{1}{2!}\sum_{\alpha,\beta}\left(\frac{\partial^2 V}{\partial S_\alpha \partial S_\beta}\right)_o S_\alpha S_\beta + \frac{1}{3!}\sum_{\alpha,\beta,\gamma}\left(\frac{\partial^3 V}{\partial S_\alpha \partial S_\beta \partial S_\gamma}\right)_o S_\alpha S_\beta S_\gamma \ldots \tag{3}$$

Usually the expansion of the $\mathbf{G}(\mathbf{S})$ matrix elements up to linear terms and the potential up to quadratic terms are the starting point to obtain a reasonable spectroscopic description. The substitution of the expansions (2) and (3) into (1), leads to a Hamiltonian of type

$$\hat{H} = \hat{H}(\hat{\mathbf{P}}, \mathbf{S}), \tag{4}$$

involving powers of $\hat{P}_\alpha, S_\beta$ and products. The curvilinear coordinates may be expanded in terms of linear symmetry adapted coordinates Q_i. These coordinates are isomorphic to the normal coordinates, a remarkable fact that allows us to deal with Q_i in every calculation. Hence we have the general form for the expansion

$$S_\alpha = \sum_i L^\alpha_i Q_i + \frac{1}{2!}\sum_{i,j} L^\alpha_{ij} Q_i Q_j + \frac{1}{3!}\sum_{i,j,k} L^\alpha_{ijk} Q_i Q_j Q_k \ldots. \tag{5}$$

The corresponding momenta are obtained through their definition

$$P_\alpha = \sum_i \frac{\partial Q_i}{\partial S_\alpha}\frac{\partial T}{\partial Q_i} = \sum_i \frac{\partial Q_i}{\partial S_\alpha} p_i. \tag{6}$$

The partial derivatives involved in (6) are obtained by inversion of the system of equations

$$\delta_{\alpha\beta} = \sum_i L^\alpha_i \left(\frac{\partial Q_i}{\partial S_\beta}\right) + \sum_{i,j} L^\alpha_{ij} Q_i \left(\frac{\partial Q_j}{\partial S_\beta}\right) + \frac{3}{3!}\sum_{i,j,k} L^\alpha_{ijk}\left(\frac{\partial Q_i}{\partial S_\beta}\right) Q_j Q_k \ldots, \tag{7}$$

which in turn are got by deriving (5) with respect to the coordinate S_β. This set of equations, however, provides a non linear solution for the derivatives. An additional expansion in powers of the symmetry adapted coordinates is required in order to obtain an approximation of the form

$$P_\alpha = \sum_i (M^{i,\alpha} + \sum_r M_r^{i,\alpha} Q_r + \sum_{r,s} M_{rs}^{i,\alpha} Q_r Q_s + \dots) p_i, \tag{8}$$

where the associated quantum operators are obtained through a symmetry projection method. Therefore the substitution of (5) and (8) into (4) yields a Hamiltonian of type

$$\hat{H} = \hat{H}(\hat{\mathbf{p}}, \mathbf{Q}), \tag{9}$$

where $\hat{p}_k = -i\hbar\partial/\partial Q_k$. The form of this Hamiltonian is not appropriate to identify the polyad(s) preserving interactions. The natural scheme is the number operator representation, also known as the algebraic representation.

A suitable algebraic representation of the Hamiltonian (9) is obtained by the introduction of the bosonic operators

$$a^\dagger_{q\Gamma\gamma} = \alpha_{q\Gamma}\ Q_{q\Gamma\gamma} - \frac{i}{2\hbar\alpha_{q\Gamma}}\ p_{q\Gamma\gamma}\ , \quad a_{q\Gamma\gamma} = \alpha_{q\Gamma}\ Q_{q\Gamma\gamma} + \frac{i}{2\hbar\alpha_{q\Gamma}}\ p_{q\Gamma\gamma}\ , \tag{10}$$

where Γ and γ are irreps associated with a group chain

$$G \supset H, \tag{11}$$

q is a multiplicity index and $\alpha^{q\Gamma}$'s are functions of the reduced mass $\mu_{q\Gamma}$ and the force constant $f^q_{\Gamma\Gamma}$

$$\alpha^2_{q,\Gamma} = \frac{1}{2\hbar} f^q_{\Gamma\Gamma}\ \mu_{q\Gamma}. \tag{12}$$

With the introduction of the bosonic operators the Hamiltonian takes thus the form

$$\hat{H}_P = \hat{H}_P(\hat{a}^\dagger_{q\Gamma\gamma}, \hat{a}_{q\Gamma\gamma}), \tag{13}$$

where the subindex P means that we assume polyad preservation by neglecting all the terms mixing states of different polyad. This algebraic representation has the advantage that a polyad preserving Hamiltonian may be proposed from the outset in a precise form. The spectroscopic parameters involved in (13) are related to the structure and force constants, and consequently the PES can be estimated from a fit of experimental vibrational levels. The matrix representation of Hamiltonian (13) can be obtained in a straightforward way in the harmonic oscillator basis $|n_1 n_2, \dots n_s\rangle$, where n_i is defined as the eigenvalue associated to the number operator $\hat{n}_{i(q\Gamma)} = \sum_\gamma \hat{a}^\dagger_{q\Gamma\gamma}\hat{a}_{q\Gamma\gamma}$. This basis can be projected to obtain a symmetry adapted basis in which the matrix representation of the Hamiltonian acquires a blocked diagonal form. An efficient and elegant approach to carry out this projection is described in Refs. [48, 49, 50, 51].

The main nondiagonal interactions that define the polyad are identified from the fundamentals and overtones of the molecule, and it is in the normal (symmetry adapted) scheme that the polyad number appears in natural form. In molecules with local mode behavior the concept of polyad has a straightforward translation. In contrast, for molecules involving strong normal behavior, like in BF_3, for instance, the polyad can not be translated into a local scheme. This is explained by the large splitting among the states coming from the same set of equivalent local oscillators as well as the appearance of redundant coordinates [38]. This fact leads to the conclusion that local mode bases cannot be proposed for these kind of molecules. Another argument in favor of this conclusion is that, in systems with strong normal behavior, starting

with local oscillators necessarily leads to the indispensableness of breaking the polyad in order to obtain the correct estimation of the force constants [39, 41, 42, 43]. In spite of these arguments, we address the possibility of using a local mode approach in cases where the normal behavior is strong enough that breaking the polyad may seem compulsory.

