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# Simulation of the Raman spectra of CO<sub>2</sub>: Bridging the gap between algebraic models and experimental spectra

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The carbon dioxide Raman spectrum is simulated within an algebraic approach based on curvilinear coordinates in a local representation. The two main advantages of the present algebraic approach are a possible connection with configuration space and the correct description of systems with either local or normal mode character. The system Hamiltonian and polarizability tensor are expanded in terms of curvilinear coordinates. The curvilinear coordinates are in turn expanded into normal coordinates, obtaining an algebraic representation in terms of normal bosonic operators. A canonical transformation maps the operators into a local algebraic representation. The final step is an anharmonization procedure to local operators. The Raman spectrum of CO<sub>2</sub> has been simulated, obtaining results close to experimental accuracy, and polarizability transition moments for the Raman spectral lines between 1150 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> are reported. The comparison between experimental and simulated spectra has provided six new CO<sub>2</sub> experimental vibrational terms. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4889995>]

## I. INTRODUCTION

Algebraic methods have been for a long time a useful tool to describe the vibrational spectrum of molecules. Usually such methods are based on harmonic oscillator bases because of their direct correspondence with normal modes.<sup>1–5</sup> A remarkable advantage of the algebraic representation is that it allows the precise identification of the most relevant interactions, in such a way that it is relatively easy to split the basis set into different subspaces that do not interact among themselves to a first approximation. These basis subsets are characterized by a pseudoquantum number called polyad.<sup>6–8</sup> This approach has proved specially useful when combined with canonical Van Vleck perturbation theory.<sup>9,10</sup> In a polyad-preserving approach the representation of the Hamiltonian is block diagonal, with each block characterized by the polyad number and the irreducible representation (irrep) of the symmetry group. This scheme remains valid as long as the description is confined to the low-lying region of the spectrum, since as energy increases both the polyad and the harmonic oscillator basis may stop being useful approximations, either because of large anharmonic effects or the occurrence of different structural minima accessible over potential barriers. In such situations breaking the polyad may represent a suitable strategy.<sup>2,3,11–16</sup> It has recently been shown how a polyad-breaking effective Hamiltonian is capable of describing the spectrum of systems with a reaction barrier (e.g., dissociation or isomerization systems).<sup>17–19</sup>

The traditional description of molecular vibrations in terms of normal modes<sup>20</sup> involves harmonic collective nuclear

motions, and works reasonably well for molecules without large mass differences in their constituents. However, when such mass differences are present, an approach based on local modes may be more convenient to explain the patterns appearing in the energy spectrum.<sup>21–29</sup> Local modes exhibit a characteristic pattern of near-degenerate states,<sup>30</sup> a fact nicely explained with the simplest version of the local theory.<sup>23</sup> The basic idea behind local models consists in expressing the Hamiltonian in terms of a set of oscillators associated with local coordinates, coupled by kinetic and potential energy terms. The recognition of the relevance of this approach was delayed due to the successful description of the overtones of H<sub>2</sub>O with an effective spectroscopic Hamiltonian in normal coordinates including a Darling–Dennison resonance term due to the near degeneracy of the symmetric and anti symmetric stretching normal modes.<sup>31</sup> After that work, a quarter of a century elapsed before the local mode concept was reintroduced.<sup>32–35</sup> Local modes are closely related to anharmonic effects, a fact that explains the heavy mixing required in the normal basis to describe the aforementioned patterns. Hence molecules having hydrogen atoms are appropriate candidates to be described in the framework of the local scheme. The search for a connection between the local and normal mode descriptions of molecular vibrations led to the establishment of the  $x$ - $K$  relations, the connection between the spectroscopic parameters of these two descriptions.<sup>36–42</sup> In particular, the equivalence of the local algebraic and the normal Darling–Dennison Hamiltonians through a SU(2) transformation was demonstrated by Lehmann and Kellman.<sup>43,44</sup>

The Morse and Pöschl-Teller potential wavefunctions are convenient bases for the local mode description, because both potentials have analytic solutions in one dimension and can model stretching or bending vibrations, respectively.<sup>45,46</sup> Indeed the study of two interacting Morse oscillators is the prototype to simulate the stretching degrees of freedom of triatomic molecules from different perspectives,<sup>23,47</sup> including classical trajectories obtained with nonlinear dynamics tools.<sup>26,48–51</sup>

From a power expansion of the Hamiltonian in terms of normal coordinates in configuration space it is possible to obtain an algebraic representation using bosonic operators in such a way that the optimized spectroscopic parameters allow the potential energy surface (PES) to be estimated.<sup>1,2</sup> When large mass differences are involved, a local description may be more useful but not necessarily including all the degrees of freedom. An example of this mixed approach treats stretching degrees of freedom as local Morse oscillators, while bending degrees of freedom are modeled using harmonic oscillators.<sup>52,53</sup> An attempt to use a local scheme for every degree of freedom may fail in extracting the correct PES. However, a scheme encompassing local or normal approaches may be attractive and useful when dealing with the PES.

Because of the relation between locality and anharmonicity, Morse functions may be the starting point to model local oscillators. In particular, this can be done in the framework of the one dimensional limit of the vibron model, that exploits the isomorphism between the one dimensional Morse potential and the  $U(2)$  dynamical algebra.<sup>54</sup> Phenomenological algebraic local models using a  $U(2)$  basis have been extensively used in the spectroscopic description of the molecular vibrations of semi-rigid molecules.<sup>54–63</sup> Phenomenological models and, in particular, anharmonic spectroscopic effective Hamiltonians, provide wavefunctions but a link to the system PES is missing. Consequently, it is not possible to extract chemical information from the molecular PES. This problem was overcome once the coordinate and momenta for the Morse and/or Pöschl-Teller (PT) functions were realized in terms of the generators of the  $U(2)$  algebra<sup>64–66</sup>—equivalent expansions were obtained before in terms of bosonic operators through a Holstein-Primakov transformation.<sup>67,68</sup> Although these potentials can be treated in a unified form through the  $U(2)$  algebra, the choice depends on their symmetry. This connection allowed the calculation of force constants and, consequently, the obtainment of a PES used to predict the spectra of isotopologues.<sup>68–75</sup> Recently, an alternative approach to solve the problem of linking with a correct coordinate space representation in the case of a spectroscopic effective Hamiltonian has been applied to the case of a polyad-breaking Hamiltonian.<sup>19</sup>

The polyad pseudo quantum number implies a linear combination of normal mode quantum numbers multiplied by positive weights.<sup>7</sup> Thus, the natural way to define a system's polyad is from a normal mode scheme, and a translation into a local scheme may not be possible. In particular, this is relevant in systems with a strong normal mode character, e.g.,  $\text{CO}_2$  and  $\text{BF}_3$ .<sup>73,76,77</sup> In such cases normal modes are the convenient framework for the system's description. If such

molecules are described as a set of interacting local oscillators two problems appear. On the first hand, the polyad in terms of local oscillators may not be well defined<sup>73</sup> and, on the second hand, a wrong estimate of the molecular force constants is obtained. This is explained by the fact that non-interacting local oscillators are not a good zeroth order Hamiltonian. In order to obtain a correct estimation of the system's force constants it is necessary to introduce interactions that break the polyad, as explained in detail in Refs. 76 and 78. In contrast, when the description can be carried out with interacting local oscillators, an algebraic description with a good estimation of the force constants is possible either in a local or normal mode scheme. From a phenomenological point of view both approaches are equivalent,<sup>79,80</sup> although only one of the cases provide realistic force constants.

In recent works it has been proved that it is possible to conserve the polyad quantum numbers and estimate the PES for any molecular degree of freedom using an algebraic approach based on  $U(2)$  algebras.<sup>76–78</sup> The basic idea is akin to the basis of previous works that connect the local and normal approaches: the traditional algebraic description in terms of bosonic operators associated with normal modes is mapped with a canonical transformation into bosonic operators isomorphic to symmetry adapted local bosonic operators, as in previous studies connecting the local and normal mode approaches. Finally, a crucial aspect of the model is that anharmonicity is considered replacing local bosonic operators with ladder operators associated with Morse or Pöschl-Teller functions. This last step is done preserving the connection between spectroscopic parameters and force constants. In our opinion this is a major advantage of the present approach.

The natural description of molecular vibrations is in terms of internal (valence) curvilinear coordinates,<sup>81,82</sup> although variable curvature coordinates have also been considered (see, e.g., Ref. 83). Symmetry-adapted combinations of these curvilinear coordinates can be expanded into a power series of the normal coordinates, that are rectilinear by definition.<sup>20</sup> A first-order approximation consists in truncating the expansion at the linear terms which implies an identification of the (now rectilinear) symmetry coordinates with linear combinations of normal coordinates. This approximation has been considered in previous applications of the  $U(2)$  algebraic approach.<sup>74</sup> However, a general approach considering curvilinear symmetry adapted coordinates is of great interest. In this contribution we review from a general perspective a local algebraic approach based on  $U(2)$  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 either curvilinear coordinates or normal coordinates. As an application, the study of the vibrational excitations of the molecule of carbon dioxide ( $^{12}\text{CO}_2$ ) in its ground electronic state is presented, considering non-linear effects in the expansion of curvilinear coordinates as a function of normal coordinates.

The present approach is applied to the Raman spectrum of carbon dioxide, a very relevant molecular species in the study of the earth's climate, combustion, planetary atmospheres, etc.<sup>84</sup> Therefore, both experimental and theoretical spectroscopic studies are needed to complete the most

currently used spectroscopic databases; e.g., HITRAN, GEISA, HITEMP, JPL, and CDSD databases. For this reason, an exhaustive spectral analysis of the absorption spectrum has been recently carried out.<sup>84–86</sup>

Due to its importance in different fields, carbon dioxide has not only been deeply studied quantum mechanically, but also using the modern methods of nonlinear classical mechanics, which have been extensively applied to the dynamics of molecular resonance spectra.<sup>79,87</sup> In particular, phase space bifurcations structure involving Fermi-like resonances has been analyzed,<sup>80,88,89</sup> and the results have been applied in particular with application to the CO<sub>2</sub> molecule.<sup>90</sup> Also catastrophe theory has been used to classify the dynamics of spectra involving the 2:1 bend-stretch Fermi resonance in carbon dioxide.<sup>91</sup>

The present study includes the analysis of the Raman spectrum transition probabilities,<sup>92</sup> which represents an exigent test for the computed vibrational eigenfunctions. The expansion of the molecular polarizability tensor as a Taylor series into either curvilinear or normal coordinates is used to describe the spectrum. The analysis of the carbon dioxide molecule using rectilinear coordinates has already been reported in a letter form.<sup>93</sup> In this work we include previously neglected nonlinear effects and we present the approach from a more general perspective, emphasizing the effect of the nonlinear contributions. In addition to this, the CO<sub>2</sub> polarizability transition moments are predicted, and used to simulate the Raman spectrum close to experimental accuracy. It is expected that this prediction provides valuable information for quantitative combustion diagnostics and could also be of help in the identification of transition signatures with spectroscopic accuracy. As a bonus, new experimental vibrational bands are reported, obtained from the comparison of the experimental and simulated Raman spectra.

