A novel connection between algebraic spectroscopic parameters and force constants in the description of vibrational excitations of linear triatomic molecules

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Abstract

A connection between an algebraic approach to the dynamics of triatomic molecules based on the $U(2) \times U(3) \times U(2)$ Lie algebra and the traditional description in configuration space is presented. The connection is established in four steps. First, the molecular Hamiltonian is expanded in symmetrized local coordinates. Second, the Hamiltonian is transformed into an algebraic representation by introducing the realization of coordinates and momenta in terms of bosonic creation and annihilation operators of normal character. The third step is to perform a canonical transformation applied to the bosons associated with the stretching degrees of freedom in order to obtain a unified representation in a local scheme. Finally, an anharmonization procedure is applied to identify the $U(2) \times U(3) \times U(2)$ dynamical algebra. The main advantage of the proposed approach is that it provides relations between the spectroscopic parameters and the molecular structure and force constants. As an application, the analysis of the vibrational excitations of CO_2 in its ground electronic state is considered. In this scheme, each stretching degree of freedom is identified as an interacting Morse oscillator, with an associated $U(2)$ dynamical algebra, and the doubly degenerate bending degree of freedom is modelled with a $U(3)$ dynamical algebra, obtaining as a final result a reasonable set of force constants.

Key words: Algebraic description: U(3) dynamical algebra, bending modes, linear molecules, carbon dioxide

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1 Introduction

Vibrational spectroscopy constitutes a powerful tool to probe the structure and dynamics of molecules in gases, liquids, and interfaces [1–4]. To this end, the use of effective Hamiltonians is crucial in the assignment of spectral lines, making possible to calculate force constants by means of perturbation methods [1,2].

Phenomenological approaches that expand the Hamiltonian in second quantization operators are a valuable alternative to traditional methods when trying to characterize molecular vibrational spectra [2,5]. They are particularly useful when the generation of the spectrum using integro-differential techniques to calculate the potential energy surface and solve the Schrödinger equation implies a formidable computing task. Although full variational methods, with exact kinetic energy operators, have been intensively developed, they are computationally very demanding and cannot be used for large, and even medium-size, molecules [6]. In contrast, because of its phenomenologic character and the possibility to take advantage of group theoretical techniques, algebraic methods are capable of providing a deep physical insight into the problem keeping the necessary calculations relatively simple. Its simplicity is maximal when a normal mode basis is used. In such case, the diagonal contribution of the Hamiltonian presents harmonic contributions as well as anharmonic terms proportional to higher powers of the normal quantum numbers, with energies given as a Dunham expansion as a first approximation [7]. In general, this simple expansion turns out to be inadequate, and couplings between zeroth-order states must be introduced. The Darling-Dennison [8] and Fermi [9] resonances are among the most striking examples of such couplings. It is important to emphasize that these methods have the remarkable feature that they provide the interaction operators in such a way that its action on the basis states can be precisely stated, without the interference of additional contributions that are usual in the traditional configuration space approach. However, there is a downside behind this simplicity: the connection with the configuration space is blurred and the information about force constants and potentials is not trivially extracted from the spectroscopic parameters.

Methods based on normal harmonic oscillator basis are useful as long as we are interested in the low lying region of the spectrum [10,11]. For highly excited vibrational states, a local perspective represents a better alternative [12–14]. Local models appear in natural form when using internal coordinates for the molecular vibrational modeling. Usually Morse oscillators [15] are associated with stretching coordinates, since they reflect more accurately than harmonic oscillators the main physical properties of a pure local bond [12]. An usual approach implies the use of Morse oscillators for the stretching degrees of freedom, keeping a harmonic approximation for the bending dynamics [16].

The present paper makes use of an algebraic approach that is a particular case of a more general set of models characterized by the use of the unitary $U(\nu+1)$ Lie algebra as a dynamical algebra [17–19] to describe systems with ν degrees of freedom . The $U(\nu+1)$ approach was for the first time proposed in the context of the description of collective states of nuclei [20–22] and it is the basis of the Interacting Boson Model (IBM), which nowadays is a very useful tool for the description of nuclear structure [23]. The basic idea behind these models consists in adding an extra boson to the ν physical bosons in such a way that the total number of bosons is kept constant. Thus, the total space is appropriately cut off, allowing the description of the system in terms of an irreducible representation of the dynamical group $U(\nu+1)$. An additional advantage is that the subalgebra chains of the dynamical algebra leading to the system's symmetry algebra provide dynamical symmetries, with precise physical meaning and analytical energy formulas [17–19]. This approach was applied for the first time in the field of molecular physics by Iachello and coworkers to describe the rotation-vibration excitations of molecular systems [24–26]. Since in this framework the ro-vibrational degrees of freedom are treated as a set of collective bosonic excitations, called vibrons, the model derived from this approach is known as the vibron model [26]. A different algebraic approach has been formulated by Michelot and Moret-Bailly to describe only vibrational degrees of freedom, where a unitary algebra $U(\nu+1)$ is proposed for each set of ν equivalent oscillators [27]. This alternative is particularly interesting because of the simplification attained not dealing with rotations and vibrations simultaneously.

¿From the original vibron model, based on the $U(4)$ Lie algebra, stems two other models: the one dimensional (1D) and two dimensional (2D) limits of the vibron model. The 1D limit of the vibron model assigns a $U(2)$ dynamical algebra to each vibrational degree of freedom [28], a description which turns out to be equivalent to the algebraic treatment of a set of interacting Morse oscillators [29,30]. Although at first Morse oscillators were considered only to be a convenient description of stretching modes, later on they were also introduced to model asymmetric bending oscillations involved in non-linear semi-rigid molecules [31–33]. For linear molecules, however, the doubly degenerate nature of the bending degrees of freedom makes appropriate a description in terms of a $U(3)$ dynamical algebra [34]. This approach can be seen as a particular case ($\nu = 2$) of the model proposed by Michelot and Moret-Bailly [27]. However, in a more general context, the 2D limit of the vibron model has proved to be particularly relevant for the description of non-rigid molecules involving bending modes [34–36]. The $U(3)$ model permits to study from a simple perspective the situations arising between the rigidly linear and rigidly bent limits, in particular the spectra of quasilinear and quasirigid molecular species [35–37]. Hereafter we refer to the 1D and 2D limits of the vibron model as the $U(2)$ model and the $U(3)$ model, respectively.

In the $U(\nu + 1)$ models, the introduction of the scalar boson hinders a connection with traditional approaches in phase space. It is not trivial to extract Born-Oppenheimer potential surfaces from the obtained results, a fundamental feature to predict the spectra of isotopic species. One possible way to assign classical variables and calculate an energy functional from the algebraic Hamiltonian is via the classical limit, making use of the coherent or intrinsic state formalism [38,39]. Although the obtained energy functionals cannot be directly associated with Born-Oppenheimer potentials, it is possible to extract useful qualitative physical information [35]. But, in order to be able to calculate molecular force constants, it is crucial to take an alternative route, establishing a correspondence between the system coordinates and momenta and the generators of the dynamical group, at least in an approximate form. In the last years, several works have appeared where this correspondence is studied. The exact connection of the $U(2)$ model with the Morse and Pöschl-Teller potentials was established in Refs. [29,30,33]. This connection opened up the possibility of obtaining force constants from the optimized values of Hamiltonian parameters [31,32,40]. More recently, an approximate relation between coordinates and momenta in terms of the generators of the $U(\nu+1)$ dynamical algebra has also been proposed [41,42]. This relation allows the calculation, for the first time, of force constant values in the framework of the model proposed by Michelot and Moret-Bailly for vibrational excitations [43,44].

The aim of the present paper is to present an explicit connection between the $U(2) \times U(3) \times U(2)$ algebraic model and the traditional treatment in terms of coordinates and momenta for triatomic linear molecules. In this way, we establish a correspondence between the algebraic Hamiltonian and the one given in configuration space, which permits the determination of force constants from the fit of experimental data. As an example, we present the results for the vibrational excitations of carbon dioxide (CO_2) in its electronic ground state. Carbon dioxide is a molecular species that has attracted a major interest in several fields, from atmospheric chemistry to molecular astrophysics. In particular, this molecular species plays a key role in the atmospheric greenhouse effect [45]. Hence, there is an extensive set of available experimental data for this molecule [46,47] and it is important to obtain a fit to these data whose quality is high enough to be considered predictive. A calculation of CO_2 force constants from spectroscopic information is available in the bibliography [48,49] making it possible to compare our results with those obtained with a different approach.

The outline of the present paper can be briefly described as follows. In Sect. 2 we present the chosen system of coordinates and the Hamiltonian in configuration space for a linear triatomic molecule. We then transform the Hamiltonian into a second quantization representation, in terms of harmonic creation and annihilation operators defined from local or internal coordinates. The basic concepts of the $U(3)$ model are presented in Sect. 3. We establish a connection between the configuration space and algebraic approaches in Sect. 4. As an application, in Sect. 5, we fit the vibrational spectrum of CO_2 and compute the force constants from the obtained spectroscopic parameters. Finally, a brief summary and a concluding discussion is given in Sect. 6.

2 Hamiltonian of triatomic XY_2 molecules

The aim of this section is to set up the Hamiltonian of a triatomic molecule as a function of harmonic creation and annihilation operators in a local scheme. To this end, we first write the Hamiltonian in terms of symmetry internal coordinates and translate it into second quantization, as a function of bosonic local creation and annihilation operators, via a canonical transformation between symmetrized and local bosons. This procedure is necessary to establish the connection with the algebraic $U(2) \times U(3) \times U(2)$ model.

In terms of internal displacement coordinates, q_k, the quantum mechanical Hamiltonian that describes the vibrational excitations of a molecule takes the form [50,51]

$$H = \frac{1}{2}\tilde{\mathbf{p}}\mathbf{G}(\mathbf{q})\mathbf{p} + V(\mathbf{q}) \quad , \tag{1}$$

where $\mathbf{q}$ and $\mathbf{p}$ are column vectors corresponding to the internal displacement coordinates and their conjugate momenta, respectively, and mass dependent potential terms have been omitted [52]. The conjugate momentum p_k is defined in the usual way

$$p_k = -i\hbar\frac{\partial}{\partial q_k} \quad . \tag{2}$$

The Wilson matrix $\mathbf{G}(\mathbf{q})$ connects the expression of the kinetic energy of the system in terms of internal and Cartesian coordinates. In the case of linear triatomic molecules, two sets of internal coordinates are needed. The first set, (q_1, q_2), spans the subspace of stretching vibrations with

$$q_i = \Delta r_i = r_i - r_e, \quad i = 1, 2 \quad ; \tag{3}$$

where r_i corresponds to the i-th bond length and r_e to the i-th bond equilibrium length. The second set, (q_a, q_b), spans the subspace of bending oscillators with the following definition [53]

$$q_a = r_e \; \mathbf{e}_Y \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2} \quad , \quad q_b = -r_e \; \mathbf{e}_X \cdot \frac{\mathbf{r}_1 \times \mathbf{r}_2}{r_1 r_2} \quad , \tag{4}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are vectors from the C-atom to each one of the O-atoms. The unit vectors $\mathbf{e}_X$ and $\mathbf{e}_Y$ lie on the direction of the X and Y-axis of the laboratory axis system, with its origin in the molecule's center of mass.

With this choice of coordinates, the $\mathbf{q}$ and $\mathbf{p}$ vectors in Eq. (1) are given by

$$\tilde{\mathbf{q}} = (q_1, q_2, q_a, q_b) \ , \quad \tilde{\mathbf{p}} = (p_1, p_2, p_a, p_b) \quad .$$

The Wilson matrix elements $||\mathbf{G}|| = g_{q_\alpha q_\beta}$ associated with the selected set of internal coordinates are presented in Appendix A.