The approach giving the answer to this question relies on applying to the bosonic operators in the Hamiltonian (13) a canonical transformation of the type

$$\hat{a}^{\dagger}_{q\Gamma\gamma} = \sum_i \hat{B}^i_{q\Gamma\gamma}\ c^{\dagger}_i, \tag{14}$$

where $\hat{c}^{\dagger}_i(\hat{c}_i)$ are bosonic operators, and the coefficients $B^i_{q\Gamma\gamma}$ correspond to the linear combinations associated with the symmetry adapted local coordinates of the corresponding subspace q. The operators $\hat{c}^{\dagger}_i(\hat{c}_i)$ are not local operators, but an isomorphism to the true local operators $\hat{a}^{\dagger}_i(\hat{a}_i)$ can be established:

$$\hat{c}^{\dagger}_i \approx \hat{a}^{\dagger}_i. \tag{15}$$

The true connection between the bosonic operators $\hat{a}^{\dagger}_{q\Gamma\gamma}$ and the true local operators $\hat{a}^{\dagger}_i(\hat{a}_i)$ is given by a Bogoliubov transformation involving creation and annihilation operators, being the relation (14) true only in the limit of weak interaction among the oscillators [43]. This fact justify the proposed isomorphism (15).

The transformation (14) preserves the polyad in the Hamiltonian. Hence the substitution of (14) into (13) leads to a Hamiltonian of type $\hat{H}_P = \hat{H}_P(\hat{c}^{\dagger}_i, \hat{c}_i)$, which through the isomorphism (15), takes the form

$$\hat{H}_P = \hat{H}_P(\hat{a}^{\dagger}_i, \hat{a}_i). \tag{16}$$

The importance of this Hamiltonian is that it can be looked as a polyad preserving Hamiltonian in a local basis, an expression impossible to be obtained starting from a local scheme in coordinates, unless a local behavior was present. The Hamiltonians (13) and (16) are equivalent since they provide the same spectrum, although in different basis connected with a linear transformation. Up to this point nothing new has been proposed. However, this treatment can be improved considerable when we carry out the anharmonization procedure [38, 41, 42]

$$a^{\dagger}_i \rightarrow b^{\dagger}_i, \qquad a_i \rightarrow b_i \quad . \tag{17}$$

where the creation and annihilation operators $b^{\dagger}_i(b_i)$ are generators of a $su(2)$ dynamical algebra [39]. Since this anharmonization has to be done in both, the Hamiltonian and the basis, the operators $b^{\dagger}_i(b_i)$ may be interpreted as ladder operators for a Morse or Pöschl-Teller potential eigenstates, $|\psi^j_{v_i}\rangle$, with matrix elements [34]

$$b^{\dagger}|\Psi^j_v\rangle = \sqrt{(v+1)(1-(v+1)/\kappa)}\ |\Psi^j_{v+1}\rangle \quad , \tag{18}$$

$$b\ |\Psi^j_v\rangle = \sqrt{v(1-v/\kappa)}\ |\Psi^j_{v-1}\rangle \quad , \tag{19}$$

where v is the stretching quantum number, $v = 0, 1, 2 \ldots j-1$, and $\kappa = 2j+1$ is related to the potential depth. The anharmonization (17) is valid for both stretching and bending degrees of freedom in non linear molecules [33, 34, 35, 36, 37, 38, 39, 40]. For linear molecules an anharmonization method based on the $su(3)$ algebra should be included in order to describe the degenerate bending modes [20, 41, 42].

We remark that this approach is a semiempirical method, which means that in principle we are unable to predict vibrational energy or intensity patterns for yet unknown systems. Experimental energies and transitions intensities are needed to carry out a vibrational description

of spectroscopic quality, whose accuracy relies on the quality of the input data. However, our algebraic approach is connected with configuration space and predictions are possible provided the force constants as well as the dipole moments.

We should stress that the steps (15) and (17) in our algebraic approach do not have in general an analogy in configuration space, only in the local mode limit. In the next section we shall present the application of this approach to the CO_2 molecule, which present a strong normal mode behavior with degenerate (bending) modes involved.

3. Application of the algebraic approach to CO_2

The first step to study the vibrational spectroscopic description of the CO_2 molecule consists in establishing the symmetry adapted coordinates. For the stretching degrees of freedom we have

$$S_1 \equiv S_{\Sigma_g^+} = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2), \tag{20}$$

$$S_3 \equiv S_{\Sigma_u^+} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2), \tag{21}$$

where $\Delta r_i = r_i - r_e$, with $i = 1, 2$, correspond to the left and right CO distances as displayed in Figure 1 with r_e being the equilibrium distance, while for the bending coordinates we consider [52, 53]

$$S_{2a} = d\ \mathbf{e}_Y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_e^2} \quad , \quad S_{2b} = -d\ \mathbf{e}_X \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_e^2} \quad , \tag{22}$$

where $d = 1$Å is a normalization length.

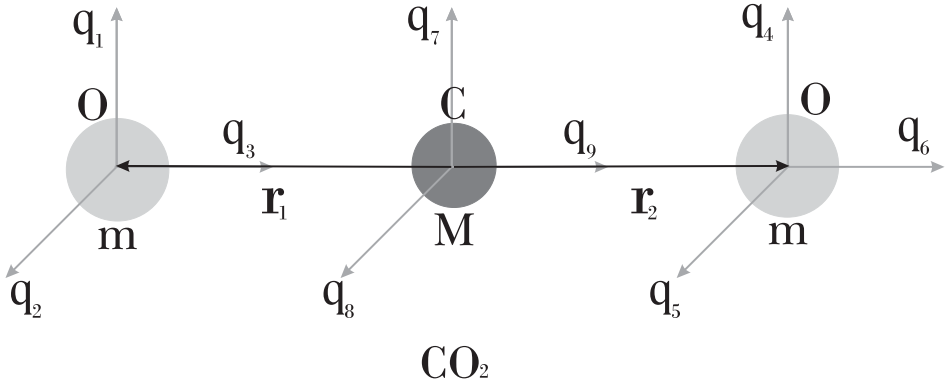

Figure 1. Mass weighted Cartesian displacement coordinates for CO_2.

For the bending modes it is convenient to introduce polar coordinates

$$S_+ = -\frac{1}{\sqrt{2}}(S_{2a} + iS_{2b}) \quad , \quad S_- = \frac{1}{\sqrt{2}}(S_{2a} - iS_{2b}) \quad , \tag{23}$$

with the corresponding conjugate momenta

$$\hat{P}_+ = -\frac{1}{\sqrt{2}}\left(\hat{P}_{2a} - i\hat{P}_{2b}\right), \quad \hat{P}_- = \frac{1}{\sqrt{2}}\left(\hat{P}_{2a} + i\hat{P}_{2b}\right) \quad . \tag{24}$$

In terms of these coordinates the expansion of the Hamiltonian equivalent to (4) may be written as

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb} \quad . \tag{25}$$

with explicit expressions given in Ref.[42].