The present work is organized as follows. First, the different sets of coordinates used in the proposed formalism are defined in Sec. II. In Sec. III we present in detail the main points of the algebraic model. Section IV is devoted to the application of our algebraic approach to the CO<sub>2</sub> molecule. The comparison of theoretical and experimental results of the CO<sub>2</sub> Raman spectrum, as well as the estimation of the derivatives of the polarizability tensor, can be found in Sec. V. Finally, in Sec. VI, a summary and concluding remarks are presented.

## II. COORDINATES

For the sake of clarity, the different sets of coordinates used in the present paper to describe the molecular vibrations of the CO<sub>2</sub> molecule are defined in first place. Three main types of coordinates will be used.

(i) *Curvilinear symmetry coordinates*  $S_\alpha$  are symmetry-adapted combinations of the internal (valence) bond-stretching and angle-bending coordinates. In the stretching degrees of freedoms case, the coordinates are

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

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

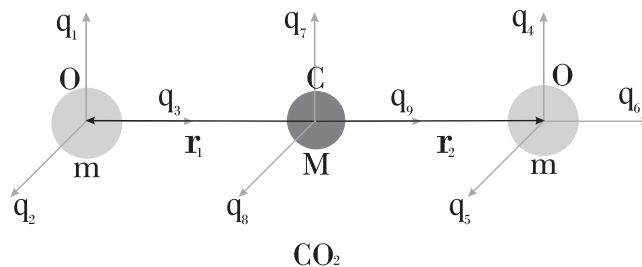


FIG. 1. Atomic masses and Cartesian coordinates for CO<sub>2</sub>.

where  $\Delta r_i = r_i - r_e$ , with  $i = 1, 2$ , corresponds to the left and right CO distances as displayed in Figure 1 with  $r_e$  being the bond equilibrium distance. The bending coordinates are<sup>82</sup>

$$S_{2a} = r_e \mathbf{e}_Y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2}, \quad S_{2b} = -r_e \mathbf{e}_X \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2}. \quad (3)$$

Another possibility, used by Tejada *et al.*,<sup>94</sup> is

$$S_{2a} = d \mathbf{e}_Y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_e^2}, \quad S_{2b} = -d \mathbf{e}_X \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_e^2}, \quad (4)$$

where  $d = 1 \text{ \AA}$  is a normalization length. The advantage of the latter definition is that its expansion into normal coordinates is finite. In our analysis we shall consider both definitions. In this case it is convenient to introduce polar coordinates

$$S_+ = -\frac{1}{\sqrt{2}}(S_{2a} + i S_{2b}), \quad S_- = \frac{1}{\sqrt{2}}(S_{2a} - i S_{2b}), \quad (5)$$

with the corresponding conjugate momenta

$$\hat{P}_+ = -\frac{1}{\sqrt{2}}(\hat{P}_{2a} - i \hat{P}_{2b}), \quad \hat{P}_- = \frac{1}{\sqrt{2}}(\hat{P}_{2a} + i \hat{P}_{2b}). \quad (6)$$

(ii) *Mass-weighted (rectilinear) normal coordinates*  $Q_\alpha$ , which are expressed in terms of the Cartesian displacement coordinates  $q_i = \Delta \xi_i$ ,  $\xi = x, y, z$ , and masses  $m$  and  $M$  of Figure 1 as

$$\begin{aligned} Q_1 &= \sqrt{\frac{m}{2}}(q_6 - q_3), \\ Q_{2a} &= \sqrt{\frac{mM}{2M_T}}[-(q_1 + q_4) + 2q_7], \\ Q_{2b} &= \sqrt{\frac{mM}{2M_T}}[-(q_2 + q_5) + 2q_8], \\ Q_3 &= \sqrt{\frac{mM}{2M_T}}[-(q_3 + q_6) + 2q_9], \end{aligned} \quad (7)$$

where  $M_T = 2m + M$ .



(iii) *Rectilinear symmetry coordinates*  $Q_i$ , which are involved in the bosonic operators associated with the harmonic oscillators:

$$\begin{aligned} Q_1 &= \frac{1}{\sqrt{m}} Q_1, \\ Q_{2a} &= \sqrt{2} \sqrt{\frac{M_T}{mM}} Q_{2a}, \\ Q_{2b} &= \sqrt{2} \sqrt{\frac{M_T}{mM}} Q_{2b}, \\ Q_3 &= \sqrt{\frac{M_T}{mM}} Q_3, \end{aligned} \quad (8)$$

given in length units.

Curvilinear symmetry coordinates,  $S_\alpha$ , may be written as a power series of the normal coordinates  $Q_\alpha$ . This expansion, up to third order, takes the form

$$\begin{aligned} S_1 &= \frac{1}{\sqrt{m}} Q_1 + \frac{1}{2\sqrt{2}} \frac{1}{r_e} \frac{M_T}{mM} Q_2^2 - \frac{1}{4} \frac{1}{r_e^2} \frac{M_T}{mM\sqrt{m}} Q_1 Q_2^2, \\ S_{2a} &= \sqrt{2} \left( \frac{d}{r_e} \right) \sqrt{\frac{M_T}{mM}} Q_{2a} + \Lambda_1 \left( \frac{d}{r_e^2} \right) \frac{1}{\sqrt{m}} \sqrt{\frac{M_T}{mM}} Q_1 Q_{2a} \\ &\quad + \Lambda_2 \frac{1}{\sqrt{2} r_e^2} \left[ \frac{1}{m} \sqrt{\frac{M_T}{mM}} Q_1^2 Q_{2a} \right. \\ &\quad \left. - \frac{M_T^2}{mM} \sqrt{\frac{M_T}{mM}} (Q_2^2 - Q_3^2) Q_{2a} \right], \\ S_{2b} &= \sqrt{2} \left( \frac{d}{r_e} \right) \sqrt{\frac{M_T}{mM}} Q_{2b} + \Lambda_1 \left( \frac{d}{r_e^2} \right) \frac{1}{\sqrt{m}} \sqrt{\frac{M_T}{mM}} Q_1 Q_{2b} \\ &\quad + \Lambda_2 \frac{1}{\sqrt{2} r_e^2} \left[ \frac{1}{m} \sqrt{\frac{M_T}{mM}} Q_1^2 Q_{2b} \right. \\ &\quad \left. - \frac{M_T^2}{mM} \sqrt{\frac{M_T}{mM}} (Q_2^2 - Q_3^2) Q_{2b} \right], \\ S_3 &= \sqrt{\frac{M_T}{mM}} Q_3 - \frac{1}{4r_e^2} \frac{M_T}{mM} \sqrt{\frac{M_T}{mM}} Q_3 Q_2^2, \end{aligned} \quad (9)$$

where  $Q_2^2 = Q_{2a}^2 + Q_{2b}^2$ . These equations are valid for the considered definitions of the bending coordinate, (3) and (4). In the case of Eq. (3) definition, one must set  $d = r_e$ ,  $\Lambda_1 = -1$ , and  $\Lambda_2 = 1$ ; while Eq. (4) definition implies  $d = 1 \text{ \AA}$ ,  $\Lambda_1 = 1$ , and  $\Lambda_2 = 0$ . The difference lays in the order of the expansions. The bending coordinates expansion is complete in Eq. (4) case, since they are quadratic in the Cartesian coordinates. In contrast, definition (3) implies an infinite series.

Finally, in terms of the  $Q_i$  coordinates of Eq. (8), the expansion (9) takes the simplified form

$$\begin{aligned} S_1 &= Q_1 + \frac{1}{4\sqrt{2}} \frac{1}{r_e} Q_2^2 - \frac{1}{8} \frac{1}{r_e^2} Q_1 Q_2^2, \\ S_{2a} &= \left( \frac{d}{r_e} \right) Q_{2a} + \Lambda_1 \left( \frac{d}{r_e^2} \right) \frac{1}{\sqrt{2}} Q_1 Q_{2a} \\ &\quad + \Lambda_2 \frac{1}{2r_e^2} \left[ Q_1^2 + Q_3^2 - \frac{1}{2} Q_2^2 \right] Q_{2a}, \\ S_{2b} &= \left( \frac{d}{r_e} \right) Q_{2b} + \Lambda_1 \left( \frac{d}{r_e^2} \right) \frac{1}{\sqrt{2}} Q_1 Q_{2b} \\ &\quad + \Lambda_2 \frac{1}{2r_e^2} \left[ Q_1^2 + Q_3^2 - \frac{1}{2} Q_2^2 \right] Q_{2b}, \\ S_3 &= Q_3 - \frac{1}{8r_e^2} Q_3 Q_2^2, \end{aligned} \quad (10)$$

where, again,  $Q_2^2 = Q_{2a}^2 + Q_{2b}^2$ .