We could expand the Wilson matrix and the potential energy in terms of the local coordinates (q_a, q_b) for the bending mode and the Morse coordinates (q_1, q_2) for the stretches. This expansion permits the identification of a set of local interacting oscillators in Eq. (1). This approach, however, is largely improved when symmetry adapted coordinates are first introduced. The difference between both approaches is presented in detail in Appendix B, as well as a justification for the convenience of using a symmetrized approach in the study of the carbon dioxide vibrational spectrum. Hence we start introducing the symmetry coordinates

$$\mathcal{Q}_{\Sigma_g} = \frac{1}{\sqrt{2}}(q_1 + q_2) \, , \qquad \mathcal{Q}_{\Sigma_u} = \frac{1}{\sqrt{2}}(q_1 - q_2) \quad , \tag{5a}$$

$$\mathcal{Q}_{+} = -\frac{1}{\sqrt{2}}(q_a + iq_b) \, , \quad \mathcal{Q}_{-} = \frac{1}{\sqrt{2}}(q_a - iq_b) \quad , \tag{5b}$$

where the coordinates associated with the stretches are labeled with the subscripts $\Sigma_{g/u}$, and the bending degrees of freedom with $+/-$. The first case is a simplification of $\Sigma^+_{g/u}$, while the bending labels are a shorthand notation for $\Pi^\pm$ [54]. Both labels refer to the irreducible representations of the point symmetry group $\mathcal{D}_{\infty h}$. In matrix form

$$\tilde{\mathcal{Q}} = \tilde{\mathbf{q}} S \quad , \tag{6}$$

where

$$\tilde{\mathcal{Q}} = \left(\mathcal{Q}_{\Sigma_u}, \mathcal{Q}_{\Sigma_g}, \mathcal{Q}_{-}, \mathcal{Q}_{+}\right) \quad , \tag{7}$$

and

$$S = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & -i & -i \end{pmatrix} \quad . \tag{8}$$

The change to symmetry coordinates transforms the Hamiltonian (1) into

$$\hat{H} = \frac{1}{2} \tilde{\mathcal{P}} \ \mathcal{G} \ \mathcal{P} + V(\mathcal{Q}) \quad , \tag{9}$$

where

$$\tilde{\mathcal{P}} = \left(\mathcal{P}_{\Sigma_u}, \mathcal{P}_{\Sigma_g}, \mathcal{P}_-, \mathcal{P}_+\right) \quad , \tag{10}$$
$$\mathcal{G} = \tilde{\mathbf{S}}\ \mathbf{G}\ \mathbf{S} \quad .$$

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

$$\hat{H} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb} \quad , \tag{11}$$

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

$$\begin{aligned} \hat{H}_s = & \frac{1}{2} g^0_{\Sigma_g\Sigma_g} \hat{\mathcal{P}}^2_{\Sigma_g} + \frac{1}{2} g^0_{\Sigma_u\Sigma_u} \hat{\mathcal{P}}^2_{\Sigma_u} + \frac{1}{2} f_{\Sigma_g\Sigma_g} \hat{\mathcal{Q}}^2_{\Sigma_g} + \frac{1}{2} f_{\Sigma_u\Sigma_u} \hat{\mathcal{Q}}^2_{\Sigma_u} \\ & + \frac{1}{4!} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} \hat{\mathcal{Q}}^4_{\Sigma_g} + \frac{1}{4!} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \hat{\mathcal{Q}}^4_{\Sigma_u} + \frac{6}{4!} f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} \hat{\mathcal{Q}}^2_{\Sigma_g} \hat{\mathcal{Q}}^2_{\Sigma_u} \quad . \end{aligned} \tag{12}$$

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

$$\begin{aligned} \hat{H}_b = & g^0_{+-} \hat{\mathcal{P}}_+ \hat{\mathcal{P}}_- + f_{+-} \hat{\mathcal{Q}}_+ \hat{\mathcal{Q}}_- + \left(\frac{\partial^2 g_{+-}}{\partial\mathcal{Q}_+ \partial\mathcal{Q}_-}\right)_0 \hat{\mathcal{P}}_+ \hat{\mathcal{Q}}_+ \hat{\mathcal{Q}}_- \hat{\mathcal{P}}_- \\ & + \frac{6}{4!} f_{++--} \hat{\mathcal{Q}}^2_+ \hat{\mathcal{Q}}^2_- \quad . \end{aligned} \tag{13}$$

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

$$\begin{aligned} \hat{H}_{sb} = & \left(\frac{\partial g_{+-}}{\partial\mathcal{Q}_{\Sigma_g}}\right)_0 \mathcal{Q}_{\Sigma_g} \hat{\mathcal{P}}_+ \hat{\mathcal{P}}_- + \left(\frac{\partial g_{\Sigma_g+}}{\partial\mathcal{Q}_+}\right)_0 \hat{\mathcal{Q}}_{\Sigma_g} \left(\hat{\mathcal{Q}}_+ \hat{\mathcal{P}}_+ + \hat{\mathcal{P}}_- \hat{\mathcal{Q}}_-\right) \\ & + \frac{6}{3!} f_{\Sigma_g+-} \hat{\mathcal{Q}}_{\Sigma_g} \hat{\mathcal{Q}}_+ \hat{\mathcal{Q}}_- + \frac{1}{2} \left(\frac{\partial^2 g_{+-}}{\partial\mathcal{Q}^2_{\Sigma_g}}\right)_0 \hat{\mathcal{Q}}^2_{\Sigma_g} \hat{\mathcal{P}}_+ \hat{\mathcal{P}}_- + \frac{1}{2} \left(\frac{\partial^2 g_{+-}}{\partial\mathcal{Q}^2_{\Sigma_u}}\right)_0 \hat{\mathcal{Q}}^2_{\Sigma_u} \hat{\mathcal{P}}_+ \hat{\mathcal{P}}_- \\ & + \frac{1}{2} \left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial\mathcal{Q}_+ \partial\mathcal{Q}_-}\right)_0 \hat{\mathcal{P}}^2_{\Sigma_g} \hat{\mathcal{Q}}_+ \hat{\mathcal{Q}}_- + \frac{1}{2} \left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial\mathcal{Q}_+ \partial\mathcal{Q}_-}\right)_0 \hat{\mathcal{P}}^2_{\Sigma_u} \hat{\mathcal{Q}}_+ \hat{\mathcal{Q}}_- \\ & + \frac{1}{2} \left(\frac{\partial^2 g_{\Sigma_g+}}{\partial\mathcal{Q}_{\Sigma_g} \partial\mathcal{Q}_+}\right)_0 \hat{\mathcal{P}}_{\Sigma_g} \hat{\mathcal{Q}}_{\Sigma_g} \left(\hat{\mathcal{Q}}_+ \hat{\mathcal{P}}_+ + \hat{\mathcal{Q}}_- \hat{\mathcal{P}}_-\right) \\ & + \frac{1}{2} \left(\frac{\partial^2 g_{\Sigma_u+}}{\partial\mathcal{Q}_{\Sigma_u} \partial\mathcal{Q}_+}\right)_0 \hat{\mathcal{P}}_{\Sigma_u} \hat{\mathcal{Q}}_{\Sigma_u} \left(\hat{\mathcal{Q}}_+ \hat{\mathcal{P}}_+ + \hat{\mathcal{Q}}_- \hat{\mathcal{P}}_-\right) + \frac{12}{4!} f_{\Sigma_g\Sigma_g+-} \hat{\mathcal{Q}}^2_{\Sigma_g} \hat{\mathcal{Q}}_+ \hat{\mathcal{Q}}_- \\ & + \frac{12}{4!} f_{\Sigma_u\Sigma_u+-} \hat{\mathcal{Q}}^2_{\Sigma_u} \hat{\mathcal{Q}}_+ \hat{\mathcal{Q}}_- \quad . \end{aligned} \tag{14}$$

The Hamiltonian (11) can be translated into an algebraic representation through the introduction of bosonic creation and annihilation operators. For the stretching degrees of freedom, these operators are defined as

$$a_\Gamma^\dagger = \alpha^\Gamma \hat{\mathcal{Q}}_\Gamma - \frac{i}{2\hbar\alpha^\Gamma}\hat{\mathcal{P}}_\Gamma \ , \quad a_\Gamma = \alpha^\Gamma \hat{\mathcal{Q}}_\Gamma + \frac{i}{2\hbar\alpha^\Gamma}\hat{\mathcal{P}}_\Gamma \quad , \tag{15}$$

where $\Gamma = \Sigma_g, \Sigma_u$ and the definitions

$$\left(\alpha^{\Sigma_g}\right)^2 = \frac{1}{2\hbar}\sqrt{\frac{f_{\Sigma_g\Sigma_g}}{g^0_{\Sigma_g\Sigma_g}}} = \frac{\mu_{\Sigma_g}}{2\hbar}\sqrt{f_{\Sigma_g\Sigma_g} g^0_{\Sigma_g\Sigma_g}} = \frac{\omega_{\Sigma_g}\mu_{\Sigma_g}}{2\hbar} \quad , \tag{16a}$$

$$\left(\alpha^{\Sigma_u}\right)^2 = \frac{1}{2\hbar}\sqrt{\frac{f_{\Sigma_u\Sigma_u}}{g^0_{\Sigma_u\Sigma_u}}} = \frac{\mu_{\Sigma_u}}{2\hbar}\sqrt{f_{\Sigma_u\Sigma_u} g^0_{\Sigma_u\Sigma_u}} = \frac{\omega_{\Sigma_u}\mu_{\Sigma_u}}{2\hbar} \quad , \tag{16b}$$

where $\mu_\Gamma = 1/g^0_{\Gamma\Gamma}$. In the case of the bending mode, the following relations apply

$$a_\pm^\dagger = \alpha^\pm \hat{\mathcal{Q}}_\pm + \frac{i}{2\hbar\alpha^\pm}\hat{\mathcal{P}}_\mp \ , \quad a_\pm = -\alpha^\pm \mathcal{Q}_\mp + \frac{i}{2\hbar\alpha^\pm}\hat{\mathcal{P}}_\pm \quad , \tag{17}$$

with

$$\left(\alpha^+\right)^2 = \left(\alpha^-\right)^2 = (\alpha)^2 = \frac{1}{2\hbar}\sqrt{\frac{f_{+-}}{g^0_{+-}}} = \frac{1}{2\hbar}\sqrt{\frac{f_{q_aq_a}}{g^0_{q_aq_a}}} \quad . \tag{18}$$

We now propose the additional canonical transformation between symmetrized and local stretching creation harmonic operators

$$a_{\Sigma_g}^\dagger = \frac{1}{\sqrt{2}}(a_1^\dagger + a_2^\dagger) \ , \quad a_{\Sigma_u}^\dagger = \frac{1}{\sqrt{2}}(a_1^\dagger - a_2^\dagger) \quad . \tag{19}$$

The corresponding relation for the annihilation operators can be trivially calculated taking the adjoint of the previous equation. The operators $\{a_i^\dagger\}$ with $i = 1, 2$, are identified with local operators. If we restrict the interactions to preserve the polyad number

$$P = 2(n_{\Sigma_g} + n_{\Sigma_u}) + (n_+ + n_-) \quad , \tag{20}$$

where $n_{\Sigma_{g/u}}$ stands for the number of quanta in the $\Sigma_{g/u}$ vibrational mode, and $n_+ + n_- = n$ is the number of quanta in the degenerate bending mode, the Hamiltonian (11) in the local harmonic representation is

$$
\begin{aligned}
\hat{H} =& \tilde{\omega}_s \sum_{i=1}^{2} \left(a_i^\dagger a_i + a_i a_i^\dagger \right) + \lambda_s \sum_{i\neq j=1}^{2} a_i^\dagger a_j + \alpha_1^s \left(\hat{n}_1^2 + \hat{n}_2^2 \right) \\
&+ \alpha_2^s \left(a_1^{\dagger 2} a_2^2 + a_2^{\dagger 2} a_1^2 + 4\hat{n}_1 \hat{n}_2 \right) + \alpha_3^s \left(\hat{n}_1 a_2^\dagger a_1 + \hat{n}_2 a_1^\dagger a_2 + H.c. \right) \\
&+ \tilde{\omega}_b \hat{n} + \alpha_1^b \hat{n}^2 + \alpha_2^b \hat{\ell}^2 + \alpha_1^{sb} \left\{ \left(a_1^\dagger + a_2^\dagger \right) a_+ a_- + H.c. \right\} \\
&+ \alpha_2^{sb} \left(\hat{n}_1 + \hat{n}_2 \right) \hat{n} + \alpha_3^{sb} \left(a_1^\dagger a_2 + a_2^\dagger a_1 \right) \hat{n} \quad ,
\end{aligned} \tag{21}
$$

with the definitions

$$
\begin{aligned}
\hat{n}_i =& a_i^\dagger a_i \ ; \quad i = 1, 2 \quad , \\
\hat{\ell} =& a_+^\dagger a_+ - a_-^\dagger a_- = \hat{n}_+ - \hat{n}_- \quad , \\
\hat{n} =& a_+^\dagger a_+ + a_-^\dagger a_- = \hat{n}_+ + \hat{n}_- \quad ,
\end{aligned} \tag{22}
$$

where $\hat{n}_i$ is the number of quanta for the i-th stretching oscillator, $\hat{n}$ is the total number of bending quanta, and $\hat{\ell}$ is the vibrational angular momentum. The expressions for the spectroscopic parameters in terms of the structure and force constants are detailed in Appendix C.

An appropriate basis to diagonalize the Hamiltonian (21) is constructed by means of the symmetry projection of the direct product of functions

$$
|n_1 n_2, n^\ell\rangle = \mathcal{N} \ (a_1^\dagger)^{n_1} (a_2^\dagger)^{n_2} (a_+^\dagger)^{\frac{n+\ell}{2}} (a_-^\dagger)^{\frac{n-\ell}{2}} |0\rangle \quad , \tag{23}
$$

with normalization constant

$$
\mathcal{N} = \frac{1}{\sqrt{n_1! n_2! (\frac{n+\ell}{2})! (\frac{n-\ell}{2})!}} \quad . \tag{24}
$$

For the sake of future reference the action of the bosonic bending operators over the kets (23) is given by

$$
a_\pm^\dagger |n_1 n_2, n^\ell\rangle = \sqrt{(n_\pm + 1)} \ |n_1 n_2, (n+1)^{\ell \pm 1}\rangle \quad , \tag{25a}
$$

$$
a_\pm |n_1 n_2, n^\ell\rangle = \sqrt{n_\pm} \ |n_1 n_2, (n-1)^{\ell \mp 1}\rangle \quad , \tag{25b}
$$

where

$$
n_\pm = \frac{n \pm \ell}{2} \quad . \tag{26}
$$

The present treatment is based on local harmonic oscillators. One of their advantages is that the force constants can be obtained from the value of the Hamiltonian parameters obtained through a fit to the available experimental data. However, the harmonic basis has some limitations. Whenever high energy regions are explored, the strong mixture of basis states makes the assignment of quantum labels difficult. A significant improvement can be obtained proposing a local mode approach for the stretches in terms of Morse oscillators, instead of harmonic oscillators, together with the incorporation of anharmonic effects for the bends. In the next section we present a local algebraic approach that is able to accomplish this task. However, this approach lacks a direct connection with configuration space and, consequently, a clear way to extract force constants from the spectroscopic parameters. This dilemma will be solved in Sect. 4, where we establish a connection between the local harmonic and the algebraic approach, taking the best of both methods.