On the other hand, as expressed by (5), the curvilinear coordinates S_α may be written in terms of a linear combination of the normal coordinates. In terms of the mass weighted Cartesian displacement coordinates $q_1 = \sqrt{m_i}\Delta\xi_i$, $\xi = x, y, z$, we have the following normal coordinates in accordance with the notation of Figure 1:

$$\mathcal{Q}_1 = \frac{1}{\sqrt{2}}(q_6 - q_3), \tag{26}$$

$$\mathcal{Q}_{2a} = \sqrt{\frac{M}{2M_T}}[-(q_1 + q_4) + 2\sqrt{\frac{m}{M}}q_7], \tag{27}$$

$$\mathcal{Q}_{2b} = \sqrt{\frac{M}{2M_T}}[-(q_2 + q_5) + 2\sqrt{\frac{m}{M}}q_8], \tag{28}$$

$$\mathcal{Q}_3 = \sqrt{\frac{m}{2M_T}}[-\sqrt{\frac{M}{m}}(q_3 + q_6) + 2q_9], \tag{29}$$

where $M_T = 2m + M$. In terms of these coordinates the curvilinear coordinates (5), up to third order, take the form

$$S_1 = \frac{1}{\sqrt{m}}\mathcal{Q}_1 + \frac{1}{2\sqrt{2}}\frac{1}{r_e}\frac{M_T}{mM}\mathcal{Q}^2 - \frac{1}{4}\frac{1}{r_e^2}\frac{M_T}{mM\sqrt{m}}\mathcal{Q}_1\mathcal{Q}^2, \tag{30}$$

$$S_{2a} = \sqrt{2}\Big(\frac{d}{r_e}\Big)\sqrt{\frac{M_T}{mM}}\mathcal{Q}_{2a} + \Big(\frac{d}{r_e^2}\Big)\frac{1}{\sqrt{m}}\sqrt{\frac{M_T}{mM}}\mathcal{Q}_1\mathcal{Q}_{2a}, \tag{31}$$

$$S_{2b} = \sqrt{2}\Big(\frac{d}{r_e}\Big)\sqrt{\frac{M_T}{mM}}\mathcal{Q}_{2b} + \Big(\frac{d}{r_e^2}\Big)\frac{1}{\sqrt{m}}\sqrt{\frac{M_T}{mM}}\mathcal{Q}_1\mathcal{Q}_{2b}, \tag{32}$$

$$S_3 = \sqrt{\frac{M_T}{mM}}\mathcal{Q}_3 - \frac{1}{4r_e^2}\frac{M_T}{mM}\sqrt{\frac{M_T}{mM}}\mathcal{Q}_3\mathcal{Q}^2, \tag{33}$$

with the definition $\mathcal{Q}^2 = \mathcal{Q}_{2a}^2 + \mathcal{Q}_{2b}^2$. In order to identify the coordinates involved in the bosonic operators associates with the harmonic oscillators, we introduce the new coordinates Q_i :

$$Q_1 = \frac{1}{\sqrt{m}}\mathcal{Q}_1 \tag{34}$$

$$Q_{2a} = \sqrt{2}\sqrt{\frac{M_T}{mM}}\mathcal{Q}_{2a} \tag{35}$$

$$Q_{2b} = \sqrt{2}\sqrt{\frac{M_T}{mM}}\mathcal{Q}_{2b} \tag{36}$$

$$Q_3 = \sqrt{\frac{M_T}{mM}}\mathcal{Q}_3, \tag{37}$$

given in lenght units. In these new coordinates the expansion (30) takes thus the simplified form

$$S_1 = Q_1 + \frac{1}{4\sqrt{2}}\frac{1}{r_e}Q^2 - \frac{1}{8}\frac{1}{r_e^2}Q_1Q^2, \tag{38}$$

$$S_{2a} = \left(\frac{d}{r_e}\right)Q_{2a} + \left(\frac{d}{r_e^2}\right)\frac{1}{\sqrt{2}}Q_1Q_{2a}, \quad (39)$$

$$S_{2b} = \left(\frac{d}{r_e}\right)Q_{2b} + \left(\frac{d}{r_e^2}\right)\frac{1}{\sqrt{2}}Q_1Q_{2b}, \quad (40)$$

$$S_3 = Q_3 - \frac{1}{8r_e^2}Q_3Q^2, \quad (41)$$

where again $Q^2 = Q_{2a}^2 + Q_{2b}^2$.

Let us now turn our attention to the Hamiltonian (25). The simplest approximation corresponds to consider the first term in the expansions (38), as it was done in Refs. [41, 42, 45]. In this case the curvilinear coordinates are basically identified with the normal coordinates (34). However, in any case, an algebraic representation is obtained by introducing the bosonic creation and annihilation operators [41, 42]

$$a_\Gamma^\dagger = \alpha^\Gamma Q_\Gamma - \frac{i}{2\hbar\alpha^\Gamma}\, p_\Gamma \ , \quad a_\Gamma = \alpha^\Gamma Q_\Gamma + \frac{i}{2\hbar\alpha^\Gamma}\, p_\Gamma \quad ; \Gamma = \Sigma_g, \Sigma_u \quad , \quad (42)$$

$$a_\pm^\dagger = \alpha^\pm Q_\pm + \frac{i}{2\hbar\alpha^\pm}\, p_\mp \ , \quad a_\pm = -\alpha^\pm Q_\mp + \frac{i}{2\hbar\alpha^\pm}\, p_\pm \quad . \quad (43)$$

where α^Γ and $\alpha^\pm$ are given by

$$(\alpha^\Gamma)^2 = \frac{1}{2\hbar} f_{\Gamma\Gamma}\mu_\Gamma; \quad \Gamma = \Sigma_g, \Sigma_u, \quad (44)$$

$$(\alpha^+)^2 = (\alpha^-)^2 = \alpha^2 = \frac{1}{2\hbar}\sqrt{\frac{f_{+-}}{g^0_{+-}}}, \quad (45)$$

with $\mu_{\Sigma_g} = 1/g^o_{\Sigma_g\Sigma_g} = m$ and $\mu_{\Sigma_u} = 1/g^o_{\Sigma_u\Sigma_u} = (2/M + 1/m)^{-1}$, while for the force constants $f_{\Sigma_g\Sigma_g} = f_{rr} + f_{rr'}$ and $f_{\Sigma_u\Sigma_u} = f_{rr} - f_{rr'}$. The resulting Hamiltonian is equivalent to the one in configuration space and it is expected to be diagonalized in a harmonic oscillator basis. The same approach can be followed when considering terms of higher order in the coordinates expansion.