### III. A GENERAL LOCAL ALGEBRAIC APPROACH

The vibrational Hamiltonian  $\hat{H}$  in terms of curvilinear internal displacement coordinates  $S_\alpha$  can be written as follows<sup>2,5,95,96</sup>

$$\hat{H} = \frac{1}{2} \tilde{\mathbf{P}} \mathbf{G}(\mathbf{S}) \mathbf{P} + V(\mathbf{S}), \quad (11)$$

where  $\mathbf{S}$  and  $\mathbf{P}$  are column vectors corresponding to the internal displacement coordinates and their conjugate momenta  $P_\alpha = -i\hbar \partial / \partial S_\alpha$ . The  $\mathbf{G}(\mathbf{S})$  matrix establishes the connection between internal and Cartesian coordinates,  $V(\mathbf{S})$  is the Born-Oppenheimer potential, and the mass-dependent potential term has been neglected. The usual approach to obtain a suitable simplified Hamiltonian 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 once an adequate convergence is achieved. In this way we have for the  $\mathbf{G}(\mathbf{S})$  matrix

$$G_{ij}(\mathbf{S}) = G_{ij}^o(\mathbf{S}) + \sum_{\alpha} \left( \frac{\partial G_{ij}}{\partial S_\alpha} \right)_o S_\alpha + \dots, \quad (12)$$

while for the potential

$$\begin{aligned} V(\mathbf{S}) &= \frac{1}{2!} \sum_{\alpha, \beta} \left( \frac{\partial^2 V}{\partial S_\alpha \partial S_\beta} \right)_o S_\alpha S_\beta \\ &\quad + \frac{1}{3!} \sum_{\alpha, \beta, \gamma} \left( \frac{\partial^3 V}{\partial S_\alpha \partial S_\beta \partial S_\gamma} \right)_o S_\alpha S_\beta S_\gamma + \dots \end{aligned} \quad (13)$$

Usually a reasonable spectrum description can be achieved with an expansion of the  $\mathbf{G}(\mathbf{S})$  matrix elements up to linear order and of the potential up to quadratic order. The substitution of the expansions (12) and (13) into (11), leads to a Hamiltonian

$$\hat{H} = \hat{H}(\mathbf{P}, \mathbf{S}), \quad (14)$$

involving powers of  $P_\alpha$  and  $S_\beta$  as well as cross-product terms. As already mentioned in Sec. II, the curvilinear coordinates

$S_\alpha$  may be expanded into rectilinear symmetry coordinates  $Q_i$  defined in (8). These coordinates are proportional to the  $Q_i$  normal coordinates, a fact that allows us to deal with  $Q_i$  heretofore. Hence, the curvilinear coordinate expansion has the general form<sup>82</sup>

$$S_\alpha = \sum_i L_i^\alpha Q_i + \frac{1}{2!} \sum_{i,j} L_{ij}^\alpha Q_i Q_j + \frac{1}{3!} \sum_{i,j,k} L_{ijk}^\alpha Q_i Q_j Q_k + \dots \quad (15)$$

The corresponding momenta are obtained using the chain rule

$$P_\alpha = \sum_i \frac{\partial Q_i}{\partial S_\alpha} \frac{\partial T}{\partial Q_i} = \sum_i \frac{\partial Q_i}{\partial S_\alpha} p_i. \quad (16)$$

The partial derivatives involved in (16) are computed by inversion of the system of equations

$$\delta_{\alpha\beta} = \sum_i L_i^\alpha \left( \frac{\partial Q_i}{\partial S_\beta} \right) + \sum_{i,j} L_{ij}^\alpha Q_i \left( \frac{\partial Q_j}{\partial S_\beta} \right) + \frac{3}{3!} \sum_{i,j,k} L_{ijk}^\alpha \left( \frac{\partial Q_i}{\partial S_\beta} \right) Q_j Q_k + \dots, \quad (17)$$

which is obtained taking the derivative of (15) with respect to coordinates  $S_\beta$ . This set of equations, however, provides a nonlinear solution for the derivatives. An additional expansion of  $Q_i$  into powers of the symmetry adapted coordinates is required in order to obtain an approximation of the form

$$P_\alpha = \sum_i \left( M^{i,\alpha} + \sum_r M_r^{i,\alpha} Q_r + \sum_{r,s} M_{rs}^{i,\alpha} Q_r Q_s + \dots \right) p_i, \quad (18)$$

where the associated quantum operators are obtained through a symmetry projection method. Therefore the substitution of (15) and (18) into (14) yields a Hamiltonian

$$\hat{H} = \hat{H}(\hat{\mathbf{p}}, \mathbf{Q}), \quad (19)$$

where  $\hat{p}_k = -i\hbar\partial/\partial Q_k$ . The identification of the polyad-preserving interactions (resonances) in coordinate space is a cumbersome task. However, introducing creation and annihilation operators, i.e., the algebraic representation, vibrational resonances come out in a concise and natural way.

A suitable algebraic representation of the Hamiltonian (19) is obtained by the introduction of the bosonic operators  $a_{q\Gamma\gamma}^\dagger (a_{q\Gamma\gamma})$ ,

$$a_{q\Gamma\gamma}^\dagger = \eta_{q\Gamma} Q_{q\Gamma\gamma} - \frac{i}{2\hbar\eta_{q\Gamma}} p_{q\Gamma\gamma}, \quad (20)$$

$$a_{q\Gamma\gamma} = \eta_{q\Gamma} Q_{q\Gamma\gamma} + \frac{i}{2\hbar\eta_{q\Gamma}} p_{q\Gamma\gamma},$$

where  $\Gamma$  and  $\gamma$  are irrep labels associated with a group chain

$$G \supset H, \quad (21)$$

$q$  is a multiplicity index, and  $\eta_{q\Gamma}$ 's depend on the reduced mass  $\mu_{q\Gamma}$  and the force constant  $f_{\Gamma\Gamma}^q$ ,

$$\eta_{q\Gamma}^2 = \frac{1}{2\hbar} \sqrt{f_{\Gamma\Gamma}^q \mu_{q\Gamma}}. \quad (22)$$

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

$$\hat{H}_P = \hat{H}_P(a_{q\Gamma\gamma}^\dagger, a_{q\Gamma\gamma}), \quad (23)$$

where the subindex  $P$  means that polyad quantum number is conserved by neglecting all terms that connect states belonging to different polyad. Thus the algebraic representation greatly simplifies the definition of a polyad preserving Hamiltonian from the outset. The spectroscopic parameters in (23) are related to the molecular geometry and force constants, and the PES can be estimated from a fit to experimental vibrational levels. A matrix representation of Hamiltonian (23) can be obtained straightforwardly in the harmonic oscillator basis,  $|\nu_1, \nu_2, \dots, \nu_s\rangle$ , where  $\nu_i$  is defined as the eigenvalue associated with the number operator  $\hat{\nu}_{i(q\Gamma)} = \sum_\gamma a_{q\Gamma\gamma}^\dagger a_{q\Gamma\gamma}$ . An alternative consists in constructing a basis  $|\bar{\nu}_1, \bar{\nu}_2, \dots, \bar{\nu}_s\rangle$ , isomorphic to the normal mode basis, defined in terms of number operators associated with a symmetry adapted basis, the latter given as a realization in terms of internal coordinates. These bases turn out to be identical unless there is multiplicity in the irreps of the normal modes, which in fact is the case for the CO<sub>2</sub> molecule. An efficient and elegant approach to deal with the general case is described in Refs. 97–100.

The non-diagonal interactions in Hamiltonian (23) define the polyad and can be identified from the energies of the fundamentals and overtones of the molecule. In molecules with a local mode behavior the concept of polyad has a straightforward translation because the coefficients attached to the modes associated with a given subspace are the same, e.g.,  $P = 2(\nu_1 + \nu_3) + \nu_2$  in H<sub>2</sub>O, where the same weight is assigned to both stretching modes. Indeed, the canonical transformation to local modes provides the polyad  $P = 2(n_1 + n_2) + n_3$ , where  $n_1$  and  $n_2$  are the local number of quanta for the stretches. In contrast, for molecules with a strong normal behavior, e.g., BF<sub>3</sub>, the polyad  $P = 4\nu_1 + 3\nu_2 + 6\nu_3 + 2\nu_4$ <sup>73</sup> involves different weights and, consequently, cannot be translated into a local scheme. In this example this is due to the large splitting among states that involve the same set of equivalent local oscillators and by the appearance of redundant coordinates.<sup>73</sup> Therefore, local bases are not well suited for the description of such molecules. Another argument that supports this conclusion is that having local oscillators as an initial basis for the description of systems with a strong normal behavior unavoidably leads to polyad breaking in order to obtain a correct estimation of the system force constants.<sup>74,76–78</sup> 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.

An approach that solves this conundrum relies on applying to the bosonic operators in the Hamiltonian (23) a canonical transformation of the type

$$a_{q\Gamma\gamma}^\dagger = \sum_i B_{q\Gamma\gamma}^i c_i^\dagger, \quad (24)$$

where  $c_i^\dagger (c_i)$  are bosonic creation (annihilation) operators, and the coefficients  $B_{q\Gamma\gamma}^i$  correspond to the linear combinations associated with the symmetry adapted local coordinates of

the corresponding subspace  $q$ . The operators  $c_i^\dagger(c_i)$  are not local operators, but an isomorphism to the true local operators  $a_i^\dagger(a_i)$  can be established:

$$c_i^\dagger \approx a_i^\dagger. \quad (25)$$

The true connection between the bosonic operators  $a_{q\Gamma\gamma}^\dagger$  and the local operators  $a_i^\dagger$  implies a Bogoliubov transformation, involving a combination of creation and annihilation operators, being the relation (24) true only in the limit of weak interaction among the oscillators.<sup>78</sup> This fact justifies the proposed isomorphism (25).

