Algebraic vibrational description of the symmetric isotopologues of CO_2: $^{13}C^{16}O_2$, $^{12}C^{18}O_2$ and $^{12}C^{17}O_2$.

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Abstract

We present a polyad-conserving local model applied to the vibrational excitations of symmetric isotopologues of carbon dioxide. The description is carried out in the framework of local internal coordinates where the stretching degrees of freedom are modeled with Morse oscillators while for the bending modes the algebraic $U(3)$ model is introduced. Three isotopologues are considered, namely $^{13}C^{16}O_2$, $^{12}C^{18}O_2$ and $^{12}C^{17}O_2$ in their electronic ground states. In all cases the most extensive experimental dataset of vibrational energies were taken into account. For the three isotopologues a Hamiltonian with interactions up to sixth order involving 16 parameters was considered. The description of the isotopologue $^{13}C^{16}O_2$ involved 110 experimental energies with a rms=0.06 cm^{-1}. On the other hand, for the isotopologue $^{12}C^{18}O_2$, only 42 experimental energies were available and a rms=0.05 cm^{-1} was obtained with 15 parameters. For the isotopologue $^{12}C^{17}O_2$, considering 28 experimental energy terms a rms=0.17 cm^{-1} was obtained. In addition, as a consequence of the normal mode behavior of these molecules, alternative polyad schemes were explored.

Keywords: Algebraic approach, vibrational excitations, isotopologues, CO_2, polyad-conserving scheme.

1. Highlights

- A polyad preserving Hamiltonian involving interactions up to sixth order is used to describe the vibrational degrees of freedom of the symmetric carbon dioxide isotopologues $^{13}C^{16}O_2$, $^{12}C^{17}O_2$ and $^{12}C^{18}O_2$.
- Different polyad schemes are explored to consider the more relevant interactions.
- The connection between the algebraic description and the configuration space is outlined.
- Predictions of the energy levels of $^{13}C^{16}O_2$, $^{12}C^{17}O_2$ and $^{12}C^{18}O_2$ have been provided up to ∼24000 cm^{-1}.

2. Introduction

Because of its importance in combustion reactions, for the evolution of planetary atmospheres and its potential greenhouse effect, carbon dioxide is the subject of a great variety of studies [1, 2, 3, 4, 5]. In particular Raman, infrared and NMR spectroscopic techniques have shown to be an invaluable tool to identify and characterize the molecule. Besides the studies on the concentration of carbon dioxide in the atmosphere, the detailed investigation of its carbon and oxygen stable isotopic composition have revealed additional information on e.g. the evolution of the carbon cycle and life as well as climate on earth [6, 7, 8], and allowed insights into many chemical reactions in the environment [9]. Due to limitations of the long predominating analytical approach of gas phase mass spectrometry [10], the investigation of the stable carbon and oxygen isotopic compositions only allowed the determination of a bulk mixed signal of the abundances of ^{12}C or ^{13}C and ^{16}O, ^{17}O or ^{18}O in a gas sample, not the precise determination of the abundances of all the isotopologues (the 12 different molecules of CO_2 differing in their isotopic composition, only $^{16}O^{12}C^{16}O$ and $^{18}O^{13}C^{18}O$ have no interfering masses of other isotopologues). But recent research has highlighted the potential of analyses of individual isotopologues, e.g. for the determination of mass-independent isotope effects, to better constrain different sources of CO_2 (microbial or from fossil fuel burning, [11]) or assessing the temperature of gas reactions in the subsurface [12], by the degree of "clumping" – the co-occurrence of the heavier isotopes of carbon and oxygen in a CO_2 molecule. But the analytical limitations in mass spectrometry are a hindrance in progress [13]. New developments in high resolution mass spectrometry [14] now allow the differentiation of a few additional isotopologues as $^{16}O^{12}C^{17}O$ and $^{16}O^{13}C^{16}O$. But the ability of spectroscopic analyses to resolve all the isotopologues has paved the way from mass spectrometry towards using IR and Raman spectroscopy as analytical tools in this field of research [15, 16, 17]. This highlights the importance of detailed studies of the ro-vibrational structure of CO_2 [18, 19, 20, 21, 22, 23, 24, 25, 26, 27]. Although much work has been done for the principal isotopologue $^{12}C^{16}O_2$, [28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39], the need of similar studies is evident for the different other isotopologues given the fact that they are usually found in mixtures of different proportions. Since the first detection of a strong resonance in the vibrational spectrum of the carbon dioxide carried by *E.Fermi* [40], a third order resonance identified where the energy transfer between longitudinal and transverse vibration modes become evident through the large energy splitting in spectrum [41, 42]. Higher order interactions have been added progressively to the Hamiltonian according to the vibrational studies involved higher excited states (see, e.g., Refs. [32, 43]).

In a series of recent works, a description of vibrational excitations of $^{12}C^{16}O_2$ was carried out with rms==0.14 cm^{-1} using an extensive data set of 178 experimental energies up to 26550 cm^{-1} including states with a maximum vibrational angular momentum value ℓ=6 [32]. Later on, the wave functions provided by this description were tested by the simulation of the Raman spectrum in the framework of the three types polyads found in the literature including the Fermi interaction [33]. Among others, McCoy & Sibert III [44] used the polyad $P_{214} = 2\nu_1 + \nu_2 + 4\nu_3$. An alternative polyad $P_{213} = 2\nu_1 + \nu_2 + 3\nu_3$ was used in the framework of variational procedures [21] and using an effective Hamiltonian [27]. The alternative polyad $P_{212} = 2\nu_1 + \nu_2 + 2\nu_3$ was also previously implemented with good results [28, 29, 30, 31]. The assessment of these three polyads was carried through the simulation of the Raman spectrum leading to the conclusion that polyad P_{212} was the best option in the framework of a polyad-preserving model. The appearance of these three alternatives for the polyad in the carbon dioxide is a consequence of the strong normal behavior of the molecule, which manifests as a large splitting of the stretching local modes due to the linear geometry but also because of the large masses of the ending oxygen atoms. As a consequence, different energy patterns for the stretching quantum numbers naturally emerge giving rise to polyads P_{214} and P_{213}. In contrast to the polyad P_{212}, although not taking into account this large splitting, this enlarges the set of interacting states for higher energies, which makes it the best alternative to describe the Raman spectrum [33]. The model used to carry out this theoretical analysis was an algebraic approach based on the $U_1(2) \times U(3) \times U_2(2)$ dynamical group keeping the connection with configuration space.

In the $U_1(2) \times U(3) \times U_2(2)$ model the stretching degrees of freedom are described with Morse oscillators whose bound states are associated with the $U(2)$ dynamical group [45, 46, 47, 48, 49, 50]. The bending degrees of freedom are treated with the 2D-vibron model which consists of the adding a scalar boson to the 2D harmonic oscillator space keeping constant the total number of bosons, which in turn establishes the Hilbert space to deal with the bending modes [49, 51]. In this model the chain $U(3) \supset SU(2)$ provides the dynamical symmetry for the linear molecules, while the chain $U(3) \supset SO(3)$ is identified with a displaced oscillator, a fact that allows the model to deal with nonrigid molecules[52, 53, 54, 55, 56, 57, 58], with interpretation linked to the coherent states formalism [59, 60, 61, 62]. Although our model deals with the $U_1(2) \times U(3) \times U_2(2)$ dynamical group [50], it is convenient to remark that we keep the connection with coordinates and momenta. Hence we start establishing the Hamiltonian in configuration space and then the stretching coordinates and momenta are expanded up to linear terms as a function of the Morse ladder operators. A similar procedure is followed for the bends, identifying the coordinates and momenta as a linear expansion of the generators of the $U(3)$ group. This approach has demonstrated its validity in describing the vibrational structure for several molecules, e.g. H_2O, SbH_3, CH_4, AsH_3, BF_3, H_2CO, HCN, O_3, SF_6 and CO_2 itself [63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73], as well as in the context of the full ro-vibrational spectrum of triatomic molecules such as H_2Se and H_2S [74, 75].

Given the success in describing the vibrational spectroscopy of the principal isotopologue $^{12}C^{16}O_2$, we decided to start with a systematic study of all isotopologues of carbon dioxide. In this contribution we encompass the isotopologues with inversion center taking into account an updated database for the available experimental vibrational terms. As for the main isotopologue, we assessed the convenience of different polyad schemes.

This paper is organized as follows. In Section 3, the used coordinates are presented as well as a discussion about the possible polyads to be taken into account in the framework of the local-to-normal transition context. Section 4 is devoted to present the Hamiltonian associated with polyad P_{212}. In Section 5, the vibrational analyses obtained for the three isotopologues $^{13}C^{16}O_2$, $^{12}C^{18}O_2$ $^{12}C^{17}O_2$ are presented. In Section 6, the use of polyad P_{214} is explored. Finally, the conclusions are drawn in Section 7.