According to the approach previously presented in §2 we proceed to establish the algebraic polyad-preserving Hamiltonian in a local basis. This goal cannot be achieved starting from configuration space because of the strong normal behavior for the stretches. This issue is addressed by introducing the canonical transformation in the stretching coordinates

$$a_{\Sigma_g}^\dagger = \frac{1}{\sqrt{2}}(c_1^\dagger + c_2^\dagger) \ , \quad a_{\Sigma_u}^\dagger = \frac{1}{\sqrt{2}}(c_1^\dagger - c_2^\dagger) \ , \quad (46)$$

where $c_i^\dagger(c_i)$ are bosonic operators isomorphic to the i-th bosonic local operators $a_i^\dagger(a_i)$. Taking into account this isomorphism, the resulting Hamiltonian takes the form

$$\begin{aligned}\hat{H} &= \tilde{\omega}_s \sum_{k=1}^{2}\left(a_k^\dagger a_k + a_k a_k^\dagger\right) + \lambda_s \sum_{k\neq j=1}^{2} a_k^\dagger a_j + \alpha_1^s\left(\hat{n}_1^2 + \hat{n}_2^2\right) \\ &+ \alpha_2^s\left(a_1^{\dagger 2}a_2^2 + a_2^{\dagger 2}a_1^2 + 4\hat{n}_1\hat{n}_2\right) + \alpha_3^s\left(\hat{n}_1 a_2^\dagger a_1 + \hat{n}_2 a_1^\dagger a_2 + H.c.\right) \\ &+ \tilde{\omega}_b\hat{n} + \alpha_1^b\hat{n}^2 + \alpha_2^b\hat{\ell}^2 + \alpha_1^{sb}\left\{\left(a_1^\dagger + a_2^\dagger\right)a_+ a_- + H.c.\right\} \\ &+ \alpha_2^{sb}\left(\hat{n}_1 + \hat{n}_2\right)\hat{n} + \alpha_3^{sb}\left(a_1^\dagger a_2 + a_2^\dagger a_1\right)\hat{n} \ , \end{aligned} \quad (47)$$

with the definitions

$$\hat{n}_k = a_k^\dagger a_k \; ; \quad k = 1, 2 \quad , \tag{48}$$

$$\hat{\ell} = a_+^\dagger a_+ - a_-^\dagger a_- = \hat{n}_+ - \hat{n}_- \quad , \tag{49}$$

$$\hat{n} = a_+^\dagger a_+ + a_-^\dagger a_- = \hat{n}_+ + \hat{n}_- \quad , \tag{50}$$

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. (47) we have restricted the interactions to preserve the polyad number $P = 2(n_{\Sigma_g} + n_{\Sigma_u}) + (n_+ + n_-)$, which establish the subspace of states connected through the transfer of two bending quanta to one stretching quantum. In the linear approximation of (38) the expressions for the spectroscopic parameters in terms of the structure and force constants are detailed in Appendix A of Ref.[42]. The diagonalization of Eq. (47) can be carried out in the harmonic oscillator local basis

$$|n_1 n_2 n_+ n_-\rangle = \frac{1}{\sqrt{n_1! n_2! n_+! n_-!}} (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} (\hat{a}_+^\dagger)^{n_+} (\hat{a}_-^\dagger)^{n_-} |0\rangle. \tag{51}$$

Instead we propose a local mode approach for the stretches in terms of Morse oscillators, together with the incorporation of anharmonic effects for the bending degrees of freedom. This goal is achieved through the introduction of the anharmonization procedure (17). Hence the operators $\{b_i^\dagger(b_i); i = 1, 2\}$ are interpreted as ladder operators for a Morse potential eigenstates with matrix elements (18).

For the bending operators $\hat{a}_\pm^\dagger(\hat{a}_\pm)$ an equivalent anharmonization procedure is performed

$$a_\pm^\dagger \rightarrow b_\pm^\dagger, \quad a_\pm \rightarrow b_\pm \quad , \tag{52}$$

but now the operators $b_\pm^\dagger(b_\pm)$ are given as a linear combination of generators of the $U(3)$ dynamical algebra [20, 21], with matrix elements [41]

$$b_\pm^\dagger |[N]; n^\ell\rangle = \sqrt{\left(\frac{n \pm \ell}{2} + 1\right)\left(1 - \frac{n}{N}\right)} \; |[N]; (n+1)^{\ell \pm 1}\rangle \quad , \tag{53}$$

$$b_\pm |[N]; n^\ell\rangle = \sqrt{\left(\frac{n \pm \ell}{2}\right)\left(1 - \frac{n-1}{N}\right)} \; |[N]; (n-1)^{\ell \mp 1}\rangle \quad , \tag{54}$$

where n and ℓ have the same meaning that in (48), and N is the total number of bosons (irrep of the $U(3)$ group) related with the anharmonicity. Note that the harmonic 2D oscillator matrix elements are recovered in the large N limit of Eq. (53), as expected. Hence applying the anharmonization procedures (17) and (52), yields the following Hamiltonian

$$\begin{aligned}
\hat{H} &= \tilde{\omega}_s \sum_{i=1}^{2} \left(b_i^\dagger b_i + b_i b_i^\dagger\right) + \lambda_s \sum_{i \neq j = 1}^{2} b_i^\dagger b_j + \alpha_1^s \left(\hat{n}_{s,1}^2 + \hat{n}_{s,2}^2\right) \\
&+ \alpha_2^s \left(b_1^{\dagger 2} b_2^2 + b_2^{\dagger 2} b_1^2 + 4 \hat{n}_{s,1} \hat{n}_{s,2}\right) + \alpha_3^s \left(\hat{n}_{s,1} b_2^\dagger b_1 + \hat{n}_{s,2} b_1^\dagger b_2 + H.c.\right) \\
&+ \tilde{\omega}_b \hat{n} + \alpha_1^b \hat{n}^2 + \alpha_2^b \hat{\ell}^2 + \alpha_1^{sb} \left\{\left(b_1^\dagger + b_2^\dagger\right) \hat{b}_+ \hat{b}_- + H.c.\right\} \\
&+ \alpha_2^{sb} \left(\hat{n}_{s,1} + \hat{n}_{s,2}\right) \hat{n} + \alpha_3^{sb} \left(b_1^\dagger b_2 + b_2^\dagger b_1\right) \hat{n},
\end{aligned} \tag{55}$$

now with the definition

$$\hat{n}_{s,i} = b_i^\dagger b_i \quad , \quad i = 1, 2 \quad , \tag{56}$$

and the connection between spectroscopic parameters and force constants is assumed to be identical to the connection previously obtained making use of the harmonic oscillator basis. This resulting Hamiltonian, although not obtained from a scheme of interacting local Morse oscillators, may be interpreted as modeling three interacting oscillators: a 2D oscillator with the $U(3)$ model (bending degrees of freedom) and two 1D Morse oscillators (stretching degrees of freedom).