The transformation (24) preserves the polyad in the Hamiltonian. Hence the substitution of (24) into (23) leads to a Hamiltonian of type  $\hat{H}_P = \hat{H}_P(c_i^\dagger, c_i)$ , which through the isomorphism (25), takes the form

$$\hat{H}_P = \hat{H}_P(a_i^\dagger, a_i). \quad (26)$$

The importance of this Hamiltonian stems from the fact that is given in a local representation and is polyad-preserving, an expression that cannot be obtained if the starting point is a Hamiltonian in coordinate space in the local scheme, unless the system has a local character. The Hamiltonians (23) and (26) 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 further improved considerably through an anharmonization procedure,<sup>73,76,77</sup>

$$a_i^\dagger \rightarrow b_i^\dagger, \quad a_i \rightarrow b_i. \quad (27)$$

where the creation (annihilation) operators  $b_i^\dagger(b_i)$  are generators of a  $U(2)$  dynamical algebra.<sup>74</sup> This anharmonization is applied both to the basis and to the Hamiltonian, and the operators  $b_i^\dagger(b_i)$  may be interpreted as ladder operators of Morse or Pöschl-Teller eigenstates  $|\psi_{v_i}^j\rangle$ , with matrix elements<sup>70</sup>

$$\begin{aligned} b^\dagger|\Psi_v^j\rangle &= \sqrt{(v+1)(1-(v+1)/\kappa)}|\Psi_{v+1}^j\rangle, \\ b|\Psi_v^j\rangle &= \sqrt{v(1-v/\kappa)}|\Psi_{v-1}^j\rangle, \end{aligned} \quad (28)$$

where  $v$  is the vibrational number of quanta,  $v = 0, 1, 2, \dots, j-1$ , and  $\kappa = 2j + 1$  is related to the potential depth. The anharmonization (27) is valid for both stretching and bending degrees of freedom in semi-rigid bent molecules.<sup>62,69-75</sup> The anharmonization method for the bending degrees of freedom of linear and non-rigid molecules is based on the two dimensional limit of the vibron model, with a  $U(3)$  dynamical algebra, to describe degenerate and large amplitude bending modes.<sup>54,76,77,101-106</sup>

We should remark that this approach is a semiempirical method, which means that in principle we are able to predict vibrational energy or intensity patterns for systems only if a minimum number of experimental energies and transitions intensities are available. The description accuracy relies on the quality of the experimental data. However, the present approach is connected with configuration space and it allows predictions via the assessment of force constants and transition operators.

We should stress that the steps (25) and (27) in our algebraic approach do not have in general an analogy in configuration space, only in the local mode limit. In Sec. IV we shall present the application of this approach to the CO<sub>2</sub> molecule, that has a strong normal character with degenerate (bending) modes involved.

#### IV. APPLICATION OF THE ALGEBRAIC APPROACH TO CO<sub>2</sub>

In the case of CO<sub>2</sub> the expansion of the Hamiltonian (14) in curvilinear symmetry coordinates,  $S_i$ , up to quartic order may be written as follows:<sup>77</sup>

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb}. \quad (29)$$

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

$$\begin{aligned} \hat{H}_s &= \frac{1}{2}g_{\Sigma_g}^0 P_{\Sigma_g}^2 + \frac{1}{2}g_{\Sigma_u}^0 P_{\Sigma_u}^2 + \frac{1}{2}f_{\Sigma_g \Sigma_g} S_{\Sigma_g}^2 + \frac{1}{2}f_{\Sigma_u \Sigma_u} S_{\Sigma_u}^2 \\ &+ \frac{1}{4!}f_{\Sigma_g \Sigma_g \Sigma_g \Sigma_g} S_{\Sigma_g}^4 + \frac{1}{4!}f_{\Sigma_u \Sigma_u \Sigma_u \Sigma_u} S_{\Sigma_u}^4 \\ &+ \frac{6}{4!}f_{\Sigma_g \Sigma_g \Sigma_u \Sigma_u} S_{\Sigma_g}^2 S_{\Sigma_u}^2. \end{aligned} \quad (30)$$

The second term,  $\hat{H}_b$ , depends solely on bending coordinates and momenta

$$\begin{aligned} \hat{H}_b &= g_{+-}^0 P_+ P_- + f_{+-} S_+ S_- + \left( \frac{\partial^2 g_{+-}}{\partial S_+ \partial S_-} \right)_0 P_+ S_+ S_- P_- \\ &+ \frac{1}{2!} \frac{1}{2} \left( \frac{\partial^2 g_{++}}{\partial S_+^2} \right)_0 (P_+ S_+ S_+ P_+ + P_- S_- S_- P_-) \\ &+ \frac{6}{4!} f_{++++} S_+^2 S_-^2. \end{aligned} \quad (31)$$

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

$$\begin{aligned} \hat{H}_{sb} &= \left( \frac{\partial g_{+-}}{\partial S_{\Sigma_g}} \right)_0 S_{\Sigma_g} P_+ P_- + \left( \frac{\partial g_{\Sigma_g+}}{\partial S_+} \right)_0 P_{\Sigma_g} (S_+ P_+ + P_- S_-) \\ &+ \frac{6}{3!} f_{\Sigma_g+-} S_{\Sigma_g} S_+ S_- + \frac{1}{2} \left( \frac{\partial^2 g_{+-}}{\partial S_{\Sigma_g}^2} \right)_0 S_{\Sigma_g}^2 P_+ P_- \\ &+ \frac{1}{2} \left( \frac{\partial^2 g_{+-}}{\partial S_{\Sigma_u}^2} \right)_0 S_{\Sigma_u}^2 P_+ P_- \\ &+ \frac{1}{2} \left( \frac{\partial^2 g_{\Sigma_g \Sigma_g}}{\partial S_+ \partial S_-} \right)_0 P_{\Sigma_g}^2 S_+ S_- + \frac{1}{2} \left( \frac{\partial^2 g_{\Sigma_u \Sigma_u}}{\partial S_+ \partial S_-} \right)_0 P_{\Sigma_u}^2 S_+ S_- \\ &+ \frac{12}{4!} f_{\Sigma_g \Sigma_g+-} S_{\Sigma_g}^2 S_+ S_- + \frac{12}{4!} f_{\Sigma_u \Sigma_u+-} S_{\Sigma_u}^2 S_+ S_-, \end{aligned} \quad (32)$$

where  $g_{\alpha\beta}$  are elements of the symmetry-adapted Wilson kinetic matrix,  $||\mathcal{G}|| = g_{\alpha\beta}$ .<sup>20</sup>

At this level the simplest approximation corresponds to consider only the linear term in the expansions (10). This approximation was considered in Refs. 76, 77, and 93 and hence the truncation in (10) makes curvilinear coordinates equivalent to normal coordinates (8).

An algebraic representation of the Hamiltonian is obtained through the substitution of the expansion (10) into (29) and the introduction of bosonic creation and annihilation operators<sup>76,77</sup>

$$\begin{aligned} a_{\Gamma}^{\dagger} &= \eta_{\Gamma} Q_{\Gamma} - \frac{i}{2\hbar\eta_{\Gamma}} p_{\Gamma}, \quad a_{\Gamma} = \eta_{\Gamma} Q_{\Gamma} + \frac{i}{2\hbar\eta_{\Gamma}} p_{\Gamma}, \\ \Gamma &= \Sigma_g, \Sigma_u, \\ a_{\pm}^{\dagger} &= \eta_{\pm} Q_{\pm} + \frac{i}{2\hbar\eta_{\pm}} p_{\mp}, \quad a_{\pm} = -\eta_{\pm} Q_{\mp} + \frac{i}{2\hbar\eta_{\pm}} p_{\pm}, \end{aligned} \quad (33)$$

where  $\eta_{\Gamma}$  and  $\eta_{\pm}$  are given by

$$\begin{aligned} (\eta_{\Gamma})^2 &= \frac{1}{2\hbar} \sqrt{f_{\Gamma\Gamma}\mu_{\Gamma}}, \quad \Gamma = \Sigma_g, \Sigma_u, \\ (\eta_{+})^2 &= (\eta_{-})^2 = \eta^2 = \frac{1}{2\hbar} \sqrt{\frac{f_{+-}}{g_{+-}^0}}, \end{aligned} \quad (34)$$

with  $\mu_{\Sigma_g} = 1/g_{\Sigma_g}^0 = m$ ,  $\mu_{\Sigma_u} = 1/g_{\Sigma_u}^0 = (2/M + 1/m)^{-1}$ , and the force constants  $f_{\Sigma_g\Sigma_g} = f_{rr} + f_{rr'}$  and  $f_{\Sigma_u\Sigma_u} = f_{rr} - f_{rr'}$ . If the linear approximation in Eq. (10) is considered, the resulting algebraic Hamiltonian is equivalent to the Hamiltonian expressed in configuration space in normal coordinates and it is usually diagonalized in a harmonic oscillator basis. The same approach can be followed when considering higher-order terms in the coordinate expansion. In this case, though the Hamiltonian interaction parameters are the same, the PES force constants change when the link between the phase space and the algebraic space is established.

Following the approach previously presented in Sec. III, we define an algebraic polyad-preserving Hamiltonian with local creation and annihilation operators. This goal cannot be achieved starting from configuration space due to the strong normal character of CO<sub>2</sub> stretching degrees of freedom. This issue is addressed by introducing the canonical transformation in the stretching coordinates

$$a_{\Sigma_g}^{\dagger} = \frac{1}{\sqrt{2}}(c_1^{\dagger} + c_2^{\dagger}), \quad a_{\Sigma_u}^{\dagger} = \frac{1}{\sqrt{2}}(c_1^{\dagger} - c_2^{\dagger}), \quad (35)$$

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

$$\begin{aligned} \hat{H} &= \tilde{\omega}_s \sum_{k=1}^2 (a_k^{\dagger} a_k + a_k a_k^{\dagger}) + \lambda_s \sum_{k \neq j=1}^2 a_k^{\dagger} a_j + \alpha_1^s (\hat{n}_1^2 + \hat{n}_2^2) \\ &+ \alpha_2^s (a_1^{\dagger 2} a_2^2 + a_2^{\dagger 2} a_1^2 + 4\hat{n}_1 \hat{n}_2) \\ &+ \alpha_3^s (\hat{n}_1 a_2^{\dagger} a_1 + \hat{n}_2 a_1^{\dagger} a_2 + H.c.) \\ &+ \tilde{\omega}_b \hat{n} + \alpha_1^b \hat{n}^2 + \alpha_2^b \hat{\ell}^2 + \alpha_1^{sb} \{(a_1^{\dagger} + a_2^{\dagger}) a_+ a_- + H.c.\} \\ &+ \alpha_2^{sb} (\hat{n}_1 + \hat{n}_2) \hat{n} + \alpha_3^{sb} (a_1^{\dagger} a_2 + a_2^{\dagger} a_1) \hat{n}, \end{aligned} \quad (36)$$

with the definitions

$$\begin{aligned} \hat{n}_k &= a_k^{\dagger} a_k; \quad k = 1, 2, \\ \hat{\ell} &= a_{+}^{\dagger} a_{+} - a_{-}^{\dagger} a_{-} = \hat{n}_{+} - \hat{n}_{-}, \\ \hat{n} &= a_{+}^{\dagger} a_{+} + a_{-}^{\dagger} a_{-} = \hat{n}_{+} + \hat{n}_{-}, \end{aligned} \quad (37)$$

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.<sup>101</sup> In Eq. (36) we have restricted the interactions to those that preserve the polyad number  $P = 2(n_{\Sigma_g} + n_{\Sigma_u}) + (n_{+} + n_{-})$ , which splits the total space into subspaces of states connected through the transfer of two bending quanta to one stretching quantum. The expressions of the spectroscopic parameters in terms of the structure and force constants in the linear approximation of Eq. (10) are detailed in Appendix A of Ref. 77. The diagonalization of the Hamiltonian operator (36) can be carried out in a harmonic oscillator local basis

$$|n_1 n_2 n_{+} n_{-}\rangle = \frac{1}{\sqrt{n_1! n_2! n_{+}! n_{-}!}} (a_1^{\dagger})^{n_1} (a_2^{\dagger})^{n_2} (a_{+}^{\dagger})^{n_{+}} (a_{-}^{\dagger})^{n_{-}} |0\rangle. \quad (38)$$

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 (27). Hence, the operators  $\{b_i^{\dagger}(b_i); i = 1, 2\}$  are interpreted as Morse potential ladder operators with matrix elements (28).