3. General considerations for the vibrational description

We start by presenting the coordinates to be used in the description of the isotopologues with inversion symmetry. All isotopologues $^{13}C^{16}O_2$, $^{12}C^{18}O_2$ and $^{12}C^{17}O_2$ have linear structure in their electronic ground state. Consequently, we follow the same assignment of internal coordinates previously proposed to describe the vibrational structure for the main isotopologue $^{12}C^{16}O_2$ in Ref. [28]. First we introduce the symmetry adapted curvilinear coordinates S_1 and S_3 associated with the stretching degrees of freedom following the normal mode labeling [41]

$$\begin{aligned} S_1 \equiv S_{\Sigma_g^+} =& \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2), \\ S_3 \equiv S_{\Sigma_u^+} =& \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2), \end{aligned} \tag{1}$$

where the local curvilinear coordinates $\Delta r_i = r_i - r_e$, with $i = 1, 2$, correspond to the displacement of the i-th CO bond with respect to the bond equilibrium length r_e. For the bending degrees of freedom we use the Cartesian coordinates [76]

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

Since the projection of the angular momentum is conserved for linear molecules, it is convenient to introduce the circular coordinates

$$S_+ = -\frac{1}{\sqrt{2}}(S_{2a} + iS_{2b}) \quad , \quad S_- = \frac{1}{\sqrt{2}}(S_{2a} - iS_{2b}) \quad , \tag{3}$$

with the corresponding conjugate momenta $P_\alpha = -i\hbar\partial/\partial S_\alpha$ given by

$$\hat{P}_+ = -\frac{1}{\sqrt{2}}(\hat{P}_{2a} - i\hat{P}_{2b}) \quad , \quad \hat{P}_- = \frac{1}{\sqrt{2}}(\hat{P}_{2a} + i\hat{P}_{2b}) \quad . \tag{4}$$

Once we have established the internal coordinates to work with we proceed to undertake general considerations to set up the Hamiltonian. The prevailing Hamiltonian to describe the vibrational degrees of freedom takes the form [77, 78, 79]

$$\hat{H} \;=\; \frac{1}{2}\tilde{\mathbf{P}}\mathbf{G}(\mathbf{S})\mathbf{P} + V(\mathbf{S}) + V'(S), \tag{5}$$

where $\mathbf{S}$ and $\mathbf{P}$ are column vectors corresponding to the internal coordinates and their conjugate momenta, with normalization

$$\int \psi(\mathbf{S})^* \psi(\mathbf{S}) dS_1 dS_2 \cdots = 1.$$

Here the pseudopotential term $V'(\mathbf{S})$, depending on the Jacobian of the transformation from Cartesian to internal coordinates, is neglected [80]. The $\mathbf{G}(\mathbf{S})$ matrix links internal and Cartesian coordinates and $V(\mathbf{S})$ is the Born-Oppenheimer potential. In principle, given a basis, the matrix elements of the Hamiltonian may be calculated once a potential is provided, through *ab initio* calculations for instance. A potential provided by *ab initio* calculations in the form of a Taylor expansion, however, besides its high computational cost, in general does not provide predictions within the experimental accuracy at the level of ro-vibrational structure demanded by high resolution spectroscopy. Consequently, an approach based on the fitting of a partial subset of *ab initio* energies and the experimental energy levels represents a practical alternative to improve the vibrational description [81, 82, 83]. On the other hand, with respect to the kinetic energy, the direct calculation of its matrix elements leading to the so called variational methods, involves multiple dimensional integrals not easy to deal with. This approach, when applied to the complete set of degrees of freedom, is possible for small molecules. For semirigid molecules with an unique potential minimum, a confident alternative consists in expanding the $\mathbf{G}(\mathbf{S})$ matrix in a Taylor series expansion in the form

$$G_{ij}(\mathbf{S}) = G_{ij}(\mathbf{0}) + \sum_{\gamma} \left(\frac{\partial G_{ij}}{\partial S_\gamma} \right)_0 S_\gamma + \ldots \ . \tag{6}$$

When the expansions of both the $\mathbf{G}(\mathbf{S})$ matrix and the potential $V(\mathbf{S})$ are inserted in the Hamiltonian (5), selected terms are expected to be kept in accordance with both symmetry and polyad considerations. The polyad is a pseudo quantum number that embraces the states that interact through the main resonances, which are defined in the normal scheme by analyzing the overtones and combinations of the spectrum [84]. We remark that a polyad in the local scheme may not be defined strictly, unless a local mode behavior is present. Hence, in order to proceed to establish the polyad-conserving Hamiltonian, it is necessary to work in the framework of a normal mode scheme and later on decide about the convenience to work with a local mode scheme.

The coordinates (1) and (2) are curvilinear coordinates and they take the form of a power expansion in terms of normal coordinates, which in turn are proportional to rectilinear symmetry coordinates [31]. A reasonable approximation for the description of the Hamiltonian consists of simplifying this expansion by considering the first term of the expansion proportional to the rectilinear normal coordinates Q_i. The importance of this simplification is that it allows the polyad to be identified in a straightforward way without losing accuracy in the description, but also because the coordinates Q_i are associated with harmonic oscillator functions. The linear approximation has been proved to be enough in establishing the polyad that allows the Hamiltonian to be set up [28, 29, 30, 31]. To achieve this goal we should start as usual with the fundamental frequencies. In Table 1 the frequencies for the isotopologues $^{13}C^{16}O_2$ (636), $^{12}C^{18}O_2$ (828) and $^{12}C^{17}O_2$ (727) are included as well as the principal isotopologue $^{12}C^{16}O_2$ (626) as a reference. For the three isotopologues, the following resonances consistent with the molecular symmetry can be identified

$$\omega_1 \approx 2\omega_2; \qquad 2\omega_1 \approx 2\omega_3; \qquad 3\omega_1 \approx 2\omega_3; \qquad 4\omega_1 \approx 2\omega_3. \tag{7}$$

As in the principal isotopologue (626), the strongest resonance corresponds to the Fermi interaction $\omega_1 \approx 2\omega_2$, while the other three resonances are of lesser importance due to both their higher order in the interactions and to the less proximity in energy of the vibrational levels. It is interesting to compare the interaction strengths by comparing the residuals between the experimental fundamental energies when the expected resonances (7) are considered for the different isotopologues. In Table 1 these differences are displayed. As noticed, the Fermi interaction is preponderant, which seems to be stronger for (636). In addition, the next more relevant resonance, according to these energy differences, would be that of which four quanta of the symmetric stretching mode is interacting with two quanta of the asymmetric stretching mode. In contrast, the resonance $2\omega_1 \approx 2\omega_3$ is the weakest relative to the others. On the one hand, the resonance $3\omega_1 \approx 2\omega_3$ is stronger for the isotopologue (636) and, on the other hand, $4\omega_1 \approx 2\omega_3$ is expected to be more important for (828). Beyond the relative importance for one or other isotopologue, the existence of these resonances leads to the following three polyads:

$$P_{212} = 2(\nu_1 + \nu_3) + \nu_2, \tag{8a}$$

$$P_{213} = 2\nu_1 + \nu_2 + 3\nu_3, \tag{8b}$$

$$P_{214} = 2\nu_1 + \nu_2 + 4\nu_3. \tag{8c}$$

where ν_i are the normal quantum numbers following the usual labeling scheme[41].

Table 1: Fundamental frequencies (in cm^{-1}) for the isotopologues of carbon dioxide in accordance with the standard notation for the normal modes. The absolute values of the residuals between the experimental values and the expected resonance (7) are given for the different isotopologues.

Frequency	$^{12}C^{16}O_2$ (626)	$^{13}C^{16}O_2$ (636)	$^{12}C^{18}O_2$ (828)	$^{12}C^{17}O_2$ (727)
ω_1 : CO symmetric stretching	1285.4	1265.82	1230.32	1258.24
ω_2 : OCO bending	667.38	648.47	657.33	662.07
ω_3 : CO antisymmetric stretching	2349.14	2283.48	2314.05	2330.59
$\lvert\omega_1 - 2\omega_2\rvert$	49	31	84	65
$\lvert 4\omega_1 - 2\omega_3\rvert$	443	496	293	371
$\lvert 3\omega_1 - 2\omega_3\rvert$	842	770	937	886
$\lvert 2\omega_1 - 2\omega_3\rvert$	2127	2035	2167	2144

In any polyad (8) the strong Fermi resonance is always included, while the other resonances define the interaction between the stretching modes in the three polyads. Polyads (8b) and (8c) are consequence of the strong normal behavior. In fact, the splitting of the levels associated with the stretching local oscillators is so large that, in principle, it is not possible to define a polyad in the local scheme. In the framework of polyads (8b) and (8c), the local scheme necessarily leads to a polyad breaking [85, 86]. Polyad P_{212} (8a) however has equal weights in the stretching modes, a feature belonging to a local mode behavior when a Darling-Dennison interaction is expected. For the principal isotopologue (626) the three polyads were tested with an unexpected result: polyad P_{212} turns out to be the slightly better for both the energy fits and the simulation of the Raman spectrum [32, 33]. This result may imply that the Darling-Dennison interaction is dominant (apart from the Fermi interaction) over the other resonances when, on the contrary, the more relevant polyad structure according to the molecular symmetry and the energy differences between the lower vibrational levels is given by P_{214}. Furthermore, for the lower excited levels, the energy level distribution of polyad P_{214} is better defined than for P_{213} and P_{212}, with a more compact energy structure, keeping an energy gap among back-to-back polyad numbers. However, when the polyad number becomes bigger for higher excited states, an increasing overlap between the energy intervals of a given polyad number happens for the three polyad structures and, therefore, that a given polyad number encompasses a broader energy range could be relevant for the spectral analysis. In fact, a given polyad number of P_{212} involves more states than the same polyad number of P_{213} and P_{214} even at the lowest energies, e.g., at polyad number 24, the number of Σ_g^+ states is 49, 28 and 21 for P_{212}, P_{214} and P_{213}, respectively [32]. So, provided that Fermi interaction is included, the good result obtained for P_{212} could be useful for highlighting that the statistical distribution of the states is rather significant as well as the other resonances.