3 Algebraic approach to triatomic molecules

The first step in the algebraic description of a system consists in identifying an appropriate dynamical algebra. Hence the Hamiltonian, and any dynamical variable, may be expanded in terms of the generators of the dynamical algebra. A fundamental feature of this approach is that the system's Hilbert space carries a specific irreducible representation of the dynamical algebra. In our case, since Morse oscillators have been shown to be useful in describing the stretching vibrational modes of a molecule, a dynamical algebra $U(2)$ is associated with each stretching coordinate [18,26,28]. In this case the representation is directly related to the depth of the potential. The 2D bending mode of a linear molecule can be described in terms of a 2D degenerate harmonic oscillator. However, as previously mentioned, in order to obtain a dynamical algebra for this 2D system using a compact group, an extra boson is added with the constraint that the total number of bosons is preserved, following the algebraic methodology presented in the introduction. In the spirit of this approach, the $U(3)$ dynamical algebra is constructed to describe the vibrational bending modes of triatomic molecules. The result is a simple model able to cope with the rigidly-linear and rigidly-bent limits as well as the situations in between these two limits [34,35,37]. The dynamical group for the complete triatomic molecule is then given by $U_1(2) \times U(3) \times U_2(2)$ [55,56]. An important feature of the algebraic approach is that every possible subalgebra chain, starting on the dynamical algebra and finishing in the symmetry algebra, constitutes what is known as a dynamical symmetry [18]. Associated with each dynamical symmetry there is an analytical solution of the system, providing a basis to diagonalize the general Hamiltonian operator.

In the $U(2)$ case, for the stretching modes, the generators of the $U_i(2)$ algebras can be associated with ladder and number operators of the Morse potential eigenfunctions [57]. The bosonic $U(3)$ Lie algebra is not related to a known potential. It can be constructed with two Cartesian boson creation and annihilation operators $\{\tau_a^\dagger, \tau_b^\dagger, \tau_a, \tau_b\}$, together with a scalar boson $\{\sigma^\dagger, \sigma\}$ [34]. To be consistent with Eq. (4), we label the Cartesian operators as a and b instead of x and y. From the physical point of view it is convenient to introduce spherical (circular) bosons

$$\tau_{\pm}^{\dagger} = \mp \frac{\tau_a^{\dagger} \pm i\tau_b^{\dagger}}{\sqrt{2}} \ , \quad \tau_{\pm} = \mp \frac{\tau_a \mp i\tau_b}{\sqrt{2}} \quad , \tag{27}$$

since they carry irreducible representations of the symmetry group $\mathcal{D}_{\infty h}$. Following Ref. [34], the nine generators of $U(3)$ may be written as combinations of the bilinear products of a creation and annihilation operator

$$\begin{aligned}
\hat{n} &= \tau_+^{\dagger}\tau_+ + \tau_-^{\dagger}\tau_- \ , & \hat{n}_\sigma &= \sigma^{\dagger}\sigma \ , \\
\hat{l} &= \tau_+^{\dagger}\tau_+ - \tau_-^{\dagger}\tau_- \ , & & \\
\hat{D}_+ &= \sqrt{2}(\tau_+^{\dagger}\sigma - \sigma^{\dagger}\tau_-) \ , & \hat{D}_- &= \sqrt{2}(-\tau_-^{\dagger}\sigma + \sigma^{\dagger}\tau_+) \ , \\
\hat{Q}_+ &= \sqrt{2}\,\tau_+^{\dagger}\tau_- \ , & \hat{Q}_- &= \sqrt{2}\,\tau_-^{\dagger}\tau_+ \ , \\
\hat{R}_+ &= \sqrt{2}(\tau_+^{\dagger}\sigma + \sigma^{\dagger}\tau_-) \ , & \hat{R}_- &= \sqrt{2}(\tau_-^{\dagger}\sigma + \sigma^{\dagger}\tau_+) \ .
\end{aligned} \tag{28}$$

The operator $\hat{l}$ can be identified as the 2D angular momentum in Eq. (22) [37]. There are two possible chains starting from $U(3)$ and ending in $SO(2)$ (i.e. that conserve 2D angular momentum):

$$U(3) \supset U(2) \supset SO(2) \rightarrow \text{Chain (Ib)} \ , \tag{29a}$$

$$U(3) \supset SO(3) \supset SO(2) \rightarrow \text{Chain (IIb)} \ , \tag{29b}$$

where the b label stands for bending. The corresponding subalgebras are composed by the following elements

$$\begin{array}{lc}
U(2) & \{\hat{n}, \hat{l}, \hat{Q}_+, \hat{Q}_-\} \\
SO(3) & \{\hat{l}, \hat{D}_+, \hat{D}_-\} \\
SO(2) & \{\hat{l}\}
\end{array} \tag{30}$$

where the $SO(3)$ elements satisfy the usual angular momentum commutation relations. Because of an automorphism of the Lie algebra $U(3)$ constructed with the scalar boson σ and the circular bosons $\tau_{\pm}$ defined in (27), there is an alternative $SO(3)$ subalgebra of $U(3)$, called $\overline{SO}(3)$, with elements [37]

$$\overline{SO}(3) \ \{\hat{l}, \hat{R}_+, \hat{R}_-\} \ . \tag{31}$$

Associated with each subalgebra, there are Casimir or invariant operators whose fundamental characteristic is that they commute with the elements of the subalgebra and, in our case, with the generators of the symmetry group. The first and second order Casimir operators for the subalgebras in Eqs. (30)

and (31) are

$$
\begin{aligned}
&\hat{C}_1[U(2)] = \hat{n} \ \ , \hat{C}_2[U(2)] = \hat{n}(\hat{n}+1), \\
&\hat{C}_2[SO(3)] = \hat{W}^2 = (\hat{D}_+\hat{D}_- + \hat{D}_-\hat{D}_+)/2 + \hat{l}^2 \,, \\
&\hat{C}_1[SO(2)] = \hat{l} \ , \hat{C}_2[SO(2)] = \hat{l}^2,
\end{aligned} \tag{32}
$$

and

$$
\hat{C}_2[\overline{SO}(3)] = \hat{R}^2 = (\hat{R}_+\hat{R}_- + \hat{R}_-\hat{R}_+)/2 + \hat{l}^2 \quad . \tag{33}
$$

With regard to the definition of a dynamical algebra for the stretching modes, a similar situation can be identified, where the possible chains are [28]

$$
U_1(2) \times U_2(2) \supset SO_1(2) \times SO_2(2) \supset SO_{12}(2) \rightarrow \text{Chain (Is)} \quad , \tag{34a}
$$
$$
U_1(2) \times U_2(2) \supset U_{12}(2) \supset SO_{12}(2) \qquad \rightarrow \text{Chain (IIs)} \quad . \tag{34b}
$$

with the associated first and second order Casimir operators

$$
\begin{aligned}
\hat{C}_1[SO_i(2)] &= \hat{J}_{z,i} \ , & \hat{C}_2[SO_i(2)] &= \hat{J}^2_{z,i} \quad , \\
\hat{C}_1[SO_{12}(2)] &= \hat{J}_{z,1} + \hat{J}_{z,2} \ , & \hat{C}_2[SO_{12}(2)] &= (\hat{J}_{z,1} + \hat{J}_{z,2})^2 \quad , \\
\hat{C}_1[U_{12}(2)] &= \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 \quad , & &
\end{aligned} \tag{35}
$$

where $i = 1, 2$. The operators $\hat{J}_{x,i}$, $\hat{J}_{y,i}$, $\hat{J}_{z,i}$, associated with the i-th stretching local mode, satisfy the usual angular momentum commutation relations [58]. It is important to emphasize that this is not a true physical angular momentum but a mathematical way of simplifying the addressed problem using well known angular momentum techniques.

Following the algebraic methodology, in general a Hamiltonian **operator** is expanded in terms of powers and products of the Casimir operators. However, in molecular systems, if the Hamiltonian goes beyond one and two-body operators, the number of interactions is greater than the number of invariant operators [59]. Consequently another prescription should be used to construct the Hamiltonian. For example, in Ref. [55], the Hamiltonian is expanded in terms of basic operators which in the harmonic limit behave as the coordinates and momenta. For the stretches these operators are

$$
\hat{S}_i = \frac{1}{\sqrt{2}}(\hat{J}_{+,i} + \hat{J}_{-,i}), \qquad \hat{P}_i = \frac{1}{\sqrt{2}}(\hat{J}_{+,i} - \hat{J}_{-,i}), \quad i = 1, 2, \tag{36}
$$

which are analogous to the usual **coordinate and momentum operators**. For the bending modes the relevant operator is

$$
\hat{\bar{R}}^2 = \hat{R}^2/\hat{N}, \tag{37}
$$

which is considered to be analogous to r^2 in configuration space [34,55] by taking into account the definition of $\hat{N}$ as the total number of bending bosons, $\hat{N} = \hat{n} + \hat{n}_\sigma$. The Hamiltonian is then expanded in terms of these oparators, providing an algebraic force field expansion [55]. Analogous to the traditional description, the algebraic Hamiltonian takes the form

$$\hat{\mathcal{H}}_{alg} = \hat{\mathcal{H}}_s + \hat{\mathcal{H}}_b + \hat{\mathcal{H}}_{sb}, \tag{38}$$

with the following explicit expressions [55]

$$\begin{aligned}
\hat{\mathcal{H}}_s = & \, a\sum_{i=1}^{2} \hat{J}_{z,i}^2 + m(\hat{P}_1\hat{P}_2 + \hat{S}_1\hat{S}_2) \\
& + b_{1,2}^{(4,0)}(\hat{S}_1^4 + \hat{S}_2^4) + b_{1,2}^{(2,2)}(\hat{S}_1^2\hat{S}_2^2) + b_{1,2}^{(1,3)}(\hat{S}_1^3\hat{S}_2 + \hat{S}_1\hat{S}_2^3), \qquad (39a)\\
\hat{\mathcal{H}}_b = & \, \omega_b\hat{n} + k_b\hat{\bar{R}}^4, \qquad (39b)\\
\hat{\mathcal{H}}_{sb} = & \, b_{(1,2),b}^{(1,2)}(\hat{S}_1 + \hat{S}_2)\hat{\bar{R}}^2 + b_{(1,2),b}^{(2,2)}(\hat{S}_1^2 + \hat{S}_2^2)\hat{\bar{R}}^2 + b_{(1,2),b}^{(1,1,2)}\hat{S}_1\hat{S}_2\hat{\bar{R}}^2 \quad , \qquad (39c)
\end{aligned}$$

where only terms that preserve the polyad (20) **are** considered. In this expression only four terms are directly given in terms of Casimir operators. In the stretching contribution $\hat{\mathcal{H}}_s$ the first term corresponds to the sum of the invariant operators $C_2[SO_i(2)] = \hat{J}_{z,i}^2$ (non interacting Morse oscillators), while the second term is connected with $\hat{C}_1[U_{12}(2)] = \hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2$**, an interaction of the Majorana type between the oscillators**. In the bending part $\hat{\mathcal{H}}_b$ both contributions correspond to the invariant operators $\hat{C}_1[U(2)] = \hat{n}$ (harmonic contribution) and $\hat{C}_2[\overline{SO}(3)]^2 = \hat{\bar{R}}^4$ (anharmonic correction), respectively. Although some other interactions may be rewritten in terms of linear combinations of powers and products of invariant operators, such **procedure hinders the physical interpretation of the spectroscopic parameters**. This fact, together with the lack of enough Casimir operators to express all the interactions, explains the convenience to express the Hamiltonian in terms of an expansion of the form (39). Hence the basic idea in the construction of the Hamiltonian (39) **consists of** starting with non interacting local oscillators and **adding** all the independent interactions up to quartic **order,** following the same prescription used in the traditional formalism in configuration space. We **discuss** the physical meaning of this expansion shortly thereafter.

The appropriate basis to diagonalize the Hamiltonian (39) corresponds to the direct product of functions associated with chains Is and Ib

$$|[N_s],[N];v_1v_2;n_\sigma,n^l\rangle = |[N_s];v_1v_2\rangle \otimes |[N];n_\sigma,n^l\rangle \quad , \tag{40}$$

where the stretching contribution $|[N_s];v_1v_2\rangle$ is the product of two identical Morse oscillators with v_i excitation quanta, characterized by a total number of bound states given by N_s

$$|[N_s]; v_i\rangle = \sqrt{\frac{(N_s - v_i)!}{N_s! v_i!}} \left(\frac{\hat{J}_{-,i}}{\sqrt{N_s}} \right)^{v_i} |[N_s]; 0\rangle \quad , \tag{41}$$

where $v_i = j - m_i$, being m_i the eigenvalue of $\hat{J}_{z,i}$. For the bending case

$$|[N]; n_\sigma, n^l\rangle = \mathcal{N}_b \; (\sigma^\dagger)^{n_\sigma} (\tau_+^\dagger)^{\frac{n+l}{2}} (\tau_-^\dagger)^{\frac{n-l}{2}} |0\rangle, \tag{42}$$

with normalization constant

$$\mathcal{N}_b = \frac{1}{\sqrt{n_\sigma! (\frac{n+l}{2})! (\frac{n-l}{2})!}}. \tag{43}$$

Note that the kets (42) may be denoted as

$$|[N]; n_\sigma, n^l\rangle = |[N]; n^l\rangle, \tag{44}$$

because of the constraint $\hat{N} = \hat{n} + \hat{n}_\sigma$. The action of the operators $\hat{J}_{\pm,i}$ over the kets (41) is known [26], as well as the action of the generators in Eq. (28) over the bending basis (42), and consequently the matrix elements of any operator involved in the Hamiltonian (39) may be calculated. Another possibility, using the same dynamical algebra, closer to the usual algebraic approach, where the Hamiltonian is expanded in terms of invariant operators can be found in Ref. [56].