The bending operators  $a_{\pm}^{\dagger}(a_{\pm})$  undergo an equivalent anharmonization procedure

$$a_{\pm}^{\dagger} \rightarrow b_{\pm}^{\dagger}, \quad a_{\pm} \rightarrow b_{\pm}, \quad (39)$$

but now the operators  $b_{\pm}^{\dagger}(b_{\pm})$  are given as a linear combination of generators of the  $U(3)$  dynamical algebra,<sup>55,101,104</sup> with matrix elements<sup>76</sup>

$$b_{\pm}^{\dagger} | [N]; n^{\ell} \rangle = \sqrt{\left(\frac{n \pm \ell}{2} + 1\right) \left(1 - \frac{n}{N}\right)} | [N]; (n+1)^{\ell \pm 1} \rangle, \quad (40)$$

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

where  $n$  and  $\ell$  have the same meaning as in Eq. (37), and  $N$  is the total number of bosons (totally symmetric irrep of the  $U(3)$  group) related with the bending degree of freedom anharmonicity. Note that in the large  $N$  limit of Eq. (40) the results for a harmonic 2D oscillator matrix elements are recovered. Hence the application of the anharmonization procedures (27) and (39) yields the following



Hamiltonian,

$$\begin{aligned} \hat{H} = & \tilde{\omega}_s \sum_{i=1}^2 (b_i^\dagger b_i + b_i b_i^\dagger) + \lambda_s \sum_{i \neq j=1}^2 b_i^\dagger b_j + \alpha_1^s (\hat{n}_{s,1}^2 + \hat{n}_{s,2}^2) \\ & + \alpha_2^s (b_1^{\dagger 2} b_2^2 + b_2^{\dagger 2} b_1^2 + 4\hat{n}_{s,1} \hat{n}_{s,2}) \\ & + \alpha_3^s (\hat{n}_{s,1} b_2^\dagger b_1 + \hat{n}_{s,2} b_1^\dagger b_2 + H.c.) \\ & + \tilde{\omega}_b \hat{n} + \alpha_1^b \hat{n}^2 + \alpha_2^b \hat{\ell}^2 + \alpha_1^{sb} \{(b_1^\dagger + b_2^\dagger) b_+ b_- + H.c.\} \\ & + \alpha_2^{sb} (\hat{n}_{s,1} + \hat{n}_{s,2}) \hat{n} + \alpha_3^{sb} (b_1^\dagger b_2 + b_2^\dagger b_1) \hat{n}, \end{aligned} \quad (41)$$

with the definition

$$\hat{n}_{s,i} = b_i^\dagger b_i, i = 1, 2. \quad (42)$$

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

The matrix representation of the Hamiltonian (41) can be obtained in a  $U(2) \times U(3) \times U(2)$  basis

$$|[N_s = 2j], [N]; v_1 v_2; n^\ell\rangle = |\psi_{v_1}^j\rangle \otimes |\psi_{v_2}^j\rangle \otimes |N; n^\ell\rangle, \quad (43)$$

although a symmetry adapted basis combined with a normal mode scheme is generally preferred.<sup>98–100</sup> In general, the diagonalization leads to eigenvectors of the form

$$|\psi_{P,j}^{\Gamma\gamma}\rangle = \sum_{v_1, v_2, v_3} C_{v_1, v_2, v_3}^{P, j, \Gamma\gamma} |P; v_1, v_2, v_3; \Gamma, \gamma\rangle \quad (44)$$

with the basis set

$$\begin{aligned} & |P; v_1, v_2, v_3; \Gamma, \gamma\rangle \\ & = \sum_{v_1, v_2, n} B_{v_1, v_2, n}^{P, v_1, v_2, v_3; \Gamma, \gamma} |\psi_{v_1}^j\rangle \otimes |\psi_{v_2}^j\rangle \otimes |N; n^\ell\rangle, \end{aligned} \quad (45)$$

where  $P$  is the polyad,  $\Gamma$  and  $\gamma$  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  $\{v_1, v_2, v_3\}$  corresponds to an approximate normal-mode labeling.<sup>98</sup> The value of the vibrational angular momentum  $\ell$  is implicit in the symmetry labels  $\Gamma$  and  $\gamma$ . The  $B$  coefficients in (45) stem from the symmetry projection procedure,<sup>98</sup> while the  $C$  components in (44) are provided by the diagonalization. We stress that the  $|\psi_{P,j}^{\Gamma\gamma}\rangle$  eigenstates (44) are obtained from an anharmonization procedure without counterpart in configuration space. We follow the usual scheme where each state is labeled as  $(v_1, v_2, v_3)$  according to its maximal squared component  $(C_{v_1, v_2, v_3}^{P, j, \Gamma\gamma})^2$  in the expansion (44). However, with this method the eigenstates may also be labeled in a local scheme, through the expansion (45). In cases with a heavy mixing of the basis elements, ambiguity arises and quite a few states may carry the same quantum labels.<sup>77,93</sup>

Truncating the expansion (10) at the linear approximation in the coordinates, the vibrational spectrum of the  $^{12}\text{CO}_2$  molecule has been described in Refs. 76 and 77 using the Hamiltonian (41). The spectroscopic parameters were optimized with an iterative nonlinear least square method.<sup>107,108</sup> The fit included 101 experimental vibrational levels<sup>109,110</sup> (encompassing terms up to polyad  $P = 9$ ) with an rms deviation of  $0.53 \text{ cm}^{-1}$ . The optimal values of the boson numbers  $N_s$  and  $N$  were found to be  $N_s = 160$  and  $N = 150$ .<sup>77</sup> From that work, the value of the force constant associated with the Fermi interaction was estimated to be  $f_{q_1 q_a q_a} = -0.9551 \text{ aJ}\text{\AA}^{-3}$ , in close agreement with Chedin results.<sup>111</sup> This value was obtained from its relation with the spectroscopic parameter  $\alpha_1^{sb} = -36.002 \text{ cm}^{-1}$  given by

$$\begin{aligned} \alpha_1^{sb} |_{lin} = & -\frac{1}{\sqrt{2}} \left( \frac{\partial g_{+-}}{\partial S_{\Sigma_g}} \right)_0 \frac{\hbar^2 \eta^2}{2\eta_{\Sigma_g}} - \frac{\hbar^2 \eta_{\Sigma_g}}{\sqrt{2}} \left( \frac{\partial g_{+\Sigma_g}}{\partial S_+} \right)_0 \\ & + \frac{1}{\sqrt{2}} \frac{6}{3!} \frac{f_{\Sigma_g+-}}{2\eta_{\Sigma_g} (2\eta)^2}, \end{aligned} \quad (46)$$

where

$$\begin{aligned} g_{+-}^0 = & -g_{q_a q_b}^0 = -g_{q_b q_a}^0; \\ g_{q_a q_a}^0 = & g_{q_b q_b}^0 = \frac{4}{M} + \frac{2}{m}; \\ \left( \frac{\partial g_{+-}}{\partial S_1} \right)_0 = & \frac{2\sqrt{2}}{r_e} \left( \frac{1}{m} + \frac{2}{M} \right); \\ \left( \frac{\partial g_{\Sigma_g+}}{\partial S_+} \right)_0 = & \frac{\sqrt{2}}{M r_e}, \end{aligned} \quad (47)$$

with an equilibrium distance  $r_e = 1.16 \text{ \AA}$ .<sup>112</sup>

In phenomenological algebraic models a test of the quality of the wavefunctions is recommended since a good energy fit does not necessarily guarantee the wavefunctions quality.<sup>19,113</sup> Indeed, the computation of line intensities with the resulting wavefunctions is a sensitive indicator of the quality of the description. This situation will be discussed in detail in Sec. V, where we introduce the description of the  $\text{CO}_2$  Raman spectrum.