In the context of the local mode theory developed during the eighties, a set of oscillators presenting weak interactions manifested through a small energy splitting may be treated as a set of interacting Morse oscillators with fundamental frequency ω and anharmonicity ωx plus a quadratic interaction λ among the oscillators [87, 88, 89, 90, 91]. In this case, the force constants may be estimated by considering a polyad-conserving Hamiltonian. However, in molecules where the local behavior is not evident, the force constant may be still estimated but breaking the polyad. It is thus convenient to have a criterion to know the locality degree. For a set of oscillators involving only one type of neighbor interactions the degree of locality (normality) may be evaluated through the parameter $\xi = \mathrm{Log}_{10}(\omega \mathrm{x}/\lambda)$ introduced by *Child and Halonen* [91] which provides insight into the nature of the molecular behavior. Hence the parameter ξ makes evident the contributions to locality of the anharmonicity as well as the energy splitting due to the strength of the coupling interaction. When only first neighbor interactions among the oscillators is present, the parameter ξ in fact manifests the degree of locality but, when more than one neighbor interactions are involved (like in octahedral molecules for instance), an alternative criterion is needed [73]. In this venue a criterion based on the splitting of the fundamentals together with the comparison between the force constants obtained in the framework of both local and normal schemes has been recently proposed [85, 86] and applied to the case of octahedral molecules [73]. Following this proposal we introduce the parameter η that is larger for a more normal behavior and is defined as [85, 86]

$$\eta = \frac{\epsilon_1 + \epsilon_2}{2}; \qquad \epsilon_1 = \left| 1 - \frac{f_{rr}^{(N)}}{f_{rr}^{(L)}} \right|; \qquad \epsilon_2 = \left| 1 - \frac{f_{rr'}^{(N)}}{f_{rr'}^{(L)}} \right|, \tag{9}$$

which involves the ratio between the quadratic force constants calculated in a local polyad-conserving Hamiltonian ($f_{rr'}^{(L)}$) and in a normal scheme ($f_{rr'}^{(N)}$). The force constants $f_{rr}^{(L)}$ and $f_{rr'}^{(L)}$ are estimated from the polyad-conserving Hamiltonian up to quadratic terms expressed in the local scheme considering the subspace of states corresponding to one quantum, while $f_{rr}^{(N)}$ and $f_{rr'}^{(N)}$ are obtained from the frequencies of the normal mode model. The basic idea is that in the pure local limit both normal and local force constants coincide. For two oscillators, the corresponding force constants can be obtained from Table 1 of Ref. [86], but for more than two oscillators equivalent expressions may be obtained [68, 73]. In our case, the locality degree involves the two stretching local oscillators so we use the expressions given in Table 1 of Ref. [86]. In Table 2 the force constants calculated in both schemes as well as the calculated values for parameter η are presented. In accordance with these results, the isotopologue 828 presents the strongest normal behavior, which is explained by the more effective energy transfer between the local modes by the increase of masses of the oxygen atoms. In contrast, the mass increase of carbon in 636 has the opposite effect going to the local behavior direction. Although in this series of isotopologues the obtained values for η can be easily understood by geometry and mass distributions, for isotopologues without center of symmetry the situation may be not so clear, as we shall present in a future work.

Table 2: Degree of locality (normality) estimate by comparing the force constants (in units of $aJ/\mathring{A}^2$) calculated from the different schemes.

Isotopologue	$f_{rr}^{(N)}$	$f_{rr}^{(L)}$	$f_{rr'}^{(N)}$	$f_{rr'}^{(L)}$	η
636	21.37	13.30	0.66	-0.29	1.94
626	21.29	13.34	0.99	-0.19	3.40
727	21.33	13.34	1.18	-0.15	4.68
828	21.40	13.32	1.31	-0.15	5.17

It is convenient to remark that in Table 2 the fundamental frequencies are used. This is a rough approximation which explains, for the main isotopologue, that the estimated force constant $f_{rr}^{(N)} \approx 21$ is large compared with the expected results $f_{rr}^{(N)} \approx 16$. This estimation however is only used to evaluate the locality degree and a more realistic force constants should involve a complete fit. We now proceed to present the analysis of the vibrational excitations.

4. Algebraic Hamiltonian: polyad P_{212}

In this section we set up the polyad-conserving Hamiltonian associated with polyad (8a), which has been proven to be the best option for the principal isotopologue (626) [32, 33]. To this end we shall alternate the local and the normal schemes in order to present the advantages of this polyad. Later on we shall identify the interaction characterizing the polyad in order to set up the allowed interactions for the other polyad schemes.

As already mentioned the feature of this polyad is that it conserves the total number of quanta in both local and normal mode schemes. This means that both polyads $P_N = 2(\nu_1+\nu_3)+\nu_2$ and $P_L = 2(n_1+n_2)+n$ coincide, where in the latter one n_1 and n_2 correspond to the number of quanta for the stretching local oscillators, while n corresponds to the bending mode which in this case coincides with ν_2.

Hence we propose that the Hamiltonian $\hat{H}_{P_{212}}$ should satisfy

$$[\hat{H}_{P_{212}}, \hat{P}_N] = [\hat{H}_{P_{212}}, \hat{P}_L] = 0. \tag{10}$$

For the sake of convenience the Hamiltonian will be expressed in terms of the following contributions:

$$\hat{H}_{P_{212}} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb} + \hat{V}_F, \tag{11}$$

where $\hat{H}_s, \hat{H}_b$ and $\hat{H}_{sb}$ contain the stretching, bending and stretching-bending interactions, respectively. In addition, because of its importance, the Fermi interaction $\hat{V}_F$ has been explicitly included. First we shall consider terms up to quartic order in the normal mode scheme. For the pure stretching contribution $\hat{H}_s$ we have

$$\begin{aligned}\hat{H}_s =& \frac{1}{2}G_{11}^0 P_1^2 + \frac{1}{2}G_{33}^0 P_3^2 + \frac{1}{2}F_{11}Q_1^2 + \frac{1}{2}F_{33}Q_3^2 \\ &+ \frac{1}{4!}F_{1111}Q_1^4 + \frac{1}{4!}F_{3333}Q_3^4 + \frac{6}{4!}F_{1133}Q_1^2Q_3^2,\end{aligned} \tag{12}$$

while for the bends

$$\begin{aligned}\hat{H}_b =& G^0_{+-}P_+P_- + F_{+-}Q_+Q_- + \left(\frac{\partial^2 G_{+-}}{\partial Q_+ \partial Q_-}\right)_0 P_+Q_+Q_-P_- + \\ &+ \frac{1}{4}\left(\frac{\partial^2 G_{++}}{\partial Q_+^2}\right)_0 (P_+Q_+Q_+P_+ + P_-Q_-Q_-P_-) + \frac{6}{4!}F_{++--}Q_+^2Q_-^2 .\end{aligned} \tag{13}$$

The stretching-bending interaction $\hat{H}_{sb}$ is given by

$$\begin{aligned}\hat{H}_{sb} =& \frac{1}{2}\left(\frac{\partial^2 G_{+-}}{\partial Q_1^2}\right)_0 P_+Q_1^2P_- + \frac{1}{2}\left(\frac{\partial^2 G_{+-}}{\partial Q_3^2}\right)_0 P_+Q_3^2P_- \\ &+ \frac{1}{2}\left(\frac{\partial^2 G_{11}}{\partial Q_+ \partial Q_-}\right)_0 P_1Q_+Q_-P_1 + \frac{1}{2}\left(\frac{\partial^2 G_{33}}{\partial Q_+ \partial Q_-}\right)_0 P_3Q_+Q_-P_3 \\ &+ \frac{12}{4!}F_{11+-}Q_1^2Q_+Q_- + \frac{12}{4!}F_{33+-}Q_3^2Q_+Q_- ,\end{aligned} \tag{14}$$

while for the Fermi interaction $\hat{V}_F$:

$$\begin{aligned}\hat{V}_F =& \left(\frac{\partial G_{+-}}{\partial Q_1}\right)_0 P_+Q_1P_- + \left(\frac{\partial G_{1+}}{\partial Q_+}\right)_0 P_1(Q_+P_+ + Q_-P_-) \\ &+ \frac{6}{3!}F_{1+-}Q_1Q_-Q_+ .\end{aligned} \tag{15}$$

The Hamiltonian (11) contains common contributions that simultaneously conserve the three polyads (8), albeit it also includes terms breaking the polyads. Additional higher order interactions characterizing polyads P_{213} and P_{214} are still missing. To identify in natural form the terms that conserve a given polyad, an algebraic representation is convenient [92]. The translation to the algebraic scheme is carried out by introducing the bosonic operators $a^\dagger_\Gamma(a_\Gamma)$ for the stretching modes and the bosonic operators $a^\dagger_\pm(a_\pm)$ for the bends [93]:

$$Q_\Gamma = \sqrt{\frac{\hbar g^0_{\Gamma\Gamma}}{2\omega_\Gamma}}(a^\dagger_\Gamma + a_\Gamma); \qquad P_\Gamma = i\sqrt{\frac{\hbar\omega_\Gamma}{2g^0_{\Gamma\Gamma}}}(a^\dagger_\Gamma - a_\Gamma) \ \ , \ \ \Gamma = 1(\Sigma_g), 3(\Sigma_u) \ , \tag{16a}$$

$$Q_\pm = \sqrt{\frac{\hbar g^0_{aa}}{2\omega}}\ (a^\dagger_\pm - a_\mp); \qquad P_\pm = -i\sqrt{\frac{\hbar\omega}{2g^0_{aa}}}\ (a^\dagger_\mp + a_\pm), \tag{16b}$$

where

$$\omega_\Gamma = \sqrt{f_{\Gamma\Gamma}g^0_{\Gamma\Gamma}}; \qquad \omega = \sqrt{f_{aa}g^0_{aa}}, \tag{17}$$

with [71, 86, 94]

$$g^0_{11} = g^0_{rr} + g^0_{rr'}; \qquad g^0_{33} = g^0_{rr} - g^0_{rr'}; \qquad g^0_{aa} = 2/m_O + 4/m_C \tag{18a}$$

$$F_{11} = f_{rr} + f_{rr'}; \qquad F_{33} = f_{rr} - f_{rr'}, \tag{18b}$$

$$g^0_{rr} = 1/m_O + 1/m_C; \qquad g^0_{rr'} = -1/m_C. \tag{18c}$$

Substitution of (16) into (11) leads to an algebraic Hamiltonian of the form

$$\hat{H}_{P_{212}} = \hat{H}_{P_{212}}(a^\dagger_1, a_1, a^\dagger_3, a_3, a^\dagger_\pm, a_\pm) \ . \tag{19}$$