By construction the algebraic Hamiltonian (39) is not directly related to the Hamiltonian (11) in configuration space. That is to say, when the harmonic limit of the algebraic Hamiltonian is considered (large N limit), the Hamiltonian (21) is not formally recovered. The reason stems from the kinetic energy term. While the Hamiltonian (21) was obtained through a Taylor expansion of both the Wilson matrix and the potential energy, in the algebraic version only the potential was expanded, keeping the Wilson matrix evaluated in equilibrium. However, we should stress that, in the harmonic limit of the algebraic Hamiltonian, both cases are completely equivalent when treated as effective Hamiltonians. In other words, when they are used to carry out a fit, both of them provide the same results, but in the algebraic case the potential surface and force constants cannot be extrapolated from the obtained spectroscopic parameters, even in the harmonic limit. When an effective Hamiltonian is expanded in terms of interactions in the second quantization representation, the spectroscopic parameters are understood to have contributions of both kinetic and potential energies, while this is not the case in the construction of the Hamiltonian (39).

In the next section, we present a connection between the Hamiltonian (21) obtained from the analysis in configuration space and the equivalent algebraic Hamiltonian in the framework of the $U_1(2) \times U(3) \times U_2(2)$ model.

4 Force constants in the algebraic approach

This section is intended to establish the connection between the conventional treatment of triatomic molecules presented in Sect. 2 and the algebraic approach $U_1(2) \times U(3) \times U_2(2)$ [55,56].

Recently, in a series of contributions [41–44], an approach to obtain reasonable force constants in the framework of the methods based on unitary groups has been proposed. The basic idea consists of mapping an $U(2)$ algebra to each oscillator. In the harmonic limit the $U(2)$ algebra is transformed to the Weyl algebra associated with the harmonic oscillator. In this way, an approximate connection between the generators of the dynamical algebra and the system coordinates and momenta may be established; a connection that makes possible a one-to-one correspondence between the algebraic approach and the traditional methods in configuration space. This approach has been already applied in the context of a set of equivalent oscillators to the description of pyramidal molecules [43,44]. The aim of the present paper is to show that it is possible to extend the same idea to the bending mode of linear molecules, calculating force constants for linear molecules from a fit to experimental data.

Following the approach given in Refs. [41,42], from the generators (28) of the unitary group $U(3)$ we identify two $SU_k(2)$ subalgebras with generators

$$\hat{J}_{+,k} = \sigma \tau_k^\dagger \quad , \tag{45a}$$

$$\hat{J}_{-,k} = \sigma^\dagger \tau_k \quad , \tag{45b}$$

$$\hat{J}_{0,k} = -\frac{1}{2}(\sigma^\dagger \sigma - \hat{n}_k) \ ; \quad k = a, b \quad , \tag{45c}$$

where $\hat{n}_k = \tau_k^\dagger \tau_k$. The operators $\{\hat{J}_{\pm,k}, \hat{J}_{0,k}\}$ have the usual angular momentum commutation relations [58]

$$[\hat{J}_{+,k}, \hat{J}_{-,k}] = 2\hat{J}_{0,k} \ ; \qquad [\hat{J}_{0,k}, \hat{J}_{\pm,k}] = \pm \hat{J}_{\pm,k} \ ; \ k = a, b \quad . \tag{45d}$$

It is important to keep in mind that, although we make use of the angular momentum algebra, the generators $\hat{J}_{\pm,k}$ and $\hat{J}_{0,k}$ are not associated with the physical angular momentum operators. For example, the action of $\hat{J}_{+,k}$ does not increment by one the value of the vibrational angular momentum. We now introduce the normalized operators

$$b_k^\dagger \equiv \frac{\hat{J}_{+,k}}{\sqrt{N}} \ ; \qquad b_k \equiv \frac{\hat{J}_{-,k}}{\sqrt{N}} \ ; \qquad k = a, b \quad , \tag{46}$$

which satisfy the commutation relations

$$[b_j, b_k^\dagger] = \delta_{jk} - \frac{\hat{n}\,\delta_{jk} + \tau_k^\dagger \tau_j}{N} \quad ; \quad [b_j^\dagger, b_k^\dagger] = [b_j, b_k] = 0 \ ; \ k = a, b \quad , \tag{47}$$

where $\hat{n} = \hat{n}_a + \hat{n}_b = \tau_+^\dagger \tau_+ + \tau_-^\dagger \tau_-$. In particular

$$[b_k, b_k^\dagger] = 1 - \frac{\hat{n} + \hat{n}_k}{N} = -\frac{2}{N} \hat{J}_{0,k} \ ; \ k = a, b \quad . \tag{48}$$

We now proceed to define the circular operators

$$b_\pm^\dagger = \mp \frac{b_a^\dagger \pm i b_b^\dagger}{\sqrt{2}} \quad , \quad b_\pm = \mp \frac{b_a \mp i b_b}{\sqrt{2}} \quad . \tag{49}$$

The action of these operators over the kets (44) is the following

$$b_\pm^\dagger |[N]; n^l\rangle = \sqrt{\left(\frac{n \pm l}{2} + 1\right)\left(1 - \frac{n}{N}\right)}\ |[N]; (n+1)^{l\pm1}\rangle \quad , \tag{50a}$$

$$b_\pm |[N]; n^l\rangle = \sqrt{\left(\frac{n \pm l}{2}\right)\left(1 - \frac{n-1}{N}\right)}\ |[N]; (n-1)^{l\mp1}\rangle \quad , \tag{50b}$$

while for the operators $\tau_\pm^\dagger(\tau_\pm)$ the corresponding matrix elements are given by (25) with the identification

$$\tau_\pm^\dagger \leftrightarrow a_\pm^\dagger \ ; \qquad \tau_\pm \leftrightarrow a_\pm \quad , \tag{51}$$

and, consequently, from Eqs. (22) and (28), $\hat{\ell} = \hat{l}$. From these results it is clear that the harmonic limit is obtained taking the large N limit, as expected. In fact, from Eq. (50) we obtain

$$\lim_{N\to\infty} b_\pm^\dagger = \tau_\pm^\dagger \quad ; \quad \lim_{N\to\infty} b_\pm = \tau_\pm \quad , \tag{52}$$

and consequently

$$\lim_{N\to\infty} [b_j, b_k^\dagger] = \delta_{jk} \ ; \quad j, k = +, - \quad . \tag{53}$$

Having in mind the calculation of force constants, it is crucial to establish the connection between the generators of the dynamical algebra and the local coordinates and momenta, at least in an approximate form. We propose the following approximation for the local coordinates, $\hat{\mathcal{Q}}_\pm$, and momenta, $\hat{\mathcal{P}}_\pm$, in the framework of the $U(3)$ model

$$\hat{\mathcal{Q}}_\pm \simeq \sqrt{\frac{\hbar}{2\omega_b \mu_b}} (d_\pm^\dagger - d_\mp) \quad , \quad \hat{\mathcal{P}}_\pm \simeq -\frac{i}{2}\sqrt{2\hbar\omega_b\mu_b} (d_\mp^\dagger + d_\pm) \quad , \tag{54}$$

where $d^\dagger_\pm(d_\pm)$ may be identified either with $b^\dagger_\pm(b_\pm)$ or $a^\dagger_\pm(a_\pm)$, following the prescription discussed in Refs.[41–44]. Here the parameters ω_b and μ_b are $\omega_b = \sqrt{f_{+-}g^0_{+-}} = \sqrt{f_{q_aq_a}g^0_{q_aq_a}}$ and $\mu_b = 1/g^0_{+-} = 1/g^0_{q_aq_a}$. A remarkable consequence of our proposal is that the correspondence $d^\dagger_\pm(d_\pm) \to b^\dagger_\pm(b_\pm)$ implies

$$\hat{\mathcal{Q}}_\pm \approx \hat{D}_\pm \quad ; \quad \hat{\mathcal{P}}_\pm \approx \hat{R}_\mp \tag{55}$$

from (28). Hence, under the approximation in Eq. (54), the coordinates and momentum operators behave as a subset of generators of $SO(3)$ and $\overline{SO}(3)$, respectively.

The proposed relation (54) represents just an approximation, not only because we are truncating to a linear expansion in terms of the operators (49), but also because the commutation relations

$$[\hat{\mathcal{Q}}_j, \hat{\mathcal{P}}_k] = i\hbar\delta_{jk} \quad , \tag{56}$$

have a correction of the order $1/N$ when the operators $d^\dagger_\pm(d_\pm)$ are substituted by $b^\dagger_\pm(b_\pm)$. Indeed, a straightforward calculation yields

$$[\hat{\mathcal{Q}}_-, \hat{\mathcal{Q}}_+] = \frac{\hbar}{2\omega_b\mu_b}\,\frac{\hat{l}}{N} \quad , \quad [\hat{\mathcal{P}}_-, \hat{\mathcal{P}}_+] = -\frac{\hbar\omega_b\mu_b}{2}\,\frac{\hat{l}}{N} \quad , \tag{57}$$

while for the coordinates and momenta

$$\left[\hat{\mathcal{Q}}_\pm, \hat{\mathcal{P}}_\pm\right] = i\hbar\left(1 - \frac{3}{2}\frac{\hat{n}}{N}\right) \quad , \tag{58a}$$

$$\left[\hat{\mathcal{Q}}_\pm, \hat{\mathcal{P}}_\mp\right] = -i\hbar\,\frac{\tau^\dagger_\pm\tau_\mp}{N} \quad . \tag{58b}$$

We know, however, that these relations should be exact in the harmonic limit, a fact that further supports the validity of the connection (54) with the configuration space.

Let us turn back to the traditional treatment presented in Sect. 2. We suggest to use the relations (54) instead of (17), in addition to substitute the operators $d^\dagger_\pm(d_\pm)$ by $a^\dagger_\pm(a_\pm)$ when number and angular momentum operators are involved. Otherwise, we use the substitution rule $d^\dagger_\pm(d_\pm) \to b^\dagger_\pm(b_\pm)$, as it is the case for Fermi interactions [41–44]. With regard to the stretching degrees of freedom, we may consider the anharmonization procedure

$$a^\dagger_i \to b^\dagger_i \quad , \quad a_i \to b_i \quad ; \quad i = 1, 2 \quad , \tag{59}$$

already used in previous works [31,32,40]. Here $b^\dagger_i(b_i)$ with $i = 1, 2$ are creation and annihilation operators acting on the Morse eigenfunctions [57]. The anharmonization (59) is equivalent to consider the linear approximation [29,30,60]

$$\frac{y_i}{\beta} \simeq \sqrt{\frac{\hbar}{2\omega_s\mu_s}}(b_i^\dagger + b_i) \quad , \quad p_i \simeq \frac{i}{2}\sqrt{2\hbar\omega_s\mu_s}(b_i^\dagger - b_i) \quad , \quad i = 1, 2 \quad , \tag{60}$$

where y_i and β are the Morse coordinate and the parameter of the Morse potential, respectively. Since in a molecule like CO_2, as shown in Appendix B, a symmetrized description is more appropriate, we cannot use (60) from the outset to obtain a Hamiltonian of the form (21). However, we are able to use (59) directly in the final algebraic Hamiltonian (21) in order to take the advantages of dealing with Morse oscillators while keeping the correct connection with the structure and force constants. Following this approach, the following Hamiltonian is obtained

$$\begin{aligned}\hat{H} =& \tilde{\omega}_s \sum_{i=1}^{2} \left(b_i^\dagger b_i + b_i b_i^\dagger\right) + \lambda_s \sum_{i\neq j=1}^{2} b_i^\dagger b_j + \alpha_1^s \left(\hat{n}_{s,1}^2 + \hat{n}_{s,2}^2\right) \\ &+ \alpha_2^s \left(b_1^{\dagger 2} b_2^2 + b_2^{\dagger 2} b_1^2 + 4\hat{n}_{s,1}\hat{n}_{s,2}\right) + \alpha_3^s \left(\hat{n}_{s,1} b_2^\dagger b_1 + \hat{n}_{s,2} b_1^\dagger b_2 + H.c.\right) \\ &+ \tilde{\omega}_b \hat{n} + \alpha_1^b \hat{n}^2 + \alpha_2^b \hat{\ell}^2 + \alpha_1^{sb} \left\{\left(b_1^\dagger + b_2^\dagger\right) b_+ b_- + H.c.\right\} \\ &+ \alpha_2^{sb} \left(\hat{n}_{s,1} + \hat{n}_{s,2}\right) \hat{n} + \alpha_3^{sb} \left(b_1^\dagger b_2 + b_2^\dagger b_1\right) \hat{n} \quad ,\end{aligned} \tag{61}$$

with the definition

$$\hat{n}_{s,i} = b_i^\dagger b_i \quad , \quad i = 1, 2 \quad . \tag{62}$$

The equations that relate the spectroscopic parameters and force constants are included in Appendix C. The first term in Eq. (61) is equivalent to two independent Morse oscillators. Hence this Hamiltonian may be interpreted as modelling three interacting oscillators: a 2D oscillator (bending degrees of freedom) and two 1D Morse oscillators (stretching degrees of freedom). In order to carry out the necessary calculations, we select the basis

$$|[N_s], [N]; v_1 v_2; n^\ell\rangle = |[N_s]; v_1 v_2\rangle \otimes |[N]; n^\ell\rangle \quad , \tag{63}$$

where $|[N]; n^\ell\rangle$ is given by (42) and for the stretches

$$|[N_s]; v_1 v_2\rangle = |[N_s]; v_1\rangle \otimes |[N_s]; v_2\rangle, \tag{64}$$

with

$$|[N_s]; v_i\rangle = \sqrt{\kappa^{v_i} \frac{(N_s - v_i)!}{v_i! N_s!}} (b_i^\dagger)^{v_i} |0\rangle, \tag{65}$$

where $N_s + 1 = \kappa$ [57]. The matrix elements of the Hamiltonian (61) are obtained by means of (50) and

$$b_i^\dagger|[N_s];v_i\rangle = \sqrt{(v_i+1)\left(1-\frac{v_i+1}{\kappa}\right)}|[N_s];v_i+1\rangle \quad , \tag{66a}$$

$$b_i|[N_s];v_i\rangle = \sqrt{v_i\left(1-\frac{v_i}{\kappa}\right)}|[N_s];v_i-1\rangle \quad . \tag{66b}$$

When the Hamiltonian (38) is written in terms of the operators $\hat{J}_{\pm,i}$, $i=1,2$, and $\tau_\pm$, it takes the same form as the Hamiltonian (61) with the correspondence

$$\tau_\pm^\dagger\sigma(\tau_\pm\sigma^\dagger) \leftrightarrow b_\pm^\dagger(b_\pm) \ , \quad \hat{J}_{-,i}(\hat{J}_{+,i}) \leftrightarrow b_i^\dagger(b_i) \quad , \quad i=1,2 \quad . \tag{67}$$

This means that both Hamiltonians should provide identical results when fitting a set of experimental vibrational energies. The algebraic approach leading to Hamiltonian (38), however, does not take into account the contribution of the kinetic energy and consequently does not provide the connection with the structure and force constants. In contrast, the present approach constitutes a reasonable method to establish a correspondence with the traditional treatments where the connection with force constants is clearly established. The next section is devoted to show the application of our approach to the specific case of carbon dioxide.