The aforementioned results were obtained under the linear approximation in the coordinates expansion. A question which arises is the effect of the neglected nonlinear terms. The inclusion of these terms is expected to modify both the PES and the polarizability function. To go beyond the linear approximation in Eq. (10) implies that the associated momenta are modified. Concerning the Hamiltonian the first step consists in obtaining the corresponding expansion in the momenta associated with (10). To this end, as discussed in Sec. III, from the chain rule (16), using (17) and truncating (18) up to first order in coordinates, the following expansions are obtained up to linear terms in the

coordinates

$$\begin{aligned}
 P_1 &= p_1 - \frac{\Lambda_1}{r_e \sqrt{2}} (\{Q_{2a}, p_{2a}\} + \{Q_{2b}, p_{2b}\}), \\
 P_{2a} &= -\frac{1}{2\sqrt{2}} \frac{1}{d} Q_{2a} p_1 + \frac{1}{d} \left( r_e - \frac{\Lambda_1}{\sqrt{2}} Q_1 \right) p_{2a}, \\
 P_{2b} &= -\frac{1}{2\sqrt{2}} \frac{1}{d} Q_{2b} p_1 + \frac{1}{d} \left( r_e - \frac{\Lambda_1}{\sqrt{2}} Q_1 \right) p_{2b}, \\
 P_3 &= p_3,
 \end{aligned} \tag{48}$$

where we have introduced the anticommutator  $\{Q, p\} = (QP + pQ)/2$  to indicate the symmetrization process for the momentum  $p_i$ . Therefore, the substitution of the expansions (10) and (48) into (29) provides a new Hamiltonian associated with curvilinear coordinates. We then proceed to get the algebraic representation of the form (41), following the anharmonization approach described in Sec. II. We should stress that relations between the spectroscopic parameters and the structure and force constants differ from the ones obtained in Ref. 77 once the nonlinear terms are considered in the  $P_\alpha$  and  $S_\beta$  expansions in terms of normal coordinates. For example, the new expression for the spectroscopic parameter associated with the Fermi interaction takes the form

$$\begin{aligned}
 \alpha_1^{sb} &= \alpha_1^{sb}|_{lin} + \Lambda_1 \frac{\hbar^2 \eta_1}{2\sqrt{2}r_e} g_{\Sigma_g^+ \Sigma_g^+}^0 - \frac{1}{2\sqrt{2}r_e} \frac{1}{8\eta_{\Sigma_g^+} \eta^2} f_{\Sigma_g^+ \Sigma_g^+} \\
 &+ \Lambda_1 f_{+-} \left\{ \frac{2d^2}{\sqrt{2}r_e^3} \frac{1}{8\eta^2 \eta_{\Sigma_g^+}} \right\} \\
 &+ g_{+-}^0 \left\{ -\frac{\sqrt{2}r_e}{4d^2} \hbar^2 \eta_{\Sigma_g^+} + \Lambda_1 \frac{\sqrt{2}}{2} \frac{r_e}{d^2 \eta_{\Sigma_g^+}} \hbar^2 \eta^2 \right\}. \tag{49}
 \end{aligned}$$

Here the force constants are derivatives with respect to curvilinear coordinates. The first term corresponds to the three contributions in the linear approximation (46), while the others come from the first and third terms in (30), and the first and second terms in (31). The force constants involved  $f_{+-}$  and  $f_{\Sigma_g^+ \Sigma_g^+}$  are expected to be consistent with this description in the sense that they should be extracted from analogue expressions of the spectroscopic parameters for  $\tilde{\omega}_s$  and  $\tilde{\omega}_b$  in Appendix A of Ref. 77. These force constants however are of lower order and consequently, as a first approximation, we may use the previous results  $f_{\Sigma_g^+ \Sigma_g^+} = 17.188 \text{ aJ}\text{\AA}^{-2}$  and  $f_{+-} = -0.5835 \text{ aJ}\text{\AA}^{-2}$ , which are consistent with the coordinates definition (3). Considering  $d = r_e$ , the expression (49) gives the Fermi constant value  $f_{q_1 q_a q_a} = -1.138 \text{ aJ}\text{\AA}^{-3}$  or  $f_{\Sigma_g^+ \Sigma_g^+} = 1.61 \text{ aJ}\text{\AA}^{-3}$  with the relation  $f_{\Sigma_g^+ \Sigma_g^+} = -\sqrt{2} f_{q_1 q_a q_a}$ . Our estimation increases the absolute value of the Fermi force constant from  $f_{q_1 q_a q_a} = -0.955 \text{ aJ}\text{\AA}^{-3}$  obtained through the linear approximation<sup>77</sup> to  $f_{q_1 q_a q_a} = -1.138 \text{ aJ}\text{\AA}^{-3}$ . Nevertheless, its value is still similar to Chedin's force constant value.<sup>111</sup>

## V. THE RAMAN SPECTRUM

Line intensities in a Raman spectrum for a gas sample are given by the transition moments of the molecular polarizability tensor  $\alpha$ . In the particular case of the  $\text{CO}_2$  molecule, the non-vanishing components of the  $\alpha$  tensor have symmetries  $\Sigma_g^+$  (trace) and  $\Sigma_g^+ \oplus \Pi_g \oplus \Delta_g$  (anisotropy). The sharp, polarized, Q-branches in the vibrational Raman spectrum of  $\text{CO}_2$  in the  $\sim 1300 \text{ cm}^{-1}$  region are totally symmetric ( $\Sigma_g^+$ ) transitions and their intensities are mainly due to the trace of the  $\alpha$  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:<sup>94</sup>

$$\begin{aligned}
 \left( \frac{\partial \sigma}{\partial \Omega} \right)_{i \rightarrow f}^{\text{trace}} &= \left( \frac{\pi}{\epsilon_0} \right)^2 \frac{(\nu_0 + \nu_i - \nu_f)^4}{Z_{vib}(T)} g_{if} |M_{if}|^2 \\
 &\times \exp(-h\nu_i/k_B T), \tag{50}
 \end{aligned}$$

where  $\epsilon_0$  is the vacuum permittivity,  $\nu_0$  is the wavenumber of the exciting radiation  $\nu_0 = 19430 \text{ cm}^{-1}$ ,<sup>92</sup>  $\nu_i$  and  $\nu_f$  are the wavenumbers of initial and final states, and  $g_{if}$  is the vibrational degeneracy of the energy levels involved in the transition.  $Z_{vib}(T) = \sum_j g_j e^{-\nu_j/k_B T}$  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  $\nu_j$  energy, and  $M_{if} = \langle \nu_i | \bar{\alpha} | \nu_f \rangle$  is the transition moment of the mean molecular polarizability  $\bar{\alpha}$  between the vibrational states  $|\nu_i\rangle$  and  $|\nu_f\rangle$ .

The computation of the cross section (50) involves the evaluation of  $M_{if}$ , which requires the previous knowledge of the molecular polarizability surface, that can be expressed as a Taylor series expansion on the vibrational coordinates

$$\begin{aligned}
 \bar{\alpha}_{\Sigma_g^+} &= \bar{\alpha}_0 + \left( \frac{\partial \bar{\alpha}}{\partial S_{\Sigma_g^+}} \right)_0 S_{\Sigma_g^+} + \frac{1}{2} \left( \frac{\partial^2 \bar{\alpha}}{\partial S_{\Sigma_g^+}^2} \right)_0 S_{\Sigma_g^+}^2 \\
 &+ \frac{1}{2} \left( \frac{\partial^2 \bar{\alpha}}{\partial S_{\Sigma_u^+}^2} \right)_0 S_{\Sigma_u^+}^2 \\
 &+ \frac{1}{2} \left( \frac{\partial^2 \bar{\alpha}}{\partial S_{2a}^2} \right)_0 (S_{2a}^2 + S_{2b}^2) + \frac{1}{2} \left( \frac{\partial^3 \bar{\alpha}}{\partial S_{\Sigma_g^+} \partial S_{2a}^2} \right)_0 \\
 &\times S_{\Sigma_g^+} (S_{2a}^2 + S_{2b}^2) \\
 &+ \frac{1}{2} \left( \frac{\partial^3 \bar{\alpha}}{\partial S_{\Sigma_g^+} \partial S_{\Sigma_u^+}^2} \right)_0 S_{\Sigma_g^+} S_{\Sigma_u^+}^2, \tag{51}
 \end{aligned}$$

where the  $\bar{\alpha}$  derivatives are unknown. The last term in Eq. (51) turns out to be negligible and, consequently, it will be omitted.<sup>94</sup> These derivatives may be determined through *ab initio* calculations,<sup>112,114</sup> but they can be also obtained from a fit to experimental transition moments.<sup>94,115</sup>

In the linear approximation the expansion in terms of normal coordinates takes the same form as (51), substituting  $S_\alpha$  by  $Q_\alpha$ . This case was previously considered by the authors to estimate the derivatives of the polarizability as well as to calculate the Raman spectrum.<sup>93</sup> In the present work we investigate nonlinearity effects in this analysis. If nonlinear terms are taken into account, substituting Eq. (10) in the expression (51), the following expansion in terms of normal coordinates

is obtained for the polarizability

$$\begin{aligned}
 \bar{\alpha}_{\Sigma_g^+} = & \bar{\alpha}_0 + \left( \frac{\partial \bar{\alpha}}{\partial S_{\Sigma_g^+}} \right)_0 \left( Q_1 + \frac{1}{4\sqrt{2}r_e} Q_2^2 - \frac{1}{8r_e^2} Q_1 Q_2^2 \right) \\
 & + \frac{1}{2} \left( \frac{\partial^2 \bar{\alpha}}{\partial S_{\Sigma_g^+}^2} \right)_0 \left( Q_1^2 + \frac{1}{32r_e^2} Q_2^4 + \frac{1}{64r_e^4} Q_1^2 Q_2^4 \right) \\
 & + \frac{1}{2\sqrt{2}r_e} Q_1 Q_2^2 - \frac{1}{4r_e^2} Q_1^2 Q_2^2 - \frac{1}{16\sqrt{2}r_e^3} Q_1 Q_2^4 \\
 & + \frac{1}{2} \left( \frac{\partial^2 \bar{\alpha}}{\partial S_{\Sigma_g^+}^2} \right)_0 \left( Q_3^2 + \frac{1}{64r_e^4} Q_3^2 Q_2^4 - \frac{1}{4r_e^2} Q_3^2 Q_2^2 \right) \\
 & + \left( \frac{\partial^2 \bar{\alpha}}{\partial S_{2a}^2} \right)_0 \left( \frac{d^2}{4r_e^4} Q_1^2 Q_2^2 + \Lambda_1 \frac{d^2}{\sqrt{2}r_e^3} Q_3^2 Q_1 + \frac{d^2}{2r_e^2} Q_2^2 \right) \\
 & - \frac{\Lambda_2}{32r_e^4} (\Lambda_1 d 4\sqrt{2} Q_1 + d 8r_e - X_s) Q_2^2 X_s \\
 & + \left( \frac{\partial^3 \bar{\alpha}}{\partial S_{\Sigma_g^+} \partial S_{2a}^2} \right)_0 \left( -\frac{d^2}{32r_e^6} Q_1^3 Q_2^4 + \left( \frac{1}{2} - \Lambda_1 \right) \right) \\
 & \times \frac{d^2}{8\sqrt{2}r_e^5} Q_1^2 Q_2^4 + \left( -\frac{1}{2} + \Lambda_1 \right) \frac{d^2}{8r_e^4} Q_1 Q_2^4 \\
 & + \frac{\Lambda_1 d^2}{\sqrt{2} r_e^3} Q_1^2 Q_2^2 + \frac{d^2}{8\sqrt{2}r_e^3} Q_2^4 + \frac{d^2}{2r_e^2} Q_1 Q_2^2 + \frac{d^2}{4r_e^4} Q_1^3 Q_2^2 \\
 & + \frac{\Lambda_2}{64r_e^6} \left[ \frac{1}{4} Q_2^2 X_p X_s^2 - d Q_2^2 (\sqrt{2}\Lambda_1 Q_1 + 2r_e) X_p X_s \right], \tag{52}
 \end{aligned}$$

where

$$\begin{aligned}
 Q_2^2 &= Q_{2a}^2 + Q_{2b}^2, \\
 X_s &= Q_2^2 - 2(Q_1^2 + Q_3^2), \\
 X_p &= \sqrt{2} Q_2^2 r_e - Q_1(Q_2^2 - 8r_e^2). \tag{53}
 \end{aligned}$$