The advantage of this representation is that we can easily identify and neglect terms that do not conserve a given polyad, keeping only the relevant interactions. The resulting polyad-conserving Hamiltonian may be diagonalized in a harmonic oscillator basis. Instead we proceed to carry out the canonical transformation for the stretches

$$a_1^\dagger = \frac{1}{\sqrt{2}}(c_1^\dagger + c_2^\dagger) \ , \qquad a_3^\dagger = \frac{1}{\sqrt{2}}(c_1^\dagger - c_2^\dagger) \ , \tag{20}$$

where $c_i^\dagger(c_i)$ are boson operators which are isomorphic to the local operators associated with the stretching local coordinates $c_i \to r_i$. With the transformation (20) the Hamiltonian (19) becomes a polyad-conserving Hamiltonian in a local scheme

$$\hat{H}_{P_{212}} = \hat{H}_{P_{212}}(c_i^\dagger, c_i, a_\pm^\dagger, a_\pm) \ ; \qquad i = 1, 2 \ , \tag{21}$$

which may be diagonalized in the harmonic oscillator local basis

$$|n_1 n_2; n^\ell\rangle = N_{\mathbf{n}} (c_1^\dagger)^{n_1} (c_2^\dagger)^{n_2} (a_+^\dagger)^{(n+l)/2} (a_-^\dagger)^{(n-l)/2} |0\rangle \ \ , \tag{22}$$

with normalization constant $N_{\mathbf{n}} = [n_1! n_2! n_+! n_-!]^{-1/2}$, where n_1 and n_2 are the local stretching harmonic quantum numbers and $n_\pm$ are related to the number of bending quanta, n, and the vibrational angular momentum, ℓ, as follows

$$\begin{aligned} \hat{\ell} =& a_+^\dagger a_+ - a_-^\dagger a_- = \hat{n}_+ - \hat{n}_- \ \ , \\ \hat{n} =& a_+^\dagger a_+ + a_-^\dagger a_- = \hat{n}_+ + \hat{n}_- \ \ . \end{aligned} \tag{23}$$

We stress that Hamiltonians (19) and (21) are equivalent. However the transformation (20) is needed in order to improve the description by introducing an anharmonization procedure at the level of the local oscillators. To accomplish this goal we introduce the mapping of the bosonic operators $c_i^\dagger(c_i)$ to the $SU(2)$ operators $b_i^\dagger(b_i)$ associated with the ladder operators of the Morse functions $|\Psi_v^j\rangle$:

$$c_i^\dagger \to b_i^\dagger, \quad c_i \to b_i \ \ , \tag{24}$$

with matrix elements

$$\begin{aligned} b_i^\dagger |\Psi_{v_i}^j\rangle =& \sqrt{(v_i+1)(1-(v_i+1)/\kappa)}\ |\Psi_{v_i+1}^j\rangle \ \ , \\ b_i\ |\Psi_{v_i}^j\rangle =& \sqrt{v_i(1-v_i/\kappa)}\ |\Psi_{v_i-1}^j\rangle \ \ , \\ \hat{v}_i |\Psi_{v_i}^j\rangle =& v |\Psi_{v_i}^j\rangle, \end{aligned} \tag{25}$$

where v_i is the vibrational quantum number for the i-th oscillator with $v_i = 0, 1, 2, \ldots, j-1$. The parameter $\kappa = 2j + 1$ is related to the potential depth and range. The operators $\{b_i^\dagger, b_i, \hat{v}_i\}$ satisfy the commutation relations

$$[b_i, b_i^\dagger] = 1 - \frac{2\hat{v}_i + 1}{\kappa}; \qquad [\hat{v}_i, b_i^\dagger] = b_i^\dagger; \qquad [\hat{v}_i, b_i] = -b_i, \tag{26}$$

which can be identified with the usual $SU(2)$ commutation relations for the angular momentum $\hat{J}_\mu$ through the identifications $\{b_i^\dagger = \hat{J}_-/\sqrt{\kappa}, b_i = \hat{J}_+/\sqrt{\kappa}, \hat{v}_i = j - \hat{J}_0\}$. In the algebraic representation the Morse Hamiltonian takes the form

$$\hat{H}_i^M = \hbar\omega_s \bigg(b_i^\dagger b_i + b_i b_i^\dagger + \frac{1}{2\kappa} \bigg), \tag{27}$$

with eigenvalues [95, 96]

$$E_M(v_i) = \hbar\omega_s\left[(v_i + 1/2) - \frac{1}{\kappa}(v_i + 1/2)^2\right], \tag{28}$$

with

$$\omega_s = \sqrt{\frac{2D\beta^2}{\mu}}; \qquad \kappa = \sqrt{\frac{8D\mu}{\hbar^2\beta^2}}, \tag{29}$$

and where D and β are the Morse potential parameters (depth and range, respectively) to be fitted and $\mu = 1/g^o_{ii}$.

The bending degrees of freedom will be described in terms of the $U(3)$ vibron model. In this context the basis is given by

$$|[N]; n^\ell\rangle \ , \tag{30}$$

where N is the total number of bosons (vibrons) which determines the dimension of the available Hilbert space for the bending degree of freedom, n stands for the number of bending bosons while ℓ corresponds to the z-component of the angular momentum or the vibrational angular momentum. In practice this model is equivalent to introduce in the interactions the following mapping for the boson harmonic oscillators $a^\dagger_\pm(a_\pm)$:

$$a^\dagger_\pm \to b^\dagger_\pm, \qquad a_\pm \to b_\pm \ \ , \tag{31}$$

with matrix elements

$$\begin{aligned} b^\dagger_\pm|[N]; n^\ell\rangle =& \sqrt{\left(\frac{n \pm \ell}{2} + 1\right)\left(1 - \frac{n}{N}\right)}|[N]; (n+1)^{\ell\pm1}\rangle \ \ , \\ b_\pm|[N]; n^\ell\rangle =& \sqrt{\left(\frac{n \pm \ell}{2}\right)\left(1 - \frac{n-1}{N}\right)}\ |[N]; (n-1)^{\ell\mp1}\rangle. \end{aligned} \tag{32}$$

For the bending number operator and the vibrational angular momentum we have

$$\hat{n}|[N]; n^\ell\rangle = n|[N]; n^\ell\rangle \ ; \qquad \hat{\ell}^2|[N]; n^\ell\rangle = \ell^2|[N]; n^\ell\rangle \ . \tag{33}$$

Introducing the mappings (24) and (31) into the Hamiltonian (21), we obtain the algebraic representation of (11):

$$\hat{H}^{[4]}_{alg} = \hat{H}_s + \hat{H}_b + \hat{H}_{sb} + \hat{V}_F, \tag{34}$$

where we have emphasized that by now only interactions up to quartic order have been taken into account. For the stretching interactions we have

$$\begin{aligned} \hat{H}_s =& \omega_s\sum_{i=1}^{2}\hat{H}^M_i + \lambda_s\hat{\Lambda} + \alpha^{(1)}_s(\hat{n}_1^2 + \hat{n}_2^2) + \alpha^{(2)}_s\hat{n}_1\hat{n}_2 \\ & + \alpha^{(3)}_s\{(\hat{n}_1 + \hat{n}_2), \hat{\Lambda}\} + d_L\hat{D}_L, \end{aligned} \tag{35}$$

where we have introduced the notation $\{\hat{A}, \hat{B}\}$ for the symmetrization of the operators

$$\{\hat{A}, \hat{B}\} = \frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A}) \ , \tag{36}$$

and the definitions

$$\begin{aligned}\hat{\Lambda} =& b_1^\dagger b_2 + b_1 b_2^\dagger \ , \\ \hat{n}_i =& b_i^\dagger b_i \qquad (i=1,2) \ .\end{aligned}$$

Here the operator $\hat{D}_L$ is the local Darling-Dennison interaction given by

$$\hat{D}_L = b_1^\dagger b_1^\dagger b_2 b_2 + H.c. \tag{37}$$

The pure bending contribution takes the following form

$$\hat{H}_b = \omega_b \hat{n} + x_{22}\hat{n}^2 + g_{22}\hat{\ell}^2 \quad . \tag{38}$$

For the stretching-bending interaction we have

$$\hat{H}_{sb} = \alpha_{sb}^{(1)}(\hat{n}_1 + \hat{n}_2)\hat{n} + \alpha_{sb}^{(2)}\hat{n}\hat{\Lambda}, \tag{39}$$

and the Fermi interaction is written as:

$$\hat{V}_F = \alpha_F \hat{F} = \alpha_F \ [(b_1^\dagger + b_2^\dagger)\, b_+\, b_- + H.c.], \tag{40}$$

Notice that in this algebraic representation we have used a local scheme with spectroscopic parameters given in terms of the structure and force constants. In a general fit, higher order force constants are very sensitive of the used model. However, the Fermi interaction is so strong that the corresponding force constant turns out to be pretty stable, a fact reflected in the spectroscopic parameters with manifested small variations. Hence we shall pay special attention to the force constant F_{1+-} derived from the spectroscopic parameter α_F through

$$\alpha_F = -\left(\frac{\partial G_{+-}}{\partial Q_1}\right)_0 \frac{\hbar\omega}{2g_{aa}^0}\sqrt{\frac{\hbar g_{11}^0}{2\omega_1}} - \left(\frac{\partial G_{1+}}{\partial Q_+}\right)_0 \hbar\sqrt{\frac{\hbar\omega_1}{2g_{11}^0}} + \frac{6}{3!}\frac{\hbar g_{aa}^0}{2\omega}\sqrt{\frac{\hbar g_{11}^0}{2\omega_1}} F_{1+-}, \tag{41}$$

where ω_1 and ω refer to the frequencies of the symmetric stretching mode and of the bending mode, respectively (17), and

$$\begin{aligned}\left(\frac{\partial G_{+-}}{\partial Q_1}\right)_0 =& -\sqrt{2}\left(\frac{\partial g_{aa}}{\partial q_1}\right)_0 = -\frac{1}{r_e}\left(\frac{2}{m_O} + \frac{4}{m_C}\right), \\ \left(\frac{\partial G_{1+}}{\partial Q_+}\right)_0 =& -\sqrt{2}\left(\frac{\partial g_{1a}}{\partial q_a}\right)_0 = \frac{1}{r_e m_C}.\end{aligned} \tag{42}$$