5 Application to carbon dioxide

We proceed to apply our approach to obtain the force constants for carbon dioxide from the set of spectroscopic constants optimized to fit the vibrational spectrum of this molecular species in its electronic ground state. In this electronic manifold, CO_2 is a linear molecule with a bond length $r_e = 1.16$ Å [61]. Thus, its point symmetry group is $\mathcal{D}_{\infty h}$, with four vibrational degrees of freedom: two stretching modes ($\Sigma_g^+ \oplus \Sigma_u^+$) and a doubly degenerate bending mode ($\Pi_g^\pm$) [11,54]. The Hamiltonian (61) has 11 spectroscopic parameters. However, as shown in Appendix C, we know that the parameters α_1^b and α_2^b depends on the same force constant f_{++--}. Thus we obtain two different estimates for the f_{++--} force constant because in the fit we considered these parameters as independent. This can be justified since, in principle, in a more complete description, additional force constants of higher order should affect differently both values.

The diagonalization of the Hamiltonian (61) is carried out in a symmetry adapted basis which is obtained by diagonalizing the representation of a complete set of operators in the basis (63) [62]. The spectroscopic parameters are optimized with an iterative non-linear least square method. The quality of the fit is expressed in terms of the rms deviation

$$rms = \left[\sum_{i=1}^{N_{exp}} (E^i_{exp} - E^i_{cal})^2 / (N_{exp} - N_{par}) \right]^{1/2} \quad , \tag{68}$$

where N_{exp} is the total number of experimental energies and N_{par} the number of parameters optimized in the fit. All the experimental data included were evenly weighted. We assign statistical uncertainties to the obtained parameters. For each parameter x_i, two types of uncertainty estimates are considered: the delta-error (δx_i) and the epsilon-error (ϵx_i). A detailed discussion on these two error estimates can be found in Ref. [42]. The fit encompasses all the experimental energies up to polyad $P = 9$. The optimal values for the boson numbers N_s and N were found to be $N_s = 160$ and $N = 150$. They were obtained by optimization using the criterion of minimum deviation. In Table C.1 we present the 101 experimental term energies for $^{12}CO_2$ and the computed energies obtained using the present approach. An rms deviation of 0.53 cm^{-1} was obtained. In addition to the experimental and calculated energies, Table C.1 includes state labels, both normal and local, as well as the square of the maximum component in each basis. The simultaneous assignment of the states in both (approximate) normal and local schemes is useful since states close to each one of the limiting situations may coexist in the spectrum.

The set of optimized spectroscopic parameters that produced the fit in Table C.1, as well as their corresponding uncertainty estimates, are presented in Table C.2. The epsilon and delta error magnitudes indicate that the parameters are well determined. In addition to this, the correlation matrix has been computed, obtaining matrix elements not greater than 0.96, which further supports that parameters are well determined.

In addition to the fit presented in Table C.1 for $^{12}CO_2$, we have carried out a calculation for the isotopomer $^{13}CO_2$, involving a fit to 63 experimental energy levels up to polyad 10 with $rms = 0.46$ cm^{-1}. In both cases, for the sake of comparison, and to clarify the advantages offered by the proposed approach, a fit with the harmonic limit of Hamiltonian (61) was carried out, obtaining an $rms = 1.0$ cm^{-1} in the $^{12}CO_2$ case and $rms = 0.9$ cm^{-1} for $^{13}CO_2$.

From the spectroscopic parameters given in Table C.2, making use of the relations given in Appendix C, we calculate the force constants that characterize the ground electronic state of carbon dioxide. The results are shown in the first column of Table C.3. The force constants derived from the fit to the isotopomer $^{13}CO_2$ are presented in the second column of Table C.3. In the third and fourth columns of the same table, the results for the harmonic limit of Hamiltonian (61) and the force constants calculated by *Chedin* [48,49] for $^{12}CO_2$ have been included. In the latter approach a normal basis is used with diagonal terms up to third order, including thereafter Fermi, l- type doubling, and Coriolis interactions with help of contact transformation theory [1,63]. As mentioned above, since we are considering effective force constants, two values for the force constant $f_{q_a q_a q_a q_a}$ were obtained due to the ambiguity in its determination (see Appendix C). The results presented in Table C.3 show that the general trend of the force constants is satisfactorily reproduced. The quadratic force constants obtained by our approach are close to the values given by Chedin, as can be noted by comparing the first and fourth columns of Table C.3. However, the accordance between our results and Chedin's force constants in the quartic order case is sensitively worse. This is an expected result, considering the difference between both approaches. Besides, the differences between the potential functions in both cases are clearly remarked by the lack of Chedin quartic bending-stretching parameters [48,49]. This could explain why the accordance for the cubic order force constants associated with the Fermi interaction are also discreet.

In order to estimate the quality of the calculated force constants of $^{12}CO_2$, we used them in the Born-Oppenheimer approximation to predict the spectroscopic parameters for the isotopomer $^{13}CO_2$. We compare the predicted values with the set of fitted spectroscopic parameters obtained from the energy levels of $^{13}CO_2$. In Table C.4 both sets are presented: the first column corresponds to the set derived from the fit and the second column corresponds to the predicted set. The resemblance of both sets of parameters constitutes an evidence of the consistency of our results. Since the sensitivity of the spectrum under parameter variations strongly depends on the nature of the affected parameter, a significant change in a parameter value does not necessarily imply a large impact in the spectrum and vice versa. For instance, the predicted parameter associated with the Fermi interaction in Table C.4 differs in only 3 cm^{-1} from the optimized value, however the predicted spectrum presents a deviation of $rms = 7.9$ cm^{-1}. But the substitution of this parameter (37.1 cm^{-1}) by its optimized value (34.1 cm^{-1}) drastically lowers the deviation to $rms = 1.7$ cm^{-1}.

Finally, in Table C.5 we present for $^{12}CO_2$ the energies predicted by our model for polyads $P = 10$ and $P = 11$ as well as the corresponding experimental energies. **The inclusion of the predicted values raises the rms from** 0.53 **cm^{-1} to XXXX**. The good quality of the predictions supports our approach to establish the Hamiltonian (61). **When the whole set of available experimental energies up to polyad** 11 **(**$N_{exp} = 122$**) is included in the fit, a deviation of** $rms = 0.67$ **cm^{-1} is obtained, a value that is comparable to the previous one. The modifications induced in the force constants are not appreciable. We present the fit up to polyad** 11 **and the predicted energies in the supplementary material.**

6 Summary and Conclusions

Based on a novel perspective on the algebraic approach to molecular spectra [41,42], we have established a connection between the $U(3)$ algebraic approach for linear molecules and the corresponding description in configuration space. The basic idea behind this connection is the identification of operators satisfying the $SU(2)$ algebra commutation relations with each Cartesian bending coordinate. This mapping between the abstract algebraic approach and the configuration space allows one to start with a Hamiltonian expressed in terms of local curvilinear coordinates and transform it into its algebraic representation. This approach has two remarkable consequences. It permits a correspondence between the interactions in the algebraic approach and the traditional formulation in terms of internal coordinates and, once the Hamiltonian parameters are optimized, a realistic approximation to the system force constants becomes available. In fact, the present approach permits to take advantage of the simplicity of the $U(3)$ algebraic methods, without losing the connection with configuration space.

As an example, the $^{12}CO_2$ molecule vibrational spectrum is studied. To describe the complete set of vibrational degrees of freedom of this molecule, the dynamical algebra $U_1(2) \times U(3) \times U_2(2)$ is proposed, where the $U(2)$ and $U(3)$ algebras are associated with the stretching degrees of freedom and the doubly degenerate bending mode, respectively. We stress that if in our description we choose as a starting point a local model of interacting Morse oscillators, the derived force constants would be inconsistent with our results unless the polyad is broken. The reason stems from the strongly normal behavior of this molecule. To obtain a reasonable approximation to the force constants it has been necessary to propose an approach where the Hamiltonian was first expressed in terms of local symmetrized coordinates and, afterwards, transformed into an algebraic representation in terms of the usual bosonic operators, with an additional canonical transformation to the local bosons. Finally, an anharmonization procedure was carried out to incorporate the creation and annihilation operators associated with the Morse ladder operators, and the operators $b^\dagger_\pm(b_\pm)$ belonging to the $U(3)$ algebra defined in Eq. (49). We want to emphasize that the present approach has the advantage of considering anharmonicities from the outset, a feature that characterizes algebraic models.

A highly accurate description of the vibrational excitations $^{12}CO_2$ was obtained, with a rms deviation of 0.53 cm^{-1}. Compared to the deviation $rms =$ 1.0 cm^{-1} obtained with the harmonic limit of the Hamiltonian (61), it implies an improvement close to 50%. The fit to the experimental energies allows the obtention of a potential energy surface in good agreement with the results of previous calculations. To test the isotopic invariance, a new set of force constants was obtained from an energy fit to the energy terms of the isotopomer

$^{13}CO_2$. The discrepancies found are reasonable, considering the approximations involved in our model. A deviation of $rms = 0.46$ cm^{-1} was obtained for the isotopomer species $^{13}CO_2$, a value that increases in the harmonic limit to $rms = 0.90$ cm^{-1}. Again, the rms increase reflects the importance of taking into account anharmonic effects.

The comparison with the results obtained for $^{12}CO_2$ using a different methodology [48,49] and the comparison of predicted and calculated spectroscopic parameters for $^{13}CO_2$ further support the present work. An evaluation of the quality of the predicted energies is also presented in Table C.5.

We believe that this approach opens up the possibility to take advantage of the benefits of the algebraic approach, keeping simultaneously a connection with the traditional description in configuration space. An example of the importance of our proposal is represented by the application to carbon dioxide, where the combination of these features allows a satisfactory description of the system with a simple model.

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A Wilson matrix elements for a linear triatomic XY_2 molecule

In this appendix the Wilson matrix elements in the set of local coordinates $\mathbf{q} = \{q_1, q_2, q_a, q_b\}$ are obtained. This task can be accomplished via the relation with the set of coordinates $\mathbf{t} = \{q_1, q_2, q_\theta, q_\chi\}$ used to describe non linear triatomic molecules, where $q_\theta = r_e \Delta\theta$ and $q_\chi = \chi$. The angle θ is the interbond angle, which is equal to 180° in the linear configuration; the angle χ is the angle between the molecular plane and the XZ plane in the laboratory axis system. The laboratory Z-axis is selected in such a way that it coincides with the z-axis in the Molecular Axis System.