The next step requires computing the matrix elements of the mean molecular polarizability  $\bar{\alpha}$  between the system wavefunctions (44). This calculation is akin to the calculation of Hamiltonian matrix elements. We first introduce an algebraic representation of  $\bar{\alpha}$  introducing the  $a^\dagger$  bosonic operators (33) followed by the canonical transformation (35) and the identification (25). Finally the anharmonization procedures (27) and (39) are applied. In this way the matrix elements of  $\bar{\alpha}$  in the basis (43) are well defined, and the transition moments  $M_{if} = |\langle v_i | \bar{\alpha} | v_f \rangle|$  can be calculated using the expansion (51) and the wavefunctions (44). The comparison of the calculated  $M_{if}^{calc}$  with those  $M_{if}^{exp}$  derived from the experimental transition intensities (50),<sup>94,116</sup> allows us to obtain estimates of the molecular polarizability derivatives of Eq. (51). To achieve this task the following root mean square deviation is defined:<sup>93</sup>

$$rms = \sqrt{\sum_{\beta} [\log |M_{\beta}^{exp}| - \log |M_{\beta}^{calc}|]^2}, \tag{54}$$

where the summation runs over all or part of the experimentally known transition pairs. The rms deviation is minimized by a suitable selection of the polarizability derivatives, using the set of values in Ref. 94 as an initial guess for the fitting procedure. In the previous work<sup>93</sup> the subindex  $\beta$  included the first six transitions presented in Table I. In this work it was necessary to consider the first nine transitions in order to reach convergence. The first three columns of Table I are the experimental and calculated frequencies of the Raman transitions, and the normal mode label assignment for the involved states. The last two columns of the table are the experimental matrix elements  $M_{if}^{exp94,116}$  and the results of the present work after the minimization of Eq. (54).

The fit to experimental transition moments allows the calculation of the derivatives of  $\bar{\alpha}$  with respect to curvilinear symmetry coordinates. These derivatives are shown in the left side panel of Table II. For the sake of comparison, we include experimental values and the derivatives obtained

TABLE I. Experimental and fitted transition moments  $|M_{if}| = |\langle v_i | \bar{\alpha} | v_f \rangle|$  of the mean polarizability of CO<sub>2</sub>. Only the first nine transitions were involved in the fit.

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

<sup>a</sup>Experimental transition wavenumbers from Ref. 94.

<sup>b</sup>Calculated wavenumbers from the fit of Ref. 77.

<sup>c</sup>The vibrational states are labeled by the ket  $|P; v_1, v_2, v_3; \Gamma\rangle$  where  $P$  is the polyad number,  $(v_1, v_2, v_3)$  are the quantum numbers in the normal-mode representation and  $\Gamma$  is the symmetry of the vibrational wavefunction.

<sup>d</sup>Experimental values from Ref. 94 in 10<sup>-42</sup> CV<sup>-1</sup> m<sup>2</sup>, otherwise is indicated.

<sup>e</sup>Fitted and predicted transition moments in 10<sup>-42</sup> CV<sup>-1</sup> m<sup>2</sup> obtained from this work.

<sup>f</sup>Experimental value from Ref. 116.

TABLE II. Derivatives of the CO<sub>2</sub> mean polarizability with respect to Eq. (4) symmetry coordinates (left panel) and dimensionless normal coordinates (right panel).

Derivative (units) <sup>a</sup>	Symmetry coordinates			Dimensionless normal coordinates			
	Linear <sup>b</sup>	Expt. <sup>c</sup>	Nonlinear <sup>d</sup>	Derivative <sup>e</sup> (10 <sup>-42</sup> CV <sup>-1</sup> m <sup>2</sup> )	Linear <sup>f</sup>	Expt. <sup>c</sup>	Nonlinear <sup>g</sup>
$(\partial\bar{\alpha}/\partial S_1)_0(10^{-30} \text{ CV}^{-1} \text{ m})$	3.15	3.15	3.181	$\bar{\alpha}'_1$	12.44	12.43	12.56
$(\partial^2\bar{\alpha}/\partial S_1^2)_0(10^{-20} \text{ CV}^{-1})$	2.549	2.9	2.634	$\bar{\alpha}''_{11}$	0.398	0.45	0.411
$(\partial^2\bar{\alpha}/\partial S_3^2)_0(10^{-20} \text{ CV}^{-1})$	0.447	0.50	0.448 <sup>h</sup>	$\bar{\alpha}''_{33}$	0.144	0.15 <sup>h</sup>	0.144
$(\partial^2\bar{\alpha}/\partial S_{2a}^2)_0(10^{-20} \text{ CV}^{-1})$	0.8395	0.36	-0.060	$\bar{\alpha}''_{+-}$	1.925	2.81	2.12
$(\partial^3\bar{\alpha}/\partial S_1\partial S_{2a}^2)_0(10^{-10} \text{ CV}^{-1} \text{ m}^{-1})$	-1.21	-1.7	-1.2	$\bar{\alpha}'''_{1+-}$	-0.110	-0.06	-0.061

<sup>a</sup>Polarizability derivatives as defined in Eq. (51).

<sup>b</sup>From Ref. 93 using the rectilinear coordinates approximation.

<sup>c</sup>Experimental values from Ref. 94.

<sup>d</sup>Present work results, obtained with a fit to experimental polarizability transition moments shown in Table I.

<sup>e</sup>Polarizability derivatives in terms of dimensionless normal coordinates as defined in Ref. 94.

<sup>f</sup>Results obtained transforming the second column derivatives to the rectilinear coordinate approximation.<sup>93</sup>

<sup>g</sup>This work, transformed from polarizability derivatives in fourth column.

<sup>h</sup>Best choice of the two experimental values of Ref. 94, according to the *ab initio* CCSD(T) value of Ref. 114.

using the linear approximation.<sup>93</sup> In general, there is a good agreement between our results and the experimental polarizability derivatives, in particular for the first three derivatives  $(\partial\bar{\alpha}/\partial S_1)$ ,  $(\partial^2\bar{\alpha}/\partial S_1^2)$ , and  $(\partial^2\bar{\alpha}/\partial S_3^2)$ . For the derivative  $(\partial^3\bar{\alpha}/\partial S_1\partial S_{2a}^2)$ , a slightly different value is obtained, but significant discrepancies appear in the bending polarizability derivatives  $(\partial^2\bar{\alpha}/\partial S_{2a}^2)$ . While the experimental value is  $(\partial^2\bar{\alpha}/\partial S_{2a}^2) = 0.36 \times 10^{-20} \text{ CV}^{-1}$ , we have obtained  $-0.06 \times 10^{-20} \text{ CV}^{-1}$ , which seems to indicate that the linear approximation is a better result. However, we have to take into account that the derivatives (51) in Ref. 94 were obtained from the derivatives with respect to 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 (15) and the chain rule to obtain

$$\bar{\alpha}'_1 \equiv \frac{\partial\bar{\alpha}}{\partial Q_1} = \frac{1}{\sqrt{m}} \frac{\partial\bar{\alpha}}{\partial S_1}, \quad (55)$$

$$\bar{\alpha}''_{11} \equiv \frac{\partial^2\bar{\alpha}}{\partial Q_1^2} = \frac{1}{m} \frac{\partial^2\bar{\alpha}}{\partial S_1^2}, \quad (56)$$

$$\bar{\alpha}''_{33} \equiv \frac{\partial^2\bar{\alpha}}{\partial Q_3^2} = \frac{M_T}{mM} \frac{\partial^2\bar{\alpha}}{\partial S_3^2}, \quad (57)$$

$$\bar{\alpha}''_{+-} \equiv \frac{\partial^2\bar{\alpha}}{\partial Q_{2a}^2} = 2 \left( \frac{d}{r_e} \right)^2 \frac{M_T}{mM} \left\{ \frac{r_e}{2\sqrt{2}d^2} \frac{\partial\bar{\alpha}}{\partial S_1} + \frac{\partial^2\bar{\alpha}}{\partial S_{2a}^2} \right\}, \quad (58)$$

$$\begin{aligned} \bar{\alpha}'''_{1+-} &\equiv \frac{\partial^3\bar{\alpha}}{\partial Q_1\partial Q_{2a}^2} \\ &= 2 \left( \frac{d}{r_e} \right)^2 \frac{M_T}{m\sqrt{m}M} \left\{ -\frac{1}{4d^2} \frac{\partial\bar{\alpha}}{\partial S_1} + \frac{r_e}{2\sqrt{2}d^2} \frac{\partial^2\bar{\alpha}}{\partial S_1^2} \right. \\ &\quad \left. + \Lambda_1 \frac{\sqrt{2}}{r_e} \frac{\partial^2\bar{\alpha}}{\partial S_{2a}^2} + \frac{\partial^3\bar{\alpha}}{\partial S_1\partial S_{2a}^2} \right\}. \end{aligned} \quad (59)$$

The derivatives with respect to the dimensionless normal coordinates used in Ref. 94 and reported in the right panel of Table II are obtained multiplying the result of Eq. (59) times a product  $\prod_i(\sqrt{2}b_i)$ , where the product runs over the coordinates involved in the derivatives, and

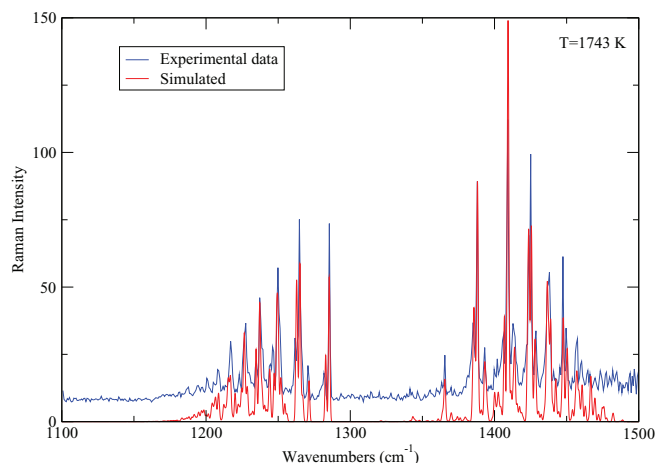
$$b_i^2 = \frac{h}{8\pi^2\nu_i}, \quad (60)$$

where  $\nu_i$  is the harmonic frequency (Hz) of the *i*th mode.