The matrix representation of the Hamiltonian (55) can be obtained in the $U(2)\times U(3)\times U(2)$ basis

$$|[N_s],[N];v_1v_2;n^\ell\rangle = |\psi^j_{v_1}\rangle \otimes |\psi^j_{v_2}\rangle \otimes |N;n^\ell\rangle \quad , \tag{57}$$

although a symmetry adapted basis combined with a normal mode scheme is preferred [49, 50, 51]. In general the diagonalization leads to eigenvectors of the form

$$|\psi^{\Gamma\gamma}_{P,j}\rangle = \sum_{\nu_1,\nu_2,\nu_3} C^{P,j,\Gamma\gamma}_{\nu_1,\nu_2,\nu_3} |P;\nu_1,\nu_2,\nu_3;\Gamma,\gamma\rangle \tag{58}$$

with the basis set

$$|P;\nu_1,\nu_2,\nu_3;\Gamma,\gamma\rangle = \sum_{v_1,v_2,n} B^{P;\nu_1,\nu_2,\nu_3;\Gamma,\gamma}_{v_1,v_2,n} \; |\psi^j_{v_1}\rangle \otimes |\psi^j_{v_2}\rangle \otimes |N;n^\ell\rangle, \tag{59}$$

where P is the polyad, Γ and γ label the irreducible representations and their components associated with the chain $\mathcal{D}_{\infty h} \supset \mathcal{C}_s$ with $\mathcal{C}_s = \{E, \sigma(xz)\}$, while the set $\{\nu_1,\nu_2,\nu_3\}$ corresponds to an approximate normal-mode labeling [49]. The B coefficients in (59) come from the symmetry projection procedure [49], while the C components in (58) are provided by the diagonalization. We stress that the eigenstates (58) are obtained from an anharmonization procedure without counterpart in configuration space. Concerning the assignment of the transitions, we follow the usual labeling scheme where each state is labeled in accordance with their maximum component in the normal scheme in the expansion (58). We can appreciate that with this method the states may be also labeled in a local scheme through (59). In cases with a strong admixture of the basis, two states may carry the same labels [42, 45].

Using the linear approximation in the coordinates, in Refs. [41, 42] the vibrational spectrum of the molecule ^{12} CO_2 has been described using the Hamiltonian (55). The spectroscopic parameters were optimized with an iterative non-linear least square method [54, 55]. The fit included 101 vibrational (encompassing terms up to polyad $P = 9$) levels with a deviation of rms= 0.53 cm^{-1}. The values for the boson numbers N_s and N were found to be $N_s = 160$ and $N = 150$ [42]. From that work the value for the force constant associated with the Fermi interaction was estimated to be $f_{q_1q_aq_a} = -0.9592$ aJÅ^{-3}, in close agreement with the Chedin's result [56].

In phenomenological algebraic models a test of the quality of the wave functions is compulsory since a good energy fit does not guarantee the wave functions quality [57]. Indeed the wave functions represent a sensitive indicator as a test of the quality of the description. This situation will be discussed in detail in the next section, when we introduce the description of the Raman spectrum.

4. Polarizability derivatives

Line intensities in a Raman spectrum for a gas sample are given by the transition moments of the molecular polarizability tensor α. In the particular case of the CO_2 molecule, the non-vanishing components of α tensor have symmetries Σ^+_g (trace) and $\Sigma^+_g \oplus \Pi_g \oplus \Delta_g$ (anisotropy). The sharp, polarized, Q-branches in the vibrational Raman spectrum of CO_2 in the $\sim$ 1300 cm^{-1} region are totally symmetric (Σ^+_g) transitions and their intensities are mainly due to the trace of the

α tensor (mean-polarizability). For the trace scattering of a gas sample at thermal equilibrium, the differential cross section can be expressed in the SI system as follows [53]

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{i\to f}^{\text{trace}} = \left(\frac{\pi}{\epsilon_0}\right)^2 \frac{(\nu_0+\nu_i-\nu_f)^4}{Z_{vib}(T)} g_{if}\,(M_{if})^2 \exp\left(-hc\nu_i/k_BT\right) \quad , \tag{60}$$

where ϵ_0 is the vacuum permitivity, ν_0 is the wave number of the exciting radiation $\nu_0 = 19430$ cm^{-1}, ν_i and ν_f are the wavenumbers of initial and final states, and g_{if} is the vibrational degeneracy of the energy levels involved in the transition. $Z_{vib}(T) = \sum_j g_j e^{-\nu_j/k_BT}$ is the vibrational partition function at the temperature T of the gas sample, where g_j is the degeneracy of the j-th state with ν_j energy, and $M_{if} = \langle\nu_i|\bar{\alpha}|\nu_f\rangle$ is the transition moment of the mean molecular polarizability $\bar{\alpha}$ between vibrational states $|\nu_i\rangle$ and $|\nu_f\rangle$.

The computation of the intensity (60) involves the molecular polarizability surface, which can be expressed as a Taylor series expansion on the vibrational coordinates

$$\begin{aligned}
\bar{\alpha}_{\Sigma_g^+} &= \bar{\alpha}_0 + \left(\frac{\partial\bar{\alpha}}{\partial S_{\Sigma_g^+}}\right)_0 S_{\Sigma_g^+} + \frac{1}{2}\left(\frac{\partial^2\bar{\alpha}}{\partial S^2_{\Sigma_g^+}}\right)_0 S^2_{\Sigma_g^+} + \frac{1}{2}\left(\frac{\partial^2\bar{\alpha}}{\partial S^2_{\Sigma_u^+}}\right)_0 S^2_{\Sigma_u^+} \\
&+ \frac{1}{2}\left(\frac{\partial^2\bar{\alpha}}{\partial S^2_{2a}}\right)_0 (S^2_{2a}+S^2_{2b}) + \frac{1}{2}\left(\frac{\partial^3\bar{\alpha}}{\partial S_{\Sigma_g^+}\partial S^2_{2a}}\right)_0 S_{\Sigma_g^+}(S^2_{2a}+S^2_{2b}) \\
&+ \frac{1}{2}\left(\frac{\partial^3\bar{\alpha}}{\partial S_{\Sigma_g^+}\partial S^2_{\Sigma_u^+}}\right)_0 S_{\Sigma_g^+} S^2_{\Sigma_u^+} \quad ,
\end{aligned} \tag{61}$$

where the derivatives are unknown. The last term in Eq. (61) turns out to be negligible and, consequently, it will be omitted [53]. These derivatives may be determined through *ab initio* calculations [58], but they can be also obtained from a fit to experimental transition moments [53, 59].