Terms up to quartic order may not be enough to obtain a description of spectroscopic quality. In fact, we found necessary to include sixth order interactions as with the following form

$$\begin{aligned}\hat{V}_{alg}^{[6]} =& \beta_s^{(1)}\{(\hat{n}_1 + \hat{n}_2), (\hat{D}_L + 2\hat{n}_1\hat{n}_2)\} + \beta_{sb}^{(1)}\{(\hat{n}_1 + \hat{n}_2), \hat{F}\} \\ &+ \beta_{sb}^{(2)}\hat{n}(\hat{D}_L + 2\hat{n}_1\hat{n}_2) + x_{123}\{\hat{\nu}_1, \hat{\nu}_3\}\hat{n},\end{aligned} \tag{43}$$

where the number operators of normal mode quanta $\hat{\nu}_i$ are given by

$$\hat{\nu}_1 = \hat{T}_g^\dagger \hat{T}_g; \quad \hat{\nu}_2 = \hat{n}; \quad \hat{\nu}_3 = \hat{T}_u^\dagger \hat{T}_u, \tag{44}$$

with definitions

$$\begin{aligned}\hat{T}_g^\dagger =&\frac{1}{\sqrt{2}}(b_1^\dagger + b_2^\dagger) \ ,\\ \hat{T}_u^\dagger =&\frac{1}{\sqrt{2}}(b_1^\dagger - b_2^\dagger) \ .\end{aligned} \tag{45}$$

The most general Hamiltonian to be considered in this work is then given by

$$\hat{H}_{P_{212}} = \hat{H}^{[4]}_{alg} + \hat{V}^{[6]}_{alg}, \tag{46}$$

where the spectroscopic parameters involved in the sixth order interaction are also expected to be given in terms of the structure and force constants.

The algebraic representation (46) deserves several comments. As we already mentioned, polyad P_{212} admits both local and normal mode representations. This explains the use of symmetrized local operators to express the interactions with exception of the interaction associated with the spectroscopic parameter x_{123}, which corresponds to the anharmonicity of sixth order involving the three normal modes. This is an advantage we have taken into account to model the best set of interactions to describe the isotopologues. One question which arises is concerned with the interactions in (34) which are proper of this polyad. To elucidate this point we notice that in the harmonic limit the following identities are given

$$4\hat{\nu}_1^2 =(\hat{n}_1+\hat{n}_2)^2 + 2(\hat{n}_1+\hat{n}_2)\hat{\Lambda} + \hat{\Lambda}^2, \tag{47a}$$

$$4\hat{\nu}_3^2 =(\hat{n}_1+\hat{n}_2)^2 - 2(\hat{n}_1+\hat{n}_2)\hat{\Lambda} + \hat{\Lambda}^2, \tag{47b}$$

$$4\hat{\nu}_1\hat{\nu}_3 =(\hat{n}_1+\hat{n}_2)^2 - \hat{\Lambda}^2, \tag{47c}$$

$$4\hat{\Lambda}^2 =(\hat{n}_1+\hat{n}_2) + (\hat{D}_L + 2\hat{n}_1\hat{n}_2), \tag{47d}$$

from which we identify the interactions $(\hat{D}_L + 2\hat{n}_1\hat{n}_2)$ and $(\hat{n}_1^2+\hat{n}_2^2+2\hat{n}_1\hat{n}_2)$ as $\hat{\nu}_i$-dependent operators, consequently, they are allowed to be included for any polyad. However, the operators $(\hat{n}_1^2+\hat{n}_2^2)$, $(\hat{n}_1\hat{n}_2)$ and the Darling-Dennison interaction $\hat{D}_L$, independently considered, characterize the polyad P_{212}.

5. Results and discussion

Here we proceed to describe the vibrational excitations of the isotopologues (636), (828) and (727) in the framework of polyad P_{212}.

Isotopologue (636)

We now start with the vibrational description of the isotopologue (636). We consider the matrix representation of the Hamiltonian (46) in a symmetry adapted basis [97, 98]. This Hamiltonian involves 16 parameters plus the anharmonicities κ_s and N_b. For the stretching modes $\kappa_s = 2j+1$ where j is the number of bound states. For the bends N_b is a parameter which goes to infinity in the harmonic limit. Finite values for N_b means that we take anharmonic effects from the outset. This is the advantage of the $U(3)$ model. The 16 parameters are optimized by a least square fit to the experimental energies for the given values of κ_s and

N_b, which are modified for each minimization procedure until the best description is reached. The fits were carried out with equal weights with the following definition of the root mean square deviation (rms) in terms of the quadratic energy deviation χ^2:

$$\text{rms} = \frac{\chi}{\sqrt{(N_{\text{exp}} - N_{\text{par}})}}; \qquad \chi^2 = \sum_{i=1}^{N_{\text{exp}}} (E^i_{\text{exp}} - E^i_{\text{cal}})^2, \tag{48}$$

where N_{exp} is the total number of fitted experimental energies and N_{par} stands for the number of parameters. During fit procedure, we distinguish two kinds of parameters. The first set are the ones involved in the Hamiltonian as multiplicative coefficients in the interactions. The second set corresponds to the anharmonicities κ_s and N_b which are implicitly involved in the matrix elements. In the fitting procedure κ_s and N_b are fixed each time the iterative least square method is applied to optimize the first set of parameters. Following this procedure, by taking different values for the set $\{\kappa_s, N_b\}$, we search for the minimum of the root mean square deviation in each fit of the first set of parameters, until we obtain the convergence for the complete set of parameters. As initial guess, the same values obtained for the main isotopologue, $\kappa_s = 159$ and $N_b = 150$, were considered. Table 3 provides the resulting parameters. To determine the significance of the fits, a statistical error analysis was carried out. Two types of uncertainty calculations are given in the same Table 3 for all the parameters denoted by x_i: the delta-uncertainty (δx_i) and the epsilon-uncertainty (ϵx_i) [99, 100]. They are defined in such a way that χ^2 does not increase more than a fraction Δ (in all fits the value was taken to be Δ=0.05) of the minimum value χ^2_{min}. The uncertainty δx_i is defined through the condition that χ^2 remains under $(1 + \Delta)$ χ^2 when x_i is chosen in the interval $[x_i - \delta x_i, x_i + \delta x_i]$ around its optimum value x_i, keeping fixed the rest of the parameters. On the other hand, ϵx_i determines the range in which x_i varies when all other parameters are optimized again. All the uncertainties are significantly smaller than the parameters themselves. This result together with the fact that the calculated correlation matrix does not show any correlation indicates that all parameters are well determined.

The optimization of the parameters was carried out taking into account an updated data set of 110 experimental energies up to approximately 25800 cm^{-1}. We have obtained an rms=0.06 cm^{-1}, which was possible by adding the sixth-order contribution (43). The result of the energy fit is displayed in Table 4. Notice that the description is rather homogeneous without large residuals in specific states. Compared with the previous fit of the principal isotopologue (626), where 19 parameters were involved taking 178 experimental energy levels with an rms=0.145 cm^{-1} [33], this description turns out to be better - with less number of parameters (16 parameters), albeit encompassing only 110 energy terms. In order to evaluate the effect of the interactions characterizing polyad P_{212}, we consider a fit omitting the Darling-Dennison interaction ($\hat{D}_L$) and putting together the terms $\hat{n}_1^2 + \hat{n}_2^2$ and $\hat{n}_1\hat{n}_2$ in the form $(\hat{n}_1 + \hat{n}_2)^2$ and adding the interaction $\hat{D}_L + 2\hat{n}_1\hat{n}_2$. So, with this restructuring of the interactions of the Hamiltonian (46), the remaining 15 parameters were made suitable with the three polyad structures before fitting. With this approach, the rms increases to 0.093 cm^{-1}. This result shows the effect of the Darling-Dennison interaction characterizing the polyad scheme (8a), which can be considered moderate, although not expected a priori according to its resonance strength.

Table 3: Optimized parameters (in cm^{-1}) involved in the Hamiltonian (46) for the vibrational description of the isotopologue (636). The parameters associated with the anharmonicity were taken to be $\kappa_s = 168$ and $N_b = 148$. The root mean square deviation obtained was rms=0.06 cm^{-1}.

Parameter	Optimized value	ϵx_i	δx_i
ω_s	1832.5139	0.0476	9.89×10^{-4}
λ_s	-478.9021	0.0170	11.46×10^{-3}
$\alpha_s^{(1)}$	0.8879	0.0446	2.34×10^{-4}
$\alpha_s^{(2)}$	-5.7117	0.1670	6.29×10^{-4}
$\alpha_s^{(3)}$	2.9812	3.99×10^{-3}	1.43×10^{-4}
d_L	-1.2056	0.0399	3.26×10^{-4}
$\beta_s^{(1)}$	-0.0121	9.98×10^{-5}	8.40×10^{-6}
ω_b	648.3692	0.0101	1.19×10^{-3}
x_{22}	0.4159	7.20×10^{-3}	2.19×10^{-4}
g_{22}	-0.2708	6.69×10^{-3}	7.52×10^{-4}
α_F	-34.5079	6.70×10^{-3}	1.04×10^{-3}
$\alpha_{sb}^{(1)}$	-6.3852	0.0169	6.69×10^{-4}
$\alpha_{sb}^{(2)}$	5.4006	0.0148	1.01×10^{-3}
$\beta_{sb}^{(1)}$	0.1312	7.83×10^{-4}	2.23×10^{-4}
$\beta_{sb}^{(2)}$	-0.0136	4.78×10^{-4}	1.54×10^{-4}
x_{123}	-0.1689	7.60×10^{-3}	1.75×10^{-3}

Table 4: Energy fit for the isotopologue $^{13}C^{16}O_2$ using the Hamiltonian (46) and including the available 110 experimental energies. The obtained root mean square deviation was rms=0.06 cm^{-1}. The residuals $\Delta = E_{\text{exp}} - E_{\text{th}}$ are also given. The coefficients correspond to the square of the maximum component in the eigenvectors. The corresponding parameters are given in Table 3.