The matrix elements $g_{q_\alpha q_\beta}$ are defined by

$$g_{q_\alpha q_\beta} = \sum_\zeta \sum_{i=1}^{3} \frac{1}{m_i} \left(\frac{\partial q_\alpha}{\partial x_{i\zeta}}\right) \left(\frac{\partial q_\beta}{\partial x_{i\zeta}}\right) \; ; \quad \zeta = x, y, z \quad . \tag{A.1}$$

In case we consider a set of internal coordinates $t_j = t_j(x)$, using the chain rule

$$\left(\frac{\partial q_\alpha}{\partial x_{i\varsigma}}\right) = \sum_j \left(\frac{\partial q_\alpha}{\partial t_j}\right)\left(\frac{\partial t_j}{\partial x_{i\varsigma}}\right) \quad , \tag{A.2}$$

we obtain the relation between the Wilson matrix elements in each system of coordinates

$$g_{q_\alpha q_\beta} = \sum_{j,k} \left(\frac{\partial q_\alpha}{\partial t_j}\right)\left(\frac{\partial q_\beta}{\partial t_k}\right) g_{t_j t_k} \quad . \tag{A.3}$$

Hence, knowing the matrix elements $g_{t_i t_j}$ of the XY_2 non linear molecule [64]

$$g_{q_1 q_1} = g_{q_2 q_2} = \frac{1}{m_X} + \frac{1}{m_Y} \quad , \tag{A.4a}$$

$$g_{q_\theta q_\theta} = r_e^2 \left\{ \frac{1}{m_Y}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) + \frac{1}{m_X}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2} - \frac{2\cos\theta}{r_1 r_2}\right)\right\} \quad , \tag{A.4b}$$

$$g_{q_1 q_2} = \frac{\cos\theta}{m_X} \quad , \tag{A.4c}$$

$$g_{q_1 q_\theta} = r_e \frac{\sin\theta}{m_X r_2} \quad , \tag{A.4d}$$

$$g_{q_2 q_\theta} = r_e \frac{\sin\theta}{m_X r_1} \quad , \tag{A.4e}$$

$$\begin{aligned} g_{q_\chi q_\chi} = g_{zz} = & \frac{r_e^2}{4\cos^2(\theta/2)} \left\{ \frac{1}{m_Y}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right) \right. \\ & \left. + \frac{1}{m_X}\left(\frac{1}{r_1^2} + \frac{1}{r_2^2} + \frac{2}{r_1 r_2}\right)\right\} \quad , \end{aligned} \tag{A.4f}$$

$$g_{q_1 q_\chi} = g_{q_2 q_\chi} = g_{q_\theta q_\chi} = 0 \quad , \tag{A.4g}$$

and the relation between both sets of bending coordinates

$$q_a = r_e \sin\theta \cos\chi \quad , \tag{A.5a}$$

$$q_b = r_e \sin\theta \sin\chi \quad , \tag{A.5b}$$

$$\sin\theta = \frac{1}{r_e}\sqrt{q_a^2 + q_b^2} \quad , \tag{A.5c}$$

$$\cos\theta = -\frac{1}{r_e}\sqrt{r_e^2 - q_a^2 - q_b^2} \quad , \tag{A.5d}$$

where $\chi = 0$ when the molecular plane lies on the laboratory XZ plane (see Eq. (4)) and $\cos\theta$ have negative values for small displacements from the linear configuration, we obtain the following non-zero independent matrix elements

$$g_{q_1q_1} = g_{q_2q_2} = \frac{1}{m_X} + \frac{1}{m_Y} \ , \tag{A.6a}$$

$$g_{q_1q_2} = \frac{\cos\theta}{m_X} = -\frac{1}{r_e m_X}\sqrt{r_e^2 - q_a^2 - q_b^2} \ , \tag{A.6b}$$

$$g_{q_1q_a} = -\frac{r_e}{m_X r_2}\cos\theta\cos\chi\sin\theta = \frac{1}{r_e}\frac{q_a}{m_X r_2}\sqrt{r_e^2 - q_a^2 - q_b^2} \ , \tag{A.6c}$$

$$g_{q_2q_a} = -\frac{r_e}{m_X r_1}\cos\theta\cos\chi\sin\theta = \frac{1}{r_e}\frac{q_a}{m_X r_1}\sqrt{r_e^2 - q_a^2 - q_b^2} \ , \tag{A.6d}$$

$$g_{q_1q_b} = -\frac{r_e}{m_X r_2}\cos\theta\sin\chi\sin\theta = \frac{1}{r_e}\frac{q_b}{m_X r_2}\sqrt{r_e^2 - q_a^2 - q_b^2} \ , \tag{A.6e}$$

$$g_{q_2q_b} = -\frac{r_e}{m_X r_1}\cos\theta\sin\chi\sin\theta = \frac{1}{r_e}\frac{q_b}{m_X r_1}\sqrt{r_e^2 - q_a^2 - q_b^2} \ , \tag{A.6f}$$

$$\begin{aligned} g_{q_aq_a} = {} & r_e\frac{r_e + \sqrt{r_e^2 - q_a^2 - q_b^2}}{2}\left\{\frac{A_{12}}{m_Y} + \frac{1}{m_X}\left(A_{12} + \frac{2}{r_1r_2}\right)\right\} \\ & - r_e^2\frac{q_a^2}{q_a^2+q_b^2}\left[\left\{\frac{r_e + \sqrt{r_e^2 - q_a^2 - q_b^2}}{2r_e}\right\}\left\{\frac{A_{12}}{m_Y} + \frac{1}{m_X}\left(A_{12} + \frac{2}{r_1r_2}\right)\right\}\right. \\ & \left. - \frac{1}{r_e^2}\left\{r_e^2 - q_a^2 - q_b^2\right\}\left\{\frac{A_{12}}{m_Y} + \frac{1}{m_X}\left(A_{12} + \frac{2\sqrt{r_e^2 - q_a^2 - q_b^2}}{r_er_1r_2}\right)\right\}\right] \end{aligned} \tag{A.6g}$$

with the definition

$$A_{12} = \frac{1}{r_1^2} + \frac{1}{r_2^2} \ .$$

The matrix element $g_{q_bq_b}$ is obtained from $g_{q_aq_a}$ by the substitution $q_a \to q_b$ and $q_b \to q_a$ in (A.6g).

B Importance of internal symmetry adapted coordinates

In this appendix we demonstrate the importance of using symmetry adapted internal coordinates for the description of the vibrational spectrum of carbon dioxide in its ground electronic state. To this end, we consider for the sake of simplicity only the stretching degrees of freedom, showing the difference that arises when symmetry internal coordinates are considered instead of non-symmetry local coordinates.

Let us start with the Hamiltonian (1) associated with the stretching modes in the harmonic approximation. The substitution of the algebraic representation of coordinates and momenta in terms of creation and annihilation operators

$$\hat{r}_i = \frac{1}{2\beta}(a_i^\dagger + a_i) \ \ , \ \ \hat{p}_i = i\hbar\beta(a_i^\dagger - a_i) \ \ ; \ \ \beta^2 = \frac{1}{2\hbar}\sqrt{\frac{f_{rr}}{g_{rr}}} \ \ , \tag{B.1}$$

allows one to express the Hamiltonian in the form

$$
\begin{aligned}
\hat{H} =& \frac{\hbar}{2}\sqrt{f_{rr}g_{rr}}\sum_{i=1}^{2}(a_i^\dagger a_i + a_i a_i^\dagger) \\
&+ \frac{\hbar}{2}\sqrt{f_{rr}g_{rr}}\left(\frac{f_{rr'}}{f_{rr}} + \frac{g_{rr'}}{g_{rr}}\right)(a_1^\dagger a_2 + a_1 a_2^\dagger) \\
&+ \frac{\hbar}{2}\sqrt{f_{rr}g_{rr}}\left(\frac{f_{rr'}}{f_{rr}} - \frac{g_{rr'}}{g_{rr}}\right)(a_1^\dagger a_2^\dagger + a_1 a_2) \quad .
\end{aligned} \tag{B.2}
$$

The first term corresponds to two independent one dimensional harmonic oscillators; the second term implies an interaction between the oscillators that conserves the total number of quanta, V. The last term does not preserve V, and usually is neglected in a local mode description. The Hamiltonian considered is then simplified to be

$$
\hat{H} = \frac{\hbar}{2}\sqrt{f_{rr}g_{rr}}\sum_{i=1}^{2}(a_i^\dagger a_i + a_i a_i^\dagger) + \frac{\hbar}{2}\sqrt{f_{rr}g_{rr}}\left(\frac{f_{rr'}}{f_{rr}} + \frac{g_{rr'}}{g_{rr}}\right)(a_1^\dagger a_2 + a_1 a_2^\dagger) \quad . \tag{B.3}
$$

Starting with the same quadratic Hamiltonian (1), expressed in terms of symmetry coordinates, a diagonal representation can be obtained introducing the bosonic operators

$$
a_\Gamma^\dagger = \alpha_\Gamma \hat{\mathcal{Q}}_\Gamma - \frac{i}{2\hbar\alpha_\Gamma}\hat{\mathcal{P}}_\Gamma \quad , \quad a_\Gamma = \alpha_\Gamma \hat{\mathcal{Q}}_\Gamma + \frac{i}{2\hbar\alpha_\Gamma}\hat{\mathcal{P}}_\Gamma \quad , \tag{B.4}
$$

where $\Gamma = \Sigma_g, \Sigma_u$. The coordinates $\mathcal{Q}_\Gamma$ are symmetry adapted coordinates (5), and the α_Γ parameters are

$$
\alpha_{\Sigma_g}^2 = \frac{1}{2\hbar}\sqrt{\frac{f_{rr} + f_{rr'}}{g_{rr} + g_{rr'}}} \quad , \quad \alpha_{\Sigma_u}^2 = \frac{1}{2\hbar}\sqrt{\frac{f_{rr} - f_{rr'}}{g_{rr} - g_{rr'}}} \quad . \tag{B.5}
$$

In this case the Hamiltonian takes the simplified form

$$
\begin{aligned}
\hat{H} =& \frac{\hbar}{2}\sqrt{(f_{rr} + f_{rr'})(g_{rr} + g_{rr'})}(a_{\Sigma_g}^\dagger a_{\Sigma_g} + a_{\Sigma_g} a_{\Sigma_g}^\dagger) \\
&+ \frac{\hbar}{2}\sqrt{(f_{rr} - f_{rr'})(g_{rr} - g_{rr'})}(a_{\Sigma_u}^\dagger a_{\Sigma_u} + a_{\Sigma_u} a_{\Sigma_u}^\dagger) \quad .
\end{aligned} \tag{B.6}
$$

We can return to a Hamiltonian of the form (B.3) introducing a canonical transformation

$$
a_{\Sigma_g}^\dagger = \frac{1}{\sqrt{2}}(a_1^\dagger + a_2^\dagger) \quad , \quad a_{\Sigma_u}^\dagger = \frac{1}{\sqrt{2}}(a_1^\dagger - a_2^\dagger) \quad , \tag{B.7}
$$

yielding to a Hamiltonian operator

$$
\begin{aligned}
\hat{H} = & \frac{\hbar}{4}\left(\sqrt{(f_{rr}+f_{rr'})(g_{rr}+g_{rr'})}+\sqrt{(f_{rr}-f_{rr'})(g_{rr}-g_{rr'})}\right) \\
& \times \sum_{i=1}^{2}(a_i^{\dagger}a_i + a_i a_i^{\dagger}) \\
& + \frac{\hbar}{2}\left(\sqrt{(f_{rr}+f_{rr'})(g_{rr}+g_{rr'})}-\sqrt{(f_{rr}-f_{rr'})(g_{rr}-g_{rr'})}\right) \\
& \times (a_1^{\dagger}a_2 + a_1 a_2^{\dagger}) \quad .
\end{aligned} \tag{B.8}
$$

¿From this result we should first note that the transformation (B.7) does not allow us to recover the original Hamiltonian (B.2), because it is such that implies that the number of quanta (polyad number) is a conserved quantity. A Bogoliubov transformation is necessary to recover (B.2). On the other hand, we should stress that the difference between the Hamiltonians (B.3) and (B.8) is given only by the different dependence on the force constants and G matrix elements of the spectroscopic parameters. This is a remarkable feature, because it implies that both Hamiltonians provide fits to experimental energies of the same quality, but the force constants derived from the optimized spectroscopic parameters are different.

Once the relation between the two descriptions is clear, the question that arises is whether there is a quantitative criterion to choose between the local and the symmetrized description in order to evaluate appropriately the force constants of a molecular system. The answer is provided by the connection between (B.2) and (B.8), which is obtained by rewriting the spectroscopic parameters in (B.8) in the form $\sqrt{1+x}$ to carry out the expansion

$$
\sqrt{1+x} = 1 + \frac{1}{2}x + \frac{1}{8}x^2 + \ldots \tag{B.9}
$$

Applying this expansion, with $x = f_{rr'}/f_{rr}$ and $x = g_{rr'}/g_{rr}$, the Hamiltonian (B.8) transforms into

$$
\begin{aligned}
\hat{H} = & \frac{\hbar}{2}\sqrt{f_{rr}g_{rr}}(1 + \frac{g_{rr'}f_{rr'}}{g_{rr}f_{rr}} + \mathcal{O}(x^2))\sum_{i=1}^{2}(\hat{a}_i^{\dagger}\hat{a}_i + a_i\hat{a}_i^{\dagger}) \\
& + \frac{\hbar}{2}\sqrt{f_{rr}g_{rr}}\left(\frac{f_{rr'}}{f_{rr}} + \frac{g_{rr'}}{g_{rr}} + \mathcal{O}(x^2)\right)(\hat{a}_1^{\dagger}\hat{a}_2 + \hat{a}_1\hat{a}_2^{\dagger}) \quad .
\end{aligned} \tag{B.10}
$$

This expression coincides with (B.3) when

$$
\frac{f_{rr'}}{f_{rr}} << 1 \ , \quad \frac{g_{rr'}}{g_{rr}} << 1 \quad . \tag{B.11}
$$

For the water molecule

$$\left(\frac{g_{rr'}}{g_{rr}}\right)^2 \simeq 2.16 \times 10^{-4}\ ,\quad \left(\frac{f_{rr'}}{f_{rr}}\right)^2 \simeq 3.76 \times 10^{-4}\quad , \tag{B.12}$$

and consequently a local approach is appropriate. In contrast, for carbon dioxide we have

$$\left(\frac{g_{rr'}}{g_{rr}}\right)^2 \simeq 0.326\ ,\quad \left(\frac{f_{rr'}}{f_{rr}}\right)^2 \simeq 0.01\quad , \tag{B.13}$$

which reflects the normal behavior that characterizes this molecule. Hence it is clear that for carbon dioxide the appropriate Hamiltonian expressed in terms of local operators should be (B.8).