In the linear approximation the expansion in terms of normal coordinates takes the same form as (61), but substituting S_α by Q_α. This case was considered previously to estimate the derivatives of the polarizability as well as to calculate the Raman spectrum [45]. Here we shall proceed to investigate the nonlinearity effects in this analysis. If non linear terms are taken into account, we have for the polarizability the following expansion in terms of normal coordinates

$$\begin{aligned}
\bar{\alpha}_{\Sigma_g^+} &= \bar{\alpha}_0 + \alpha_1\left(Q_1 + \frac{1}{4\sqrt{2}r_e}Q^2 - \frac{1}{8r_e^2}Q_1Q^2\right) \\
&+ \frac{1}{2}\alpha_{11}\left(Q_1^2 + \frac{1}{32r_e^2}Q^2 + \frac{1}{64r_e^4}Q_1^2Q^4 + \frac{1}{2\sqrt{2}r_e}Q_1Q^2 - \frac{1}{4r_e^2}Q_1^2Q^2 - \frac{1}{16\sqrt{2}r_e^3}Q_1Q^4\right) \\
&+ \frac{1}{2}\alpha_{33}\left(Q_3^2 + \frac{1}{64r_e^4}Q_3^2Q^4 - \frac{1}{4r_e^2}Q_3^2Q^2\right) \\
&+ \alpha_{22}\left(\frac{d^2}{4r_e^4}Q_1^2Q^2 + \frac{d^2}{\sqrt{2}r_e^3}Q^2Q_1 + \frac{d^2}{2r_e^2}Q^2\right) \\
&+ \alpha_{122}\Big(-\frac{d^2}{32r_e^6}Q_1^3Q^4 + \Big(-\frac{1}{2}\Big)\frac{d^2}{16\sqrt{2}r_e^5}Q_1^2Q^4 + \frac{d^2}{4r_e^4}Q_1^3Q^2 + \Big(\frac{1}{2}\Big)\frac{d^2}{16r_e^4}Q_1Q^4 \\
&\qquad + \frac{d^2}{\sqrt{2}\,r_e^3}Q_1^2Q^2 + \frac{d^2}{8\sqrt{2}r_e^3}Q^4 + \frac{d^2}{2r_e^2}Q_1Q^2\Big),
\end{aligned} \tag{62}$$

with the following definitions for the derivatives

$$\alpha_1 = \left(\frac{\partial\bar{\alpha}}{\partial S_{\Sigma_g^+}}\right)_0; \quad \alpha_{11} = \left(\frac{\partial^2\bar{\alpha}}{\partial S^2_{\Sigma_g^+}}\right)_0; \quad \alpha_{33} = \left(\frac{\partial^2\bar{\alpha}}{\partial \mathcal{S}^2_{\Sigma_u^+}}\right)_0,$$

$$\alpha_{22} = \left(\frac{\partial^2\bar{\alpha}}{\partial S_{2a}^2}\right)_0; \quad \alpha_{122} = \left(\frac{\partial^3\bar{\alpha}}{\partial\mathcal{S}_{\Sigma_g^+}\partial S_{2a}^2}\right)_0. \tag{63}$$

We now have the task of computing the matrix elements of the mean molecular polarizability $\bar{\alpha}$ between the system wavefunctions (58). The approach to follow is similar to the calculation of the matrix elements of the Hamiltonian. We first introduce an algebraic representation of $\bar{\alpha}$ introducing the bosonic operators (42). Then the cannonical transformation (46) together with the identification (15) is carried out. Finally the anharmonizations (17) and (52) are applied. In this way the matrix elements of the $\bar{\alpha}$ in the basis (57) is well defined, and the transition moments $M_{if} = |\langle\nu_i|\bar{\alpha}|\nu_f\rangle|$ can be calculated using the expansion (61) and the wavefunctions (58). The comparison of the calculated M_{if}^{calc} with those M_{if}^{exp} derived from the experimental transition intensities (60) [53, 60], allows us to obtain estimates of the molecular polarizability derivatives Eq. (63). To achieve this task the following root mean square deviation is defined [45]

$$rms = \sqrt{\sum_\beta [\log|M_\beta^{exp}| - \log|M_\beta^{calc}|]^2} \tag{64}$$

which is minimized by a suitable selection of the polarizability derivatives, using the values in Ref. [53] as initial guesses for the fitting procedure. In the previous work the subindex β run over the first six transitions presented in Table 1. In this work it was necessary to consider the first nine transitions in order to obtain convergence. At the left (first three columns) of Table 1 the experimental and calculated frequencies of the Raman transitions as well as the states involved in the transitions are displayed. At the right the experimental matrix elements M_{if}^{exp} [53, 60] and the calculated ones after the minimization of Eq. (64) are given.

The fit allows the derivatives of $\bar{\alpha}$ with respect to nonlinear symmetry adapted coordinates to be estimated. These derivatives are displayed in the left panel of Table 2. For comparison we include the experimental values as well as the derivatives obtained using the linear approximation [45]. In general, there is a good agreement between our results and the experimental polarizability derivatives, in particular for the first three derivatives α_1, α_{11} and α_{33}. For the derivative α_{122} a slightly different value is obtained, but significant discrepancies appear in the bending polarizability derivatives. While the experimental one takes the value $\alpha_{122} = 0.36$, we obtained $\alpha_{122} = -0.06$. At this point the linear approximation seems to represent a better result. However, we have to take into account that the derivatives (63) in Ref.[53] were obtained from the derivatives with respect to the dimensionless normal coordinates and consequently a much better physical comparison is expected to be obtained by calculating such derivatives. The connection between both sets of derivatives is established using the expansion (5) and the chain rule to obtain

$$\bar{\alpha}_1' \equiv \frac{\partial\bar{\alpha}}{\partial\mathcal{Q}_1} = \frac{1}{\sqrt{m}}\frac{\partial\bar{\alpha}}{\partial S_1} \tag{65}$$