Polyad^a	Normal state^b	Normal coefficient^b	Local state^c	Local coefficient^c	Experimental energy^d [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
Symmetry Σ_g							
2	0, 2, 0	0.688	0, 0, 1, 1	0.688	1265.828	1265.841	-0.013
2	1, 0, 0	0.688	1, 0, 0, 0	0.688	1370.062	1370.062	0.
4	0, 4, 0	0.474	0, 0, 2, 2	0.474	2507.530	2507.501	0.029
4	2, 0, 0	0.592	0, 0, 2, 2	0.335	2645.068	2645.060	0 .008
4	1, 2, 0	0.478	1, 0, 1, 1	0.478	2750.596	2750.555	0.041
4	0, 0, 2	1.	1, 1, 0, 0	0.505	4543.548	4543.508	0.040
6	1, 4, 0	0.391	1, 0, 2, 2	0.391	4145.767	4145.830	-0.063
6	0, 2, 2	0.728	1, 1, 1, 1	0.368	5766.180	5766.235	-0.055
6	1, 0, 2	0.728	3, 0, 0, 0	0.541	5872.551	5872.550	0.002
8	0, 0, 4	1.	2, 2, 0, 0	0.382	8993.507	8993.442	0.065
12	0, 0, 6	1.	3, 3, 0, 0	0.322	13350.170	13350.121	0.045
16	0, 0, 8	0.999	4, 4, 0, 0	0.284	17613.910	17613.927	-0.014
20	0, 0, 10	0.999	5, 5, 0, 0	0.259	21785.250	21785.304	-0.056
24	0, 0, 12	0.998	6, 6, 0, 0	0.240	25864.800	25864.755	0.043
Symmetry Σ_u							
2	0, 0, 1	1.	1, 0, 0, 0	1.	2283.487	2283.468	0.019
4	0, 2, 1	0.708	1, 0, 1, 1	0.708	3527.737	3527.772	-0.034

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Table 4 – *Continued from previous page*

Polyad[a]	Normal state[b]	Normal coefficient[b]	Local state[c]	Local coefficient[c]	Experimental energy[d] [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
4	1, 0, 1	0.708	2, 0, 0, 0	0.708	3632.910	3632.906	0.004
6	0, 4, 1	0.493	1, 0, 2, 2	0.493	4748.060[g]	4748.048	0.012
6	2, 0, 1	0.571	3, 0, 0, 0	0.432	4887.385[g]	4887.412	-0.027
6	1, 2, 1	0.468	2, 0, 1, 1	0.468	4991.352[g]	4991.358	0.007
6	0, 0, 3	1.	2, 1, 0, 0	0.757	6780.211[m]	6780.153	0.058
8	1, 4, 1	0.469	2, 0, 2, 2	0.469	5951.602[m]	5951.519	0.083
8	2, 2, 1	0.395	1, 0, 3, 3	0.353	6119.620[m]	6119.609	0.011
8	3, 0, 1	0.607	4, 0, 0, 0	0.313	6241.968[g]	6242.023	-0.055
8	2, 2, 1	0.379	2, 0, 2, 2	0.376	6363.621[m]	6363.642	-0.021
8	0, 2, 3	0.748	2, 1, 1, 1	0.566	7981.180[j]	7981.265	-0.085
8	1, 0, 3	0.748	3, 1, 0, 0	0.385	8089.021[j]	8089.030	0.010
10	1, 6, 1	0.428	2, 0, 3, 3	0.428	7142.160[e]	7142.057	0.103
10	3, 2, 1	0.364	1, 0, 4, 4	0.322	7332.205[e]	7332.186	0.019
10	4, 0, 1	0.493	4, 1, 0, 0	0.271	7481.574[e]	7481.515	0.058
10	4, 0, 1	0.381	4, 1, 0, 0	0.210	7600.121[e]	7600.245	-0.124
10	2, 4, 1	0.382	2, 0, 3, 3	0.300	7749.083[e]	7749.228	-0.145
10	0, 4, 3	0.533	2, 1, 2, 2	0.403	9158.876[h]	9158.874	0.002
10	2, 0, 3	0.523	5, 0, 0, 0	0.320	9302.138[h]	9302.192	-0.053
10	1, 2, 3	0.439	5, 0, 0, 0	0.257	9404.128[h]	9404.133	0.005
10	0, 0, 5	1.	3, 2, 0, 0	0.637	11183.480	11183.416	0.061
12	3, 4, 1	0.317	1, 0, 5, 5	0.264	8529.673[k]	8529.732	-0.059
12	5, 0, 1	0.549	5, 1, 0, 0	0.274	8835.571[h]	8835.403	0.168
12	2, 2, 3	0.425	2, 1, 3, 3	0.276	10491.440[g]	10491.379	0.056
12	3, 0, 3	0.619	6, 0, 0, 0	0.387	10616.830[g]	10616.815	0.013
12	2, 2, 3	0.401	5, 0, 1, 1	0.245	10730.980[g]	10730.868	0.114
12	0, 2, 5	0.785	3, 2, 1, 1	0.500	12341.030[l]	12341.183	-0.154
12	1, 0, 5	0.785	5, 1, 0, 0	0.392	12452.600[l]	12452.673	-0.078
14	2, 0, 5	0.466	6, 1, 0, 0	0.208	13623.890	13623.937	-0.047
14	2, 0, 5	0.488	6, 1, 0, 0	0.218	13725.590	13725.522	0.071
14	0, 0, 7	0.999	4, 3, 0, 0	0.563	15493.630	15493.607	0.018
18	0, 0, 9	0.999	5, 4, 0, 0	0.512	19711.100	19711.139	-0.044
22	0, 0, 11	0.999	6, 5, 0, 0	0.474	23836.450	23836.486	-0.035
Symmetry Π_g							
3	0, 1, 1	1.	1, 0, 1, 0	1	2920.238	2920.270	-0.033
5	0, 3, 1	0.646	1, 0, 2, 1	0.646	4147.232	4147.257	-0.025
5	1, 1, 1	0.646	2, 0, 1, 0	0.646	4287.698	4287.681	0.017
7	1, 3, 1	0.464	2, 0, 2, 1	0.464	5357.004	5356.966	0.038
7	2, 1, 1	0.554	3, 0, 1, 0	0.419	5519.924	5519.944	-0.020
7	1, 3, 1	0.481	2, 0, 2, 1	0.481	5662.258	5662.238	0.021
7	0, 1, 3	1.	2, 1, 1, 0	0.757	7393.590	7393.598	-0.008
9	1, 5, 1	0.460	2, 0, 3, 2	0.460	6552.925	6552.833	0.092

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Table 4 – *Continued from previous page*

Polyad^{a}	Normal state^{b}	Normal coefficient^{b}	Local state^{c}	Local coefficient^{c}	Experimental energy^{d} [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
9	0, 7, 1	0.363	1, 0, 4, 3	0.363	6736.696	6736.709	-0.013
9	3, 1, 1	0.525	4, 0, 1, 0	0.271	6892.116	6892.147	-0.031
9	2, 3, 1	0.386	2, 0, 3, 2	0.363	7046.031	7046.070	-0.039
11	0, 1, 5	1.	3, 2, 1, 0	0.637	11773.600	11773.596	0.008
15	0, 1, 7	0.999	4, 3, 1, 0	0.563	16060.640	16060.624	0.019
19	0, 1, 9	0.999	5, 4, 1, 0	0.512	20255.150	20255.101	0.049
Symmetry Π_u							
1	0, 1, 0	1.	0, 0, 1, 0	1.	648.478	648.514	-0.036
3	0, 3, 0	0.630	0, 0, 2, 1	0.630	1896.538	1896.547	-0.009
3	1, 1, 0	0.630	0, 0, 2, 1	0.370	2037.093	2037.070	0.023
5	1, 3, 0	0.472	0, 0, 3, 2	0.408	3127.353	3127.292	0.062
5	2, 1, 0	0.564	0, 0, 3, 2	0.394	3289.701	3289.700	0.01
5	1, 3, 0	0.487	1, 0, 2, 1	0.487	3433.771	3433.678	0.093
5	0, 1, 2	1.	1, 1, 1, 0	0.505	5168.599^{g}	5168.620	-0.021
7	1, 5, 0	0.458	0, 0, 4, 3	0.260	4344.042^{i}	4344.065	-0.023
7	3, 1, 0	0.515	0, 0, 4, 3	0.259	4683.134^{g}	4683.119	0.015
7	0, 3, 2	0.663	1, 1, 2, 1	0.335	6374.504^{m}	6374.547	-0.043
7	1, 1, 2	0.663	3, 0, 1, 0	0.492	6515.120^{m}	6515.091	0.029
9	3, 3, 0	0.366	0, 0, 5, 4	0.296	5750.562^{f}	5750.707	-0.145
9	4, 1, 0	0.475	0, 0, 5, 4	0.269	5922.731^{m}	5922.716	0.016
9	2, 5, 0	0.377	1, 1, 3, 2	0.186	6257.018^{m}	6256.814	0.203
9	1, 3, 2	0.456	1, 1, 3, 2	0.223	7563.301^{e}	7563.242	0.058
9	2, 1, 2	0.542	4, 0, 1, 0	0.406	7726.954^{e}	7726.951	0.003
9	1, 3, 2	0.473	3, 0, 2, 1	0.351	7867.831^{e}	7867.794	0.038
9	0, 1, 4	1.	2, 2, 1, 0	0.382	9595.246	9595.243	0.003
11	5, 1, 0	0.321	0, 0, 6, 5	0.256	7150.401^{e}	7150.452	-0.051
11	5, 1, 0	0.453	0, 0, 6, 5	0.213	7316.631^{e}	7316.549	0.082
11	4, 3, 0	0.332	0, 0, 6, 5	0.149	7486.776^{e}	7486.897	-0.121
11	2, 7, 0	0.352	1, 1, 4, 3	0.174	7682.389^{e}	7682.314	0.075
13	0, 1, 6	1.	3, 3, 1, 0	0.322	13928.720	13928.707	0.015
17	0, 1, 8	0.999	4, 4, 1, 0	0.285	18169.430	18169.402	0.029
Symmetry Δ_g							
2	0, 2, 0	1.	0, 0, 2, 0	1.	1297.263	1297.319	-0.056
4	0, 4, 0	0.600	0, 0, 3, 1	0.600	2531.678	2531.696	-0.017
4	1, 2, 0	0.600	0, 0, 3, 1	0.400	2700.264	2700.216	0.048
6	0, 2, 2	1.	1, 1, 2, 0	0.505	5793.992	5794.023	-0.031
Symmetry Δ_u							
4	0, 2, 1	1.	1, 0, 2, 0	1.	3557.312	3557.363	-0.051
6	0, 4, 1	0.615	1, 0, 3, 1	0.615	4770.975	4770.988	-0.013
6	1, 2, 1	0.615	2, 0, 2, 0	0.615	4938.835	4938.791	0.043
8	1, 4, 1	0.478	2, 0, 3, 1	0.478	5970.942^{m}	5970.900	0.042