C Relation between algebraic spectroscopic parameters and force constants

In this appendix we present the relation of the spectroscopic parameters associated with the Hamiltonian (21) with the molecular structure and force constants. For the stretching parameters we have

$$\begin{aligned}
\tilde{\omega}_s =& \frac{1}{2}\hbar\omega_{\Sigma_g} + \frac{1}{2}\hbar\omega_{\Sigma_u} + \frac{9}{2}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} + \frac{9}{2}\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \\
&+ \frac{1}{2}\frac{6}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2(2\alpha^{\Sigma_u})^2} f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} - \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial\mathcal{Q}^2_{\Sigma_g}}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_g})^2} \\
&- \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial\mathcal{Q}_+\partial\mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_g}\right)^2}{(2\alpha)^2} - \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2(2\alpha)^2} f_{\Sigma_g\Sigma_g+-} \\
&- \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial\mathcal{Q}^2_{\Sigma_u}}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_u})^2} - \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial\mathcal{Q}_+\partial\mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_u}\right)^2}{(2\alpha)^2} \\
&- \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_u})^2(2\alpha)^2} f_{\Sigma_u\Sigma_u+-}\quad ,
\end{aligned} \tag{C.1}$$

$$
\begin{aligned}
\lambda_s =& \frac{1}{2}\hbar\omega_{\Sigma_g} - \frac{1}{2}\hbar\omega_{\Sigma_u} + 6\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} - 6\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \\
& - \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}^2_{\Sigma_g}}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_g})^2} - \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_g}\right)^2}{(2\alpha)^2} \\
& - \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2(2\alpha)^2} f_{\Sigma_g\Sigma_g+-} + \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}^2_{\Sigma_u}}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_u})^2} \\
& + \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_u}\right)^2}{(2\alpha)^2} + \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_u})^2(2\alpha)^2} f_{\Sigma_u\Sigma_u+-} \quad ,
\end{aligned} \tag{C.2}
$$

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

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

$$
\alpha_3^s = 3\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_g})^4} f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} - 3\frac{1}{4!}\frac{1}{(2\alpha^{\Sigma_u})^4} f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} \quad . \tag{C.5}
$$

On the other hand, for the purely bending parameters

$$
\begin{aligned}
\tilde{\omega}_b =& \hbar\omega + \frac{\hbar^2}{4}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 + \frac{6}{4!}\frac{1}{(2\alpha)^4} f_{++--} - \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}^2_{\Sigma_g}}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_g})^2} \\
& - \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_g}\right)^2}{(2\alpha)^2} - \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_g})^2(2\alpha)^2} f_{\Sigma_g\Sigma_g+-} - \frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}^2_{\Sigma_u}}\right)_0 \frac{\hbar^2\alpha^2}{(2\alpha^{\Sigma_u})^2} \\
& - \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_u}\right)^2}{(2\alpha)^2} - \frac{12}{4!}\frac{1}{(2\alpha^{\Sigma_u})^2(2\alpha)^2} f_{\Sigma_u\Sigma_u+-} \ ,
\end{aligned} \tag{C.6}
$$

$$
\alpha_1^b = \frac{\hbar^2}{8}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 + \frac{3}{2}\frac{6}{4!}\frac{1}{(2\alpha)^4} f_{++--} \ , \tag{C.7}
$$

$$
\alpha_2^b = \frac{\hbar^2}{8}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 - \frac{1}{2}\frac{6}{4!}\frac{1}{(2\alpha)^4} f_{++--} \ , \tag{C.8}
$$

while for the stretching-bending interaction parameters

$$\alpha_1^{sb} = -\frac{1}{\sqrt{2}}\left(\frac{\partial g_{+-}}{\partial \mathcal{Q}_{\Sigma_g}}\right)_0 \frac{\hbar^2\alpha^2}{2\alpha^{\Sigma_g}} - \frac{1}{\sqrt{2}}\left(\frac{\partial g_{+\Sigma_g}}{\partial \mathcal{Q}_+}\right)_0 \hbar^2\alpha^{\Sigma_g} + \frac{1}{\sqrt{2}}\frac{6}{3!}\frac{1}{2\alpha^{\Sigma_g}\left(2\alpha\right)^2} f_{\Sigma_g+-} \tag{C.9}$$

$$\alpha_2^{sb} = -\frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_{\Sigma_g}^2}\right)_0 \frac{\hbar^2\alpha^2}{\left(2\alpha^{\Sigma_g}\right)^2} - \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_g}\right)^2}{\left(2\alpha\right)^2} - \frac{12}{4!}\frac{1}{\left(2\alpha^{\Sigma_g}\right)^2\left(2\alpha\right)^2} f_{\Sigma_g\Sigma_g+-} \tag{C.10}$$

$$\alpha_3^{sb} = -\frac{1}{2}\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_{\Sigma_u}^2}\right)_0 \frac{\hbar^2\alpha^2}{\left(2\alpha^{\Sigma_u}\right)^2} - \frac{1}{2}\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 \frac{\hbar^2\left(\alpha^{\Sigma_u}\right)^2}{\left(2\alpha\right)^2} - \frac{12}{4!}\frac{1}{\left(2\alpha^{\Sigma_u}\right)^2\left(2\alpha\right)^2} f_{\Sigma_u\Sigma_u+-} \tag{C.11}$$

The derivatives of the elements of the transformed Wilson matrix $\mathcal{G}$ are connected with the original Wilson matrix G in the following form

$$\begin{aligned}
\left(\frac{\partial g+-}{\partial \mathcal{Q}_{\Sigma_g}}\right)_0 &= \sqrt{2}\left(\frac{\partial g_{q_a q_a}}{\partial q_1}\right)_0 \\
\left(\frac{\partial g+\Sigma_g}{\partial \mathcal{Q}_+}\right)_0 &= -\sqrt{2}\left(\frac{\partial g_{q_1 q_a}}{\partial q_a}\right)_0 \\
\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 &= \left(\frac{\partial^2 g_{q_a q_a}}{\partial q_a^2}\right)_0 \\
\left(\frac{\partial^2 g_{\Sigma_g\Sigma_g}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 &= -\left(\frac{\partial^2 g_{\Sigma_u\Sigma_u}}{\partial \mathcal{Q}_+\partial \mathcal{Q}_-}\right)_0 = -\left(\frac{\partial^2 g_{q_1 q_2}}{\partial q_a^2}\right)_0 \\
\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_{\Sigma_g}^2}\right)_0 &= -\left(\frac{\partial^2 g_{q_a q_a}}{\partial q_1^2}\right)_0 - \left(\frac{\partial^2 g_{q_a q_a}}{\partial q_1\partial q_2}\right)_0 \\
\left(\frac{\partial^2 g_{+-}}{\partial \mathcal{Q}_{\Sigma_u}^2}\right)_0 &= -\left(\frac{\partial^2 g_{q_a q_a}}{\partial q_1^2}\right)_0 + \left(\frac{\partial^2 g_{q_a q_a}}{\partial q_1\partial q_2}\right)_0 \quad .
\end{aligned} \tag{C.12}$$

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

$$
\begin{aligned}
f_{\Sigma_g\Sigma_g} &= f_{q_1q_1} + f_{q_1q_2} \ , \\
f_{\Sigma_u\Sigma_u} &= f_{q_1q_1} - f_{q_1q_2} \ , \\
f_{+-} &= -f_{q_aq_a} \ , \\
f_{\Sigma_g+-} &= -\sqrt{2} f_{q_1q_aq_a} \ , \\
f_{++--} &= \frac{2}{3} f_{q_aq_aq_aq_a} \ , \\
f_{\Sigma_g\Sigma_g\Sigma_g\Sigma_g} &= \frac{1}{2} f_{q_1q_1q_1q_1} + 2 f_{q_1q_1q_1q_2} + \frac{3}{2} f_{q_1q_1q_2q_2} \ , \\
f_{\Sigma_u\Sigma_u\Sigma_u\Sigma_u} &= \frac{1}{2} f_{q_1q_1q_1q_1} - 2 f_{q_1q_1q_1q_2} + \frac{3}{2} f_{q_1q_1q_2q_2} \ , \\
f_{\Sigma_g\Sigma_g\Sigma_u\Sigma_u} &= \frac{1}{2} f_{q_1q_1q_1q_1} - \frac{1}{2} f_{q_1q_1q_2q_2} \ , \\
f_{\Sigma_g\Sigma_g+-} &= -f_{q_1q_1q_aq_a} - f_{q_1q_2q_aq_a} \ , \\
f_{\Sigma_u\Sigma_u+-} &= -f_{q_1q_1q_aq_a} + f_{q_1q_2q_aq_a} \ .
\end{aligned}
\tag{C.13}
$$

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Table C.1

Energies (in cm^{-1}) of $^{12}CO_2$ provided by the fit using the Hamiltonian (61). The rms deviation obtained is 0.53 cm^{-1}.

State[a]	Polyad	State[b] (normal)	Contribution (normal)	State[c] (local)	Contribution (local)	Energies Exp.[d]	Theor.	Δ E
Symmetry	Σ_g^+							
1	2	1 0 0	0.510	0 0 1 1	0.490	1285.41[e]	1286.21	-0.80
2	2	0 2 0	0.510	0 0 1 1	0.510	1388.18[e]	1387.73	0.46
1	4	1 2 0	0.515	0 0 2 2	0.290	2548.37	2549.37	-1.01
2	4	2 0 0	0.660	0 0 2 2	0.335	2671.14	2671.31	0.41
3	4	1 2 0	0.481	0 0 2 2	0.375	2797.14	2796.21	0.93
4	4	0 0 2	1.00	1 1 0 0	0.503	4673.33[e]	4673.2	0.12
1	6	1 4 0	0.434	1 0 2 2	0.434	3792.70	3793.11	-0.41
2	6	3 0 0	0.515	0 0 3 3	0.247	3942.49	3942.43	0.06
3	6	3 0 0	0.387	0 0 3 3	0.310	4064.27	4064.26	0.02
4	6	1 4 0	0.458	0 0 3 3	0.280	4225.10	4224.12	0.97
5	6	0 2 2	0.547	1 1 1 1	0.275	5915.21	5915.33	-0.11
6	6	1 0 2	0.547	1 1 1 1	0.228	6016.69	6016.63	0.06
2	8	3 2 0	0.336	0 0 4 4	0.184	5197.25	5196.22	1.03
4	8	3 2 0	0.372	0 0 4 4	0.303	5475.57	5476.08	-0.52
6	8	1 2 2	0.509	3 0 1 1	0.379	7133.82	7133.44	0.38
7	8	2 0 2	0.661	4 0 0 0	0.495	7259.74	7259.71	0.03
8	8	1 2 2	0.491	3 0 1 1	0.366	7377.68	7378.12	-0.44
Symmetry	Σ_u^+							
1	2	0 0 1	1.000	1 0 0 0	1.000	2349.14[e]	2349.08	0.07
1	4	0 2 1	0.518	1 0 1 1	0.518	3612.84[e]	3613.29	-0.45
2	4	1 0 1	0.518	2 0 0 0	0.518	3714.78[e]	3714.53	0.25
1	6	1 2 1	0.513	2 0 1 1	0.513	4853.62[e]	4853.92	-0.30
2	6	2 0 1	0.662	3 0 0 0	0.500	4977.83[e]	4977.91	-0.08
3	6	1 2 1	0.487	2 0 1 1	0.487	5099.66[e]	5099.44	0.22
4	6	0 0 3	1.00	2 1 0 0	0.754	6972.58[e]	6972.49	0.09
1	8	1 4 1	0.444	2 0 2 2	0.444	6075.98[e]	6075.27	0.71
2	8	3 0 1	0.486	1 0 3 3	0.262	6227.92[e]	6227.46	0.46
3	8	3 0 1	0.418	1 0 3 3	0.299	6347.85[e]	6348.19	-0.34
4	8	1 4 1	0.455	2 0 2 2	0.455	6503.08[e]	6503.53	-0.45
5	8	0 2 3	0.575	2 1 1 1	0.434	8192.55[e]	8192.43	0.12
6	8	1 0 3	0.575	2 1 1 1	0.321	8293.95[e]	8294.13	-0.18

[a] The state position from lower to higher energy inside the polyad for a given symmetry.
[b] The third and fourth columns, with headings State and Contribution, indicate the main component of the eigenfunction in the normal basis (ν_1 ν_2 ν_3) and the square value of this largest contribution respectively.
[c] The fifth and sixth columns, with headings State and Contribution, indicate the main component of the eigenfunction in the local basis (v_1 v_2 n_+ n_-) and the square value of this largest contribution respectively.
[d] Experimental vibrational energies are taken from Ref. [46], otherwise is indicated.

[e] Experimental energies were taken from Ref. [47].

Table 1. Continuation.