$$\bar{\alpha}_{11}' \equiv \frac{\partial^2\bar{\alpha}}{\partial\mathcal{Q}_1^2} = \frac{1}{m}\frac{\partial^2\bar{\alpha}}{\partial S_1^2} \tag{66}$$

$$\bar{\alpha}_{33}' \equiv \frac{\partial^2\bar{\alpha}}{\partial\mathcal{Q}_3^2} = \frac{M_T}{mM}\frac{\partial^2\bar{\alpha}}{\partial S_3^2} \tag{67}$$

$$\bar{\alpha}_{+-}' \equiv \frac{\partial^2\bar{\alpha}}{\partial\mathcal{Q}_{2a}^2} = 2\left(\frac{d}{r_e}\right)^2\frac{M_T}{mM}\left\{\frac{r_e}{2\sqrt{2}d^2}\frac{\partial\bar{\alpha}}{\partial S_1} + \frac{\partial^2\bar{\alpha}}{\partial S_{2a}^2}\right\} \tag{68}$$

$$\bar{\alpha}_{1+-}' \equiv \frac{\partial^3\bar{\alpha}}{\partial\mathcal{Q}_1\partial\mathcal{Q}_{2a}^2} = 2\left(\frac{d}{r_e}\right)^2\frac{M_T}{m\sqrt{m}M}\left\{\frac{1}{4d^2}\frac{\partial\bar{\alpha}}{\partial S_1} + \frac{r_e}{2\sqrt{2}d^2}\frac{\partial^2\bar{\alpha}}{\partial S_1^2} + \Lambda_1\frac{\sqrt{2}}{r_e}\frac{\partial^2\bar{\alpha}}{\partial S_{2a}^2} + \frac{\partial^3\bar{\alpha}}{\partial S_1\partial S_{2a}^2}\right\} \tag{69}$$

The derivatives with respect to the dimenssionless normal coordinates used in Ref.[53] are obtained by multiplying for a product $\prod_i \sqrt{2}b_i$, where i runs over the coordinates involved in the derivatives, and

$$b_i^2 = \frac{h}{8\pi^2\omega_i c}, \tag{70}$$

where $\omega_i = 1/\lambda_i$ is the wave number associated with the i-th mode.

Table 1. Experimental and fitted transition moments $|M_{if}| = |\langle\nu_i|\bar{\alpha}|\nu_f\rangle|$ of the mean polarizability of CO_2. The first six transitions were involved in the fit while the last five are predictions. The labeling was chosen to be the normal mode scheme (ν_1, ν_2, ν_3).

ν $(\mathrm{cm}^{-1})^a$	ν $(\mathrm{cm}^{-1})^b$	$\lvert\nu_i\rangle^c \longrightarrow \lvert\nu_f\rangle$ transition	$\lvert M_{if}\rvert = \lvert\langle\nu_i\rvert\bar{\alpha}\lvert\nu_f\rangle\rvert^d$	$\lvert M_{if}\rvert = \lvert\langle\nu_i\rvert\bar{\alpha}\lvert\nu_f\rangle\rvert^e$
1285.4	1286.29	$\lvert 0;000;\Sigma_g^+\rangle \longrightarrow \lvert 2;100;\Sigma_g^+\rangle$	5.58	5.59
1388.2	1387.54	$\lvert 0;000;\Sigma_g^+\rangle \longrightarrow \lvert 2;020;\Sigma_g^+\rangle$	6.79	6.89
2548.4	2549.53	$\lvert 0;000;\Sigma_g^+\rangle \longrightarrow \lvert 4;120;\Sigma_g^+\rangle$	0.088	0.084
2671.1	2671.11	$\lvert 0;000;\Sigma_g^+\rangle \longrightarrow \lvert 4;200;\Sigma_g^+\rangle$	0.114	0.116
2797.1	2795.98	$\lvert 0;000;\Sigma_g^+\rangle \longrightarrow \lvert 4;120;\Sigma_g^+\rangle$	0.026	0.026
4673.3	4673.17	$\lvert 0;000;\Sigma_g^+\rangle \longrightarrow \lvert 4;002;\Sigma_g^+\rangle$	0.050^f	0.050
1265.1	1266.04	$\lvert 1;010;\Pi_u\rangle \longrightarrow \lvert 3;110;\Pi_u\rangle$	5.4	5.41
1409.5	1408.54	$\lvert 1;010;\Pi_u\rangle \longrightarrow \lvert 3;030;\Pi_u\rangle$	7.2	7.06
2514.1	2515.01	$\lvert 1;010;\Pi_u\rangle \longrightarrow \lvert 5;130;\Pi_u\rangle$	0.095	0.098
2671.9	2671.93	$\lvert 1;010;\Pi_u\rangle \longrightarrow \lvert 5;210;\Pi_u\rangle$	...	0.109
2833.3	2831.93	$\lvert 1;010;\Pi_u\rangle \longrightarrow \lvert 5;130;\Pi_u\rangle$	≤ 0.03	0.016

[a] Experimental transition frequency [53].
[b] Theoretical frequency calculated from the fitted vibrational term values of Ref. [42].
[c] The vibrational states are labeled by the ket $|P;\nu_1,\nu_2,\nu_3;\Gamma\rangle$ where P is the polyad number, (ν_1,ν_2,ν_3) are the quantum numbers of the normal-mode representation and Γ is the symmetry of the vibrational wavefunction.
[d] Experimental values from Ref. [53] in $10^{-42}\mathrm{CV}^{-1}\mathrm{m}^2$ otherwise is indicated.
[e] Fitted and predicted values of the transition moment in $10^{-42}\mathrm{CV}^{-1}\mathrm{m}^2$ obtained from this work.
[f] Value derived from *Chrysos et al.* [60].

In the right panel of Table 2 we compare our results with the mean polarizability derivatives with respect to dimensionless normal coordinates obtained by *Tejeda et al.* in Ref. [53]. As in the previous case, the first three derivatives are very close to the experimental, which means that the non linear effects are basically negligible. In contrast for the second derivative with respect to the bending coordinate, $\bar{\alpha}''_{+-}$, and $\bar{\alpha}''_{1+-}$, the nonlinear effects turn out to be significant. In the linear approximation the derivative $\bar{\alpha}''_{+-}$ is 31 % smaller than the experimental value of *Tejeda et al.*, but when the non linear terms are incorporated the derivative becomes closer to the expected value lowering the error to 25 %. This improvement is not reflected in the left panel. From the technical point of view this fact is explained by the appearance of the derivative $\partial\bar{\alpha}/\partial S_1$ in (68) as a consequence of nonlinearity. This term is not negligible compared with $\partial^2\bar{\alpha}/\partial S_{2a}^2$. With respect the derivative $\bar{\alpha}''_{1+-}$ the improvement is slightly better. The error decreases from 8.4 % to 1.6 %.