Continued on next page

Table 4 – *Continued from previous page*

Polyad[a]	Normal state[b]	Normal coefficient[b]	Local state[c]	Local coefficient[c]	Experimental energy[d] [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
8	2, 2, 1	0.544	1, 0, 4, 2	0.421	6155.418[m]	6155.451	-0.033
8	1, 4, 1	0.487	2, 0, 3, 1	0.487	6326.036[m]	6325.997	0.039
8	0, 2, 3	1.	2, 1, 2, 0	0.757	8007.331	8007.333	-0.001
10	0, 8, 1	0.370	1, 0, 5, 3	0.370	7359.687[e]	7359.788	-0.101
10	3, 2, 1	0.487	1, 0, 5, 3	0.277	7540.523[e]	7540.699	-0.177
10	2, 4, 1	0.387	2, 0, 4, 2	0.361	7720.079[e]	7720.209	-0.130
Symmetry Φ_g							
5	0, 3, 1	1.	1, 0, 3, 0	1.	4194.706	4194.747	-0.041
7	0, 5, 1	0.594	1, 0, 4, 1	0.594	5397.252	5397.243	0.009
7	1, 3, 1	0.594	2, 0, 3, 0	0.594	5588.026	5587.958	0.068
Symmetry Φ_u							
3	0, 3, 0	1.	0, 0, 3, 0	1.	1946.35	1946.414	-0.064
5	0, 5, 0	0.581	0, 0, 4, 1	0.581	3169.442	3169.449	-0.007
5	1, 3, 0	0.581	0, 0, 4, 1	0.419	3361.400	3361.338	0.062
Symmetry Γ_g							
4	0, 4, 0	1.	0, 0, 4, 0	1.	2595.759	2595.798	-0.039
Symmetry Γ_u							
6	0, 4, 1	1.	1, 0, 4, 0	1.	4832.437	4832.420	0.017
Symmetry H_g							
7	0, 5, 1	1.	1, 0, 5, 0	1.	5470.470	5470.383	0.087
Symmetry H_u							
5	0, 5, 0	1.	0, 0, 5, 0	1.	3245.446	3245.474	-0.027

[a] Polyad P_{212} of the state. [b] The second and third columns, with headings normal state and coefficient, assign normal-mode labels $(\nu_1\nu_2\nu_3)$ to the energy level according to the square value of the largest contribution in this basis. [c] The fourth and fifth columns, with headings local state and coefficient, assign local-mode labels $(1/\sqrt{2}[(v_1v_2n_+n_-)\pm(v_2v_1n_+n_-)])$ to the energy level and its squared maximum component in the local basis is shown. [d] Experimental vibrational energies are taken from Ref. [19], otherwise indicated. [e] Ref. [101], [f] Ref. [27], [g] Ref. [102], [h] Ref. [103], [i] Ref. [104], [j] Ref. [23], [k] Ref. [105], [l] Ref. [106], [m] Ref. [107].

Isotopologue (828)

For the isotopologue $^{12}C^{18}O_2$, there are 42 available experimental energies. Since for this isotopologue the energy terms are not so abundant we have explored the possibility of reducing the number of parameters involved in (46). In Table 5 we present three fits where the number of parameters used in the calculations were increased from 12 to 15, where it was taking into account 42 experimental energies. At the bottom of the table, the rms is indicated together with the quadratic energy deviation χ^2, more sensitive to quantify the goodness of the fit. Although a fit with 16 parameters has been carried out, the fit with 15 parameters (Fit 3) is equally good and it can be taken as a suitable description to future studies. Fit 2 involving 13 parameters, although reasonable, has two times the rms deviation Fit 3. We should also mention the effect of the higher order interactions over the parameters d_L, $\alpha_s^{(1)}$

Table 5: Optimized parameters (in cm^{-1}) involved in the Hamiltonian (46) for the vibrational description of the isotopologue (828). Three fits are presented which differ in the number of spectroscopic parameters. In all cases the parameters associated with the anharmonicity of the potentials are assumed to be $\kappa_s = 166$ and $N_b = 172$.

Parameter	Fit 1	Fit 2	Fit 3
ω_s	1802.68	1806.01	1807.42
λ_s	-533.13	-532.10	-531.98
$\alpha_s^{(1)}$	7.0411	4.3030	2.8559
$\alpha_s^{(2)}$	-30.0754	-21.0632	-15.0741
$\alpha_s^{(3)}$	3.4737	3.2923	3.2556
d_L	4.0012	2.1750	0.8144
$\beta_s^{(1)}$	-	-	-0.0139
ω_b	657.82	657.12	657.137
x_{22}	-0.1154	0.1097	0.0846
g_{22}	0.1103	0.1068	0.1247
α_F	-36.90	-37.37	-37.39
$\alpha_{sb}^{(1)}$	-5.6591	-5.9077	-5.8198
$\alpha_{sb}^{(2)}$	7.3168	6.4546	6.5037
$\beta_{sb}^{(1)}$	-	0.1627	0.1622
$\beta_{sb}^{(2)}$	-	-	-
x_{123}	-	-	-0.0783
rms (cm^{-1})	0.6498	0.0938	0.0498
N$_{par}$	12	13	15
χ^2 (cm^{-2})	12.668	0.2555	0.0706

and $\alpha_s^{(2)}$. As it is noted from Fit 1 to Fit 3, these parameters are strongly affected: while $\alpha_s^{(1)}$ and $\alpha_s^{(2)}$ diminish up to half of their original value, the Darling-Dennison interaction $\hat{D}_L$ goes down to the fifth part of its initial value for Fit 1. In contrast, the other parameters remain without noticeable changes. This means that the interactions $\alpha_s^{(1)}$ and $\alpha_s^{(2)}$ together with the Darling-Dennison absorb the effect of higher order terms when they are missing. In this case it is necessary to consider the higher order terms since, otherwise, the spectroscopic parameters may not properly reflect the physical interactions. In Table 6 the parameters for Fit 3 together with their uncertainties are presented, while in Table 7 the theoretical and experimental levels are displayed.

Table 6: Parameters (in cm^{-1}) associated with Fit 3 in Table 5 for the isotopologue $^{12}C^{18}O_2$, with the corresponding uncertainties.

Parameter	Optimized value	ϵx_i	δx_i
ω_s	1807.4185	0.8340	0.0017
λ	-531.9815	0.0260	0.0026
$\alpha_s^{(1)}$	2.8559	0.8220	0.0006
$\alpha_s^{(2)}$	-15.0741	3.1900	0.0032
$\alpha_s^{(3)}$	3.2556	0.0039	0.0006
d_L	0.8144	0.8020	0.0022
$\beta_s^{(1)}$	-0.0139	0.0010	0.0001
ω_b	657.1372	0.0132	0.0014
x_{22}	0.0846	0.0100	0.0003
g_{22}	0.1247	0.0112	0.0020
α_F	-37.3956	0.0145	0.0012
$\alpha_{sb}^{(1)}$	-5.8198	0.0213	0.0009
$\alpha_{sb}^{(2)}$	6.5043	0.0243	0.0016
$\beta_{sb}^{(1)}$	0.1622	0.0013	0.0003
x_{123}	-0.0783	0.0092	0.0022
rms (cm^{-1})	0.0498	-	-

Table 7: Energy fit for the isotopologue $^{12}C^{18}O_2$ using the Hamiltonian (46) and including the 42 available experimental energies. The obtained root mean square deviation was rms=0.050 cm^{-1}. The corresponding parameters are given in Table 6.

Polyad^a	Normal state^b	Normal coefficient^b	Local state^c	Local coefficient^c	Experimental energy^d [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
Symmetry Σ_g							
2	1, 0, 0	0.721	1, 0, 0, 0	0.721	1230.324	1230.363	-0.039
2	0, 2, 0	0.721	0, 0, 1, 1	0.721	1347.093	1347.137	-0.044
4	1, 2, 0	0.431	1, 0, 1, 1	0.431	2447.054	2447.073	-0.019
4	0, 0, 2	1.	1, 1, 0, 0	0.500	4603.699^h	4603.678	0.021
Symmetry Σ_u							
2	0, 0, 1	1.	1, 0, 0, 0	1.	2314.046	2314.047	-0.
4	1, 0, 1	0.699	2, 0, 0, 0	0.699	3525.203^h	3525.247	-0.044
4	0, 2, 1	0.699	1, 0, 1, 1	0.699	3638.064^h	3638.086	-0.022
6	1, 2, 1	0.447	2, 0, 1, 1	0.447	4721.922^i	4721.936	-0.014
6	2, 0, 1	0.541	3, 0, 0, 0	0.406	4833.254^i	4833.285	-0.031
6	0, 4, 1	0.507	1, 0, 2, 2	0.507	4989.235^i	4989.194	0.041
6	0, 0, 3	1.	2, 1, 0, 0	0.750	6868.979	6868.920	0.058
8	2, 2, 1	0.399	2, 0, 2, 2	0.325	5903.040^e	5903.009	0.031
8	3, 0, 1	0.618	4, 0, 0, 0	0.309	6024.504	6024.528	-0.025
8	2, 2, 1	0.434	1, 0, 3, 3	0.372	6166.625	6166.602	0.023
8	1, 4, 1	0.468	2, 0, 2, 2	0.468	6359.572	6359.501	0.071
8	1, 0, 3	0.650	3, 1, 0, 0	0.325	8041.530^i	8041.548	-0.019
8	0, 2, 3	0.650	2, 1, 1, 1	0.488	8147.517^i	8147.547	-0.030