State[a]	Polyad	State[b] (normal)	Contribution (normal)	State[c] (local)	Contribution (local)	Energies Exp.[d]	Theor.	Δ E
Symmetry Π_g								
1	3	0 1 1	1.000	1 0 1 0	1.00	3004.01[e]	3004.02	-0.01
1	5	1 1 1	0.508	2 0 1 0	0.508	4247.71	4248.18	-0.48
2	5	0 3 1	0.508	1 0 2 1	0.508	4390.63	4390.33	0.30
1	7	1 3 1	0.510	2 0 2 1	0.510	5475.07[e]	5475.1	-0.02
2	7	2 1 1	0.594	3 0 1 0	0.448	5632.76[e]	5632.91	-0.15
3	7	1 3 1	0.487	2 0 2 1	0.487	5790.58[e]	5790.53	0.05
4	7	0 1 3	1.00	2 1 1 0	0.755	7602.51[e]	7602.52	-0.00
1	9	1 5 1	0.407	2 0 3 2	0.407	6688.17[e]	6686.71	1.47
2	9	3 1 1	0.470	1 0 4 3	0.283	6863.56[e]	6863.09	0.47
3	9	3 1 1	0.385	1 0 4 3	0.338	7023.67[e]	7024.43	-0.75
4	9	1 5 1	0.442	2 0 3 2	0.442	7203.83[e]	7204.89	-1.06
5	9	0 3 3	0.533	2 1 2 1	0.402	8803.27	8802.99	0.27
6	9	1 1 3	0.533	2 1 2 1	0.353	8944.15	8944.54	-0.39
Symmetry Π_u								
1	1	0 1 0	1.000	0 0 1 0	1.000	667.38[e]	667.453	-0.07
1	3	1 1 0	0.529	0 0 2 1	0.471	1932.47	1933.4	-0.93
2	3	0 3 0	0.529	0 0 2 1	0.529	2076.86[e]	2076.21	0.65
1	5	1 3 0	0.509	1 0 2 1	0.509	3181.46	3182.37	-0.90
2	5	2 1 0	0.592	0 0 3 2	0.400	3339.36	3339.53	-0.17
3	5	1 3 0	0.483	0 0 3 2	0.353	3500.67	3499.66	1.02
4	5	0 1 2	1.00	1 1 1 0	0.503	5315.71[e]	5315.67	0.05
1	7	1 5 0	0.395	1 0 3 2	0.395	4416.15	4416.04	0.11
2	7	3 1 0	0.486	0 0 4 3	0.271	4591.12	4591.05	0.07
3	7	3 1 0	0.364	0 0 4 3	0.345	4753.45	4753.62	-0.17
4	7	1 5 0	0.446	0 0 4 3	0.254	4938.38	4937.64	0.74
5	7	0 3 2	0.512	1 1 2 1	0.258	6537.96	6538.01	-0.05
6	7	1 1 2	0.512	1 1 2 1	0.245	6679.71	6679.74	-0.03
4	9	3 3 0	0.360	0 0 5 4	0.307	6179.01	6180.15	-1.14
5	9	1 7 0	0.397	1 0 4 3	0.397	6388.08	6388.55	-0.46
6	9	1 3 2	0.509	3 0 2 1	0.380	7743.7	7742.87	0.83
7	9	2 1 2	0.595	4 0 1 0	0.446	7901.48	7901.53	-0.05
8	9	1 3 2	0.490	3 0 2 1	0.365	8056.02	8056.85	-0.82

Table 1. Continuation.

State^{a}	Polyad	State^{b} (normal)	Contribution (normal)	State^{c} (local)	Contribution (local)	Energies Exp.^{d}	Theor.	Δ E
Symmetry Δ_g								
1	2	0 2 0	1.000	0 0 2 0	1.000	1335.13^{e}	1335.25	-0.12
1	4	1 2 0	0.541	0 0 3 1	0.459	2585.02	2585.97	-0.95
2	4	0 4 0	0.541	0 0 3 1	0.541	2760.72	2760.	0.73
1	6	1 4 0	0.505	1 0 3 1	0.505	3821.98	3822.72	-0.73
2	6	2 2 0	0.561	0 0 4 2	0.427	4007.91	4008.13	-0.21
3	6	1 4 0	0.483	0 0 4 2	0.348	4197.36	4196.4	0.96
4	6	0 2 2	1.00	1 1 2 0	0.503	5958.51	5958.48	0.04
2	8	3 2 0	0.473	0 0 5 3	0.279	5245.47	5245.43	0.04
5	8	1 2 2	0.507	1 1 3 1	0.248	7166.05	7165.92	0.12
6	8	0 4 2	0.507	1 1 3 1	0.255	7338.15	7338.3	-0.15
Symmetry Δ_u								
1	4	0 2 1	1.000	1 0 2 0	1.000	3659.27^{e}	3659.3	-0.03
1	6	1 2 1	0.524	2 0 2 0	0.524	4887.99	4888.39	-0.41
2	6	0 4 1	0.524	1 0 3 1	0.524	5061.78	5061.5	0.28
1	8	1 4 1	0.507	2 0 3 1	0.507	6103.68^{e}	6103.36	0.33
2	8	2 2 1	0.564	1 0 4 2	0.429	6288.49^{e}	6288.72	-0.23
3	8	1 4 1	0.487	2 0 3 1	0.487	6474.53^{e}	6474.76	-0.23
4	8	0 2 3	1.00	2 1 2 0	0.755	8232.89	8232.89	-0.00
Symmetry Φ_g								
1	5	0 3 1	1.000	1 0 3 0	1.000	4314.91	4314.93	-0.01
1	7	1 3 1	0.536	2 0 3 0	0.536	5531.30	5531.57	-0.26
2	7	0 5 1	0.536	1 0 4 1	0.536	5730.61	5730.39	0.22
1	9	1 5 1	0.504	2 0 4 1	0.504	6736.79	6736.04	0.75
2	9	2 3 1	0.546	1 0 5 2	0.444	6944.87	6945.02	-0.16
3	9	1 5 1	0.486	2 0 4 1	0.486	7154.75	7155.1	-0.35
4	9	0 3 3	1.00	2 1 3 0	0.755	8863.68	8863.61	0.07

Table 1. Continuation.

State[a]	Polyad	State[b] (normal)	Contribution (normal)	State[c] (local)	Contribution (local)	Energies Exp.[d]	Theor.	Δ E
Symmetry Φ_u								
1	3	0 3 0	1.000	0 0 3 0	1.000	2003.25	2003.39	-0.15
1	5	1 3 0	0.551	0 0 4 1	0.449	3240.62	3241.53	-0.90
2	5	0 5 0	0.551	0 0 4 1	0.551	3442.22	3441.49	0.73
3	7	1 5 0	0.482	0 0 5 2	0.349	4890.10	4889.3	0.79
4	7	0 3 2	1.00	1 1 3 0	0.503	6601.71	6601.63	0.09
Symmetry Γ_g								
1	4	0 4 0	1.000	0 0 4 0	1.000	2671.72	2671.88	-0.73
1	6	1 4 0	0.560	0 0 5 1	0.440	3898.33	3899.14	-0.82
2	6	0 6 0	0.560	0 0 5 1	0.560	4122.27	4121.61	0.66
Symmetry Γ_u								
1	6	0 4 1	1.000	1 0 4 0	1.000	4970.93	4970.9	0.03
1	8	1 4 1	0.546	2 0 4 0	0.546	6176.65	6176.79	-0.14
2	8	0 6 1	0.546	1 0 5 1	0.546	6398.07	6397.93	0.14
Symmetry Hg								
1	7	0 5 1	1.000	1 0 5 0	1.000	5627.25	5627.21	0.04
2	9	0 7 1	0.555	1 0 6 1	0.555	7064.52	7064.59	-0.07
Symmetry Hu								
1	5	0 5 0	1.000	0 0 5 0	1.000	3340.72	3340.71	0.01
Symmetry Ig								
1	6	0 6 0	1.000	0 0 6 0	1.000	4010.07	4009.88	0.19
Symmetry Iu								
1	8	0 6 1	1.000	1 0 6 0	1.000	6283.98	6283.87	0.10

Table C.2

Parameters of the Hamiltonian (61) in cm^{-1} obtained in the fit to 101 vibrational energies for $^{12}CO_2$. The statistical error analysis has been included in the last two columns, where the Epsilon and Delta errors are shown.

Parameter	Fit	Errors	
		Epsilon	Delta
$\tilde{\omega}_s$	1684.4	0.3030	0.0304
λ_s	-508.16	0.2351	0.0459
α_1^s	1.4526	0.0827	0.0132
α_2^s	-0.6122	0.0136	0.0061
α_3^s	3.872	0.0825	0.0259
$\tilde{\omega}_b$	667.28	0.1335	0.0170
α_1^b	0.8584	0.0691	0.0034
α_2^b	-0.6870	0.0704	0.0067
α_1^{sb}	36.005	0.0396	0.0175
α_2^{sb}	-7.6167	0.1487	0.0127
α_3^{sb}	4.9365	0.1544	0.0197

Table C.3

Force constants for carbon dioxide computed using the expressions given in App. C.

Force constant	$^{12}CO_2$ (a)	$^{13}CO_2$ (b)	$^{12}CO_2$ (c)	$^{12}CO_2$ (d)
$f_{q_1q_1}(aJ\AA^{-2})$	15.98	16.00	15.98	16.01
$f_{q_1q_2}(aJ\AA^{-2})$	1.5310	1.5465	1.5589	1.2526
$f_{q_1q_1q_1q_1}(aJ\AA^{-4})$	189.61	170.51	-581.51	681.87
$f_{q_1q_1q_1q_2}(aJ\AA^{-4})$	152.73	141.18	32.935	12.27
$f_{q_1q_1q_2q_2}(aJ\AA^{-4})$	59.367	53.658	26.232	36.702
$f_{q_aq_a}(aJ\AA^{-2})$	0.5721	0.57153	0.57227	0.5818
$f_{q_aq_aq_aq_a}(aJ\AA^{-4})$	3.3714	3.1593	2.9722	0.75
	-7.1862	-7.6319	-8.1737	-
$f_{q_1q_aq_a}(aJ\AA^{-3})$	-5.4013	-5.2114	-5.3550	-0.8874
$f_{q_1q_1q_aq_a}(aJ\AA^{-4})$	-19.549	-16.884	-16.079	–
$f_{q_1q_2q_aq_a}(aJ\AA^{-4})$	-32.880	-30.814	-31.481	–

(a) Force constants derived from the spectroscopic parameters given in Tab. C.2.
(b) Results for $^{13}CO_2$ from a fit to the available vibrational levels using Hamiltonian (61).
(c) Force constants computed from the spectroscopic parameters obtained fitting the harmonic limit of the model Hamiltonian (61) to the vibrational spectrum of $^{12}\mathrm{CO}_2$.

(d) Force constants obtained by Chedin **[48,49]**.

Table C.4

Comparison of the fitted and predicted spectroscopic parameters of the carbon dioxide isotopomer $^{13}CO_2$.

Parameter	*Fit*	*Prediction*
$\tilde{\omega}_s$	1832.3	1830.6
λ_s	-474.22	-475.12
α_1^s	1.2700	1.4656
α_2^s	-0.5283	-0.5406
α_3^s	3.5215	3.7584
$\tilde{\omega}_b$	648.06	648.37
α_1^b	0.5900	0.8276
α_2^b	-0.3915	-0.6322
α_1^{sb}	34.100	37.100
α_2^{sb}	-6.6485	-7.6930
α_3^{sb}	4.9729	4.7022

Note. The first column shows the spectroscopic parameters of the Hamiltonian (61) obtained from a fit to the experimental spectrum, involving 63 states up to polyad 10, of the carbon dioxide **isotopomer** $^{13}CO_2$ (column b, Table C.3). The predicted parameters, calculated using the force constants of $^{12}CO_2$ (column (a) in Tab. C.3) are included in the second column.

Table C.5

Predicted energies (in cm^{-1}) of $^{12}CO_2$ provided by the fit up to polyad 9 using the Hamiltonian (61). See footnotes of Table C.1

State[a]	Polyad	State[b] (normal)	Contribution (normal)	State[c] (local)	Contribution (local)	Energies Exp.[d]	Pred.	ΔE
Symmetry Σ_u^+								
1	10	2 4 1	0.385	2 0 3 3	0.333	7283.98	7281.18	2.80
2	10	3 2 1	0.353	1 0 4 4	0.199	7460.52[e]	7458.87	1.65
3	10	4 0 1	0.568	4 1 0 0	0.316	7593.69[e]	7593.34	0.35
4	10	3 2 1	0.376	1 0 4 4	0.290	7734.45[e]	7736.06	-1.61
5	10	1 6 1	0.408	2 0 3 3	0.408	7920.84	7922.97	-2.13
6	10	1 2 3	0.503	2 1 2 2	0.270	9388.99	9388.05	0.94
7	10	2 0 3	0.655	5 0 0 0	0.404	9516.97	9516.81	0.16
8	10	1 2 3	0.493	3 1 1 1	0.251	9631.35	9632.40	1.05
Symmetry Π_g								
2	11	3 3 1	0.297	2 0 4 3	0.217	8080.89	8079.84	1.05
3	11	4 1 1	0.486	4 1 1 0	0.270	8250.63	8250.91	-0.28
4	11	3 3 1	0.360	1 0 5 4	0.297	8425.00	8427.57	-2.57
6	11	1 3 3	0.507	3 1 2 1	0.258	9987.48	9985.81	1.67
7	11	2 1 3	0.594	5 0 1 0	0.367	10145.51	10145.50	0.01
8	11	1 3 3	0.492	3 1 2 1	0.251	10297.05	10298.70	-1.65
Symmetry Π_u								
5	11	3 5 0	0.289	0 0 6 5	0.273	7616.62	7619.89	-3.27
Symmetry Δ_u								
1	10	1 6 1	0.383	2 0 4 2	0.383	7307.65	7305.42	2.23
2	10	3 2 1	0.461	1 0 5 3	0.290	7505.22	7504.78	0.44
3	10	3 2 1	0.364	1 0 5 3	0.360	7694.42	7695.63	-1.21
4	10	1 6 1	0.436	2 0 4 2	0.436	7897.57	7899.36	-1.79
5	10	0 4 3	0.510	2 1 3 1	0.384	9419.19	9418.69	0.50
6	10	1 2 3	0.510	2 1 3 1	0.370	9589.93	9590.53	-0.60