In the right panel of Table II we compare our results with the mean polarizability derivatives with respect to dimensionless normal coordinates obtained by Tejada *et al.* in Ref. 94. As in the previous case, the first three derivatives are close to the experimental values, which means that nonlinear effects are basically negligible. In contrast, nonlinear effects turn out to be significant for the derivatives with respect to the bending coordinate,  $\bar{\alpha}''_{+-}$ , and  $\bar{\alpha}'''_{1+-}$ . In the linear approximation the derivative  $\bar{\alpha}''_{+-}$  is 31% smaller than the experimental value of Tejada *et al.*, but once nonlinear terms are incorporated the derivative becomes closer to the expected value, lowering the error to 25%. This improvement cannot be appreciated in the left panel of Table II. This fact is explained by the appearance of the derivative  $\partial\bar{\alpha}/\partial S_1$  in (58), which is not present in the linear approximation. It turns out that this term is not negligible compared with  $\partial^2\bar{\alpha}/\partial S_{2a}^2$ , giving rise to the result for  $\bar{\alpha}''_{+-}$  displayed in Table II. In turn, the derivative  $\bar{\alpha}'''_{1+-}$  comes to a good agreement with the experiment.

The results displayed in Table II for the derivatives show the sensitiveness of the polarizability with respect to nonlinear effects, specially in the bending coordinates case. The difference between our results and the ones obtained by Tejada *et al.*<sup>94</sup> can be attributed to the different approach followed to obtain the eigenstates. In Ref. 94 the derivatives with respect to the normal coordinates were fitted using perturbation theory through the eigenfunctions of Chedin's results. It is worth mentioning that if the latter procedure is applied to our calculated transition moments in Table I, a value of  $\bar{\alpha}''_{+-} = 2.28 \times 10^{-42} \text{ C m}^2 \text{ V}^{-1}$  is obtained, very close to the



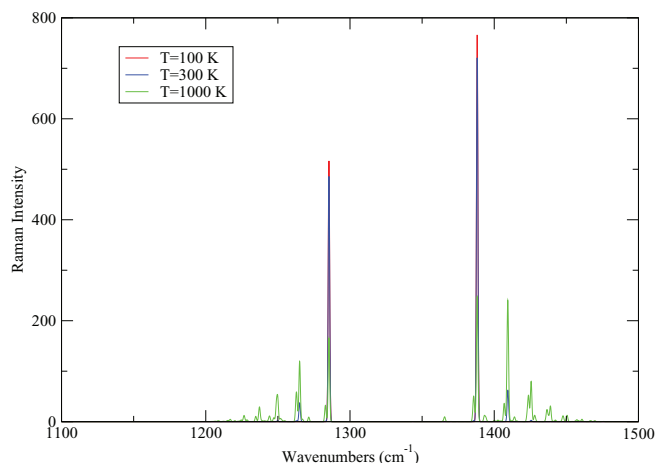
FIG. 2. Experimental and simulated Raman spectrum of CO<sub>2</sub>.

value  $2.12 \times 10^{-42} \text{C m}^2 \text{V}^{-1}$  of our fit. This is an indication of the consistency of the methodology employed in this work.

We now use the expansion (51) to simulate the Raman spectrum of CO<sub>2</sub> at high temperature. In Figure 2 we present the calculated spectrum of carbon dioxide at 1743 K in the range of energies 1150–1460 cm<sup>-1</sup>, along with the experimental one.<sup>92</sup> The procedure followed to simulate the spectrum consists in calculating the transition moments between all pairs of vibrational states with the same symmetry such that their energy difference falls in the range of energies experimentally scanned. Then, scattering cross sections are calculated through Eq. (50) and the transition lines are convoluted using a Gaussian profile up to the experimental bandwidth (1.2 cm<sup>-1</sup>). In order to find new experimental vibrational terms, calculated line positions in Figure 2 were replaced by experimental values when available. This procedure allowed us to identify unassigned lines in the experimental spectrum and, with the help of the computed frequencies and intensities, to obtain a number of new experimental vibrational terms, with an estimated uncertainty of 0.8 cm<sup>-1</sup>. The new experimental vibrational terms, with energies around 5000 cm<sup>-1</sup>, are given in Table III, labeled according to Ref. 117. Three of them are compared with other experimental vibrational terms<sup>118</sup> not used in the current fit, to check the predictions of the current algebraic model.

TABLE III. New experimental vibrational terms of CO<sub>2</sub> obtained in the present work from the analysis of the Raman spectrum, labelled following the notation of Ref. 117. The estimated accuracy of the new levels is 0.8 cm<sup>-1</sup>.

$\nu$ (cm <sup>-1</sup> )	$\nu_1, \nu_2^\ell, \nu_3$	Ref. 119
4557.7	(1 5 <sup>5</sup> 0) <sub>2</sub>	4557.595
4677.0	(2 3 <sup>3</sup> 0) <sub>2</sub>	4676.791
4800.9	(1 5 <sup>5</sup> 0) <sub>1</sub>	4801.365
5115.3	(2 4 <sup>4</sup> 0) <sub>3</sub>	
5218.7	(1 6 <sup>6</sup> 0) <sub>2</sub>	
5330.6	(4 0 <sup>0</sup> 0) <sub>3</sub>	
5345.6	(2 4 <sup>4</sup> 0) <sub>2</sub>	
5436.5	(3 2 <sup>2</sup> 0) <sub>2</sub>	
5644.9	(3 2 <sup>2</sup> 0) <sub>1</sub>	

FIG. 3. Simulated Raman spectrum of CO<sub>2</sub> at 100, 300, and 1000 K.

Finally, to illustrate the predictive power of our analysis we display in Figure 3 the simulated Raman CO<sub>2</sub> spectrum at temperatures  $T = 100, 300,$  and  $1000$  K. We provide a table which includes the calculated transitions in the frequency range 1100–1500 cm<sup>-1</sup>.<sup>119</sup> For each transition and symmetry, the calculated lower and upper vibrational term values, the frequency, and the polarizability transition moment are given. The transition line assignment has been performed according to Ref. 77.

## VI. CONCLUSIONS

In this work a general algebraic approach to describe the vibrational spectrum of semirigid molecules with either normal or local vibrational dynamics has been presented. The main feature of our approach is that the PES can be estimated for semirigid molecules using a local basis with preservation of the polyad, allowing the consideration of anharmonic effects from the outset.

The algebraic method has been applied to the vibrational spectrum of the CO<sub>2</sub> molecule. Although this molecule has already been studied within this approach, the results are extended to include the effect of curvilinear coordinates. Carbon dioxide is an example where the general approach presented in Sec. III is applied in its wider sense, since CO<sub>2</sub> has a linear geometry and presents a normal mode behavior. The current approach could be extended to more complex molecular systems, presenting either a local-mode or a normal-mode behavior.

Since the CO<sub>2</sub> molecule is linear, the local-mode description is introduced via a canonical transformation in the stretching degrees of freedom that, 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 through an anharmonization procedure in the local basis, while the  $U(3)$  model appears because of the anharmonization in the 2D harmonic oscillator. The inclusion of nonlinear terms in the coordinates expansion changes the force constant of the Fermi interaction, departing from Chedin's

value, a fact that is explained due to non-perturbative effects in (49).

The polarizability function is expanded in terms of curvilinear symmetry coordinates, and then transformed into an expansion in terms of (rectilinear) normal coordinates through Eq. (15). This allows us to obtain its algebraic representation by the introduction of normal mode bosonic operators. As was done for the Hamiltonian, the anharmonization procedure is applied, making possible to compute Raman transition matrix elements using algebraic eigenstates.

The CO<sub>2</sub> Raman spectrum has been simulated close to the experimental accuracy through a fit of the derivatives of the mean polarizability with respect to the curvilinear symmetry coordinates. The obtained polarizability function derivatives with respect to the stretching coordinates agree satisfactorily with previous results based on a linear expansion. Nonlinear effects appear chiefly in the derivatives with respect to the bending coordinates, with new values that improve the agreement with experimental results.

The eigenstates provided by the diagonalization of Hamiltonian with the spectroscopic parameter values in Ref. 77 and the computed 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<sub>2</sub> for combustion flames diagnostics. With this aim, a supplementary table<sup>119</sup> with a set of computed frequencies in the range 1100–1500 cm<sup>-1</sup> and polarizability transition moments is provided. Finally, by comparing the experimental and simulated Raman CO<sub>2</sub> spectra, a number of new experimental vibrational terms around 5000 cm<sup>-1</sup> are reported.

The present work is the result of a continuous effort, that lasts a couple of decades, trying to establish a connection between the modeling of molecular spectra using algebraic methods based on unitary algebras and the traditional approach in configuration space.

The application of the algebraic approach to the vibrational spectrum of carbon dioxide is a clear example of a case where a normal mode behavior hinders a description in terms of local oscillators in configuration space, and how this is solved in the suggested algebraic framework.

The CO<sub>2</sub> analysis involves testing the system wavefunctions through the description of the Raman spectrum, including a systematic and general approach to take into account nonlinear effects. Hence, the present work clearly demonstrates the possibility of taking advantage of algebraic methods based on unitary algebras to provide a spectroscopic description of molecules, keeping a connection with coordinates and momenta. Still a significant endeavor is needed to obtain at the quantum mechanical level the connection with configuration space for non-rigid molecular species.

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