The results displayed in Table 2 for the derivatives show the sensitiveness of the polarizability with respect to the nonlinearity. Only the derivatives involving the bending coordinates are affected by the non linear terms. The differences between our results and the ones obtained by *Tejada et al* can be attributed to the approach followed to obtain the eigenstates. In Ref.[53] the derivatives with respect to the normal coordinates were fitted using perturbation theory through the eigenfunctions of the Chedin's results. It is worth mentioning that if the latter procedure is applied to our calculated transition moments in Table 1, the value of $\bar{\alpha}''_{+-} = 2.28 \times 10^{-42}$ C m^2 V^{-1} is obtained, very close to the value 2.12×10^{-42} C m^2 V^{-1} of our fit. This is an indication of the consistency of the methodology employed in this work.

Table 2. Derivatives of the mean polarizability of CO_2 with respect to the symmetry coordinates (left panel) and dimensionless normal coordinates (right panel).

Symmetry coordinates				Dimensionless normal coordinates			
Derivative (units) [a]	Linear [b]	Exp [c]	Nonlinear [d]	Derivative [e] ($10^{-42}CV^{-1}m^2$)	Linear [f]	Exp [d]	Nonlinear
$(\partial\bar{\alpha}/\partial S_{\Sigma_g})_0(10^{-30}\,CV^{-1}m)$	3.15	3.15	3.181	$\bar{\alpha}'_1$	12.44	12.43	12.56
$(\partial^2\bar{\alpha}/\partial S^2_{\Sigma_g})_0(10^{-20}\,CV^{-1})$	2.549	2.9	2.634	$\bar{\alpha}''_{11}$	0.398	0.45	0.411
$(\partial^2\bar{\alpha}/\partial S^2_{\Sigma_u})_0(10^{-20}\,CV^{-1})$	0.447	0.50	0.448 [g]	$\bar{\alpha}''_{33}$	0.144	0.15 [g]	0.144
$(\partial^2\bar{\alpha}/\partial S^2_{2a})_0(10^{-20}\,CV^{-1})$	0.8395	0.36	−0.060	$\bar{\alpha}''_{+-}$	1.925	2.81	2.12
$(\partial^3\bar{\alpha}/\partial S_{\Sigma_g}\partial S^2_{2a})_0(10^{-10}\,CV^{-1}m^{-1})$	−1.21	−1.7	−1.2	$\bar{\alpha}'''_{1+-}$	−0.110	−0.06	−0.061

[a] Polarizability function derivatives as defined in Eq. (61).
[b] Values obtained in this work by a fitting of experimental polarizability transition moments (see Table 1).
[c] Refs. [?, 58].
[d] Experimental values [53].
[e] Polarizability function derivatives in terms of dimensionless normal coordinates as defined in Ref. [53].
[f] Polarizability derivative values given in second column after transforming them from symmetry coordinates to dimensionless normal coordinates.
[g] Best choice of the two available experimental values of *Tejeda et al.* [53] according to the *ab initio* CCSD(T) value provided in Ref. [58].

5. Conclusions

In this work a general algebraic approach to describe the vibrational spectroscopy of molecules presenting both normal and local mode behaviors has been presented. The main feature of our approach is that the PES can be estimated for every kind of semirigid molecule using a local basis with preservation of the polyad, allowing anharmonic effects to be introduced from the outset. This approach is not analogous to any method in configuration space, since any trial to obtain a PES from a local basis necessarily leads to brake the polyad when a normal mode behavior is present. Although in this work we present an application to CO_2, the current approach could be extended to deal with more complex molecular systems presenting either a local-mode or a normal-mode behavior.

In the present work we have applied the algebraic method to the description of the CO_2 molecule. Although this molecule has already been studied in the framework of this approach, here we present the general approach in detail with the extension to include non linear coordinates. Since CO_2 molecule is linear, the local-mode description is introduced via a canonical transformation in the stretching degrees of freedom, after an anharmonization procedure, gives rise to the $U(2) \times U(3) \times U(2)$ model. The model basis set is built as the direct product of two 1D local Morse potential wavefunctions for the stretching and a 2D quasi-rigid bender wavefunction. The Morse functions are introduced as a consequence of the anharmonzation procedure in the local basis while the U(3) model appears because of the anharmonization in the 2D harmonic oscillator. Our analysis starts with a summary of the previous results obtained for the energy fits and their consequences in the estimation of the PES as well as in the quality of the eigenstates. An attempt to improve the Fermi force constant through the non linear effects fails due to their non perturbative effects at the level of approximation.

The polarizability function is expanded in terms of non linear symmetry coordinates, which through the use of the transformation (5) to normal coordinates, is transformed into an expansion in terms of normal coordinates. This allows us to obtain its algebraic representation by the introduction of the bosonic operators associated with the normal modes. In similar form to the Hamiltonian, thereafter the anharmonization procedure is applied. This makes possible to compute the Raman transition matrix elements using the algebraic eigenstates. The

polarizability function derivatives with the stretching coordinates obtained agree with previous estimations based an a linear expansion. The non linear effects manifest in the calculations of the derivatives associated with the bending coordinates, which moves in the right direction to agree with the experimental results.

The eigenstates provided by the Hamiltonian parameter values in Ref. [42] along with the polarizability derivatives allow us to reproduce most of the available experimental Raman intensities. This is a stringent test for the calculated wavefunctions opening up the possibility of simulations of high temperature Raman spectra of CO_2 for combustion flames diagnostics [61].

Although in this contribution the main focus of interest was the particular molecule of CO_2, this approach is general and it can be applied to any semi-rigid molecular system either linear or nonlinear. However, it does not mean that the quality of the description would be similar, because ro-vibrational interactions and/or polyad breaking interactions may appear as fundamental ingredients.

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Estimado Manolo Tena,

Muchisimas gracias por esta atencion.

deseo decirle que toda la semana he estado completamente en tension sin poder dormir por este problema. Como Usted sabe,tenia la cita con el abogado representante de la demanda y Usted me dijo que la pospusiera.

Quiero pedirle disculpas debido a que decidi asistir solo para saber lo que querian. Yo se que esto fue indevido dado el consejo que Usted me dio, pero me volvia loco solo el pensar que la propiedad de mi papa estaba ya por venderse. Tenia que saber la situacion en la que estaba el terreno. La incertidumbre me tenia en zozobra. Solo escuche lo que desaban y me retire.

Le pido disculpas y espero que comprenda y me perdone.