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Table 7 – *Continued from previous page*

Polyad[a]	Normal state[b]	Normal coefficient[b]	Local state[c]	Local coefficient[c]	Experimental energy[d] [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
10	2, 4, 1	0.371	3, 0, 2, 2	0.278	7069.726[f]	7069.786	-0.060
10	4, 0, 1	0.527	4, 1, 0, 0	0.296	7209.007[f]	7208.976	0.032
10	4, 0, 1	0.350	1, 0, 4, 4	0.226	7341.527[f]	7341.469	0.058
10	0, 8, 1	0.358	1, 0, 4, 4	0.358	7522.321[f]	7522.413	-0.092
10	1, 6, 1	0.447	2, 0, 3, 3	0.447	7744.476[f]	7744.513	-0.037
12	1, 0, 5	0.596	5, 1, 0, 0	0.298	12460.070[g]	12460.076	-0.007
12	0, 2, 5	0.596	3, 2, 1, 1	0.373	12560.670[g]	12560.673	0.002
Symmetry Π_g							
3	0, 1, 1	1.	1, 0, 1, 0	1.	2959.131[h]	2959.144	-0.013
Symmetry Π_u							
1	0, 1, 0	1.	0, 0, 1, 0	1.	657.3288	657.3466	-0.018
3	1, 1, 0	0.665	0, 0, 2, 1	0.335	1868.704	1868.653	0.051
3	0, 3, 0	0.665	0, 0, 2, 1	0.665	2024.530	2024.559	-0.029
5	0, 1, 2	1.	1, 1, 1, 0	0.500	5236.555[i]	5236.601	-0.046
7	1, 1, 2	0.628	3, 0, 1, 0	0.471	6409.310	6409.308	0.002
7	0, 3, 2	0.628	1, 1, 2, 1	0.314	6558.038 [i]	6558.059	-0.021
9	4, 1, 0	0.354	0, 0, 5, 4	0.253	5779.755[e]	5779.774	-0.019
9	1, 7, 0	0.433	0, 0, 5, 4	0.229	6230.081	6230.067	0.014
9	1, 3, 2	0.472	3, 0, 2, 1	0.354	7569.909[f]	7569.844	0.065
9	2, 1, 2	0.546	4, 0, 1, 0	0.409	7720.857[f]	7720.876	-0.019
9	1, 3, 2	0.466	1, 1, 3, 2	0.214	7898.035[f]	7898.017	0.018
Symmetry Δ_g							
2	0, 2, 0	1.	0, 0, 2, 0	1.	1315.084	1315.112	-0.028
4	1, 2, 0	0.637	0, 0, 3, 1	0.363	2511.813	2511.708	0.105
Symmetry Δ_u							
4	0, 2, 1	1 .	1, 0, 2, 0	1.	3604.653[h]	3604.661	-0.008
8	2, 2, 1	0.525	1, 0, 4, 2	0.416	6133.452	6133.444	0.009
8	1, 4, 1	0.470	2, 0, 3, 1	0.470	6339.456	6339.420	0.036
Symmetry Φ_u							
3	0, 3, 0	1.	0, 0, 3, 0	1.	1973.247	1973.296	-0.049

[a] Polyad P_{212} of the state. [b] The second and third columns, with headings normal state and coefficient, assign normal-mode labels $(\nu_1\nu_2\nu_3)$ to the energy level according to the square value of the largest contribution in this basis. [c] The fourth and fifth columns, with headings local state and coefficient, assign local-mode labels $(1/\sqrt{2}[(v_1 v_2 n_+ n_-) \pm (v_2 v_1 n_+ n_-)])$ to the energy level and its squared maximum component in the local basis is shown. [d] Experimental vibrational energies are taken from Ref. [23], otherwise indicated. [e] Ref. [108], [f] Ref. [109], [g] Ref. [110], [h] Ref. [19], [i] Ref. [111].

Isotopologue (727)

For this isotopologue there are 28 confirmed experimental energies. Again this number is low but enough to carry out a fit providing confident wave functions. In Table 8 three

Table 8: Optimized parameters (in cm^{-1}) involved in the Hamiltonian (46) for the vibrational description of the isotopologue (727). Three fits are presented differing in the number of spectroscopic parameters. In all cases the parameters associated with the anharmonicity of the potentials are taken to be $\kappa_s = 156$ and $N_b = 146$.

Parameter	Fit 1	Fit 2	Fit 3
ω_s	1833.69	1837.53	1836.8365
λ_s	-523.79	-524.37	-521.9588
$\alpha_s^{(1)}$	3.3788	-0.69015	1.7985
$\alpha_s^{(2)}$	-13.1675	2.8924	-8.1125
$\alpha_s^{(3)}$	3.2909	3.5079	3.1396
d_L	-	-4.0433	-0.9635
$\beta_s^{(1)}$	-	-	-0.0259
ω_b	662.68	662.778	661.9532
x_{22}	0.2172	0.3030	-0.0758
g_{22}	-0.2209	-0.3701	0.3357
α_F	-36.4102	-36.3318	-37.1807
$\alpha_{sb}^{(1)}$	-6.4679	-6.6979	-5.7075
$\alpha_{sb}^{(2)}$	6.5835	-	6.9436
$\beta_{sb}^{(1)}$	-	-	0.1339
$\beta_{sb}^{(2)}$	-	-	0.0149
x_{123}	-	-	0.1320
rms (cm^{-1})	0.554	0.553	0.17
χ^2 (cm^{-2})	5.242	4.899	0.34

fits are presented using the Hamiltonian (46) with 11 parameters (Fits 1 and 2) and 16 parameters (Fit 3). Fits 1 and 2 provide the same deviation rms=0.55 cm^{-1}, although the difference is given by the incorporation of the Darling-Dennison interaction $\hat{D}_L$. Even though the parameter d_L cannot be assumed to be negligible, the effect over the quality of the fit is not significant and it substitutes $\alpha_{sb}^{(2)}$. However when the epsilon and delta uncertainties are analyzed, the parameter d_L displays an epsilon uncertainty larger than the parameter itself. This means that the Darling-Dennison interaction, when it is included instead of those of higher order, is highly correlated. When we carried out a fit with the full set of interactions (Fit 3) involved in the Hamiltonian (46), all the parameters are well determined. The deviation is reduced to rms=0.17 cm^{-1} with uncertainty errors displayed in Table 9. The experimental and theoretical energies, together with the residuals are displayed in Table 10.

It is important to notice that three more experimental energies have been reported by Ref. [115] belonging to symmetry Π_g. However when they are incorporated in the fit the rms increases from 0.55 cm^{-1} to 8.2 cm^{-1}. Thus, these three energies were not considered in the fit but used to assess the predictions. On the other hand, two of those experimental energies were updated by Ref. [118] reporting different energy values. In Table 11 we show those energies given by Ref. [115] and Ref. [118]. We compare both values with the predicted energies obtained from the fit given in Table 10 and we can conclude that our predictions agree with those in Ref. [118]. This comparison is useful to assess the predictive power of this approach in the assignments of new experimental energy levels.

Table 9: Parameters and uncertainties (in cm^{-1}) obtained for the energy fit (Fit 3 of Tab. 8) of the isotopologue $^{12}\text{C}^{17}\text{O}_2$ using the full set of parameters involved in the Hamiltonian (46). As in the previous fits the parameters associated with the anharmonicity of the potentials were taken to be $\kappa_s = 156$ and $N_b = 146$.

Parameter	Optimized value	ϵx_i	δx_i
ω_s	1836.8365	0.5680	0.0015
λ	-521.9588	0.0368	0.0023
$\alpha_s^{(1)}$	1.7985	0.5670	0.0005
$\alpha_s^{(2)}$	-8.1125	2.2400	0.0029
$\alpha_s^{(3)}$	3.1396	0.0175	0.0006
d_L	-0.9635	0.5520	0.0021
$\beta_s^{(1)}$	-0.0259	0.0009	0.0001
ω_b	661.9532	0.0168	0.0016
x_{22}	-0.0758	0.0108	0.0003
g_{22}	0.3357	0.0151	0.0036
α_F	-37.1807	0.0081	0.0013
$\alpha_{sb}^{(1)}$	-5.7075	0.0227	0.0011
$\alpha_{sb}^{(2)}$	6.9436	0.0225	0.0018
$\beta_{sb}^{(1)}$	0.1339	0.0011	0.0003
$\beta_{sb}^{(2)}$	0.0149	0.0052	0.0004
x_{123}	0.1320	0.0299	0.0033
rms (cm^{-1})	0.17	-	-

Table 10: Energy fit for the isotopologue $^{12}\text{C}^{17}\text{O}_2$ using the Hamiltonian (46) and including 28 available experimental energies. The obtained root mean square deviation was rms=0.17 cm $^{-1}$. The corresponding parameters are given in Table 9.

Polyad^a	Normal state^b	Normal coefficient^b	Local state^c	Local coefficient^c	Experimental energy^d [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
Symmetry Σ_g							
2	1, 0, 0	0.640	0, 0, 1, 1	0.360	1258.235	1257.983	0.252
2	0, 2, 0	0.640	0, 0, 1, 1	0.640	1364.940	1364.564	0.377
Symmetry Σ_u							
2	0, 0, 1	1.	1, 0, 0, 0	1.	2330.593	2330.723	-0.130
4	1, 0, 1	0.600	2, 0, 0, 0	0.600	3568.472^e	3568.489	-0.017
4	0, 2, 1	0.600	1, 0, 1, 1	0.600	3672.698^e	3672.614	0.084
6	1, 2, 1	0.491	2, 0, 1, 1	0.491	4787.572	4787.492	0.080
6	2, 0, 1	0.624	3, 0, 0, 0	0.469	4901.033	4900.901	0.133
6	1, 2, 1	0.474	2, 0, 1, 1	0.474	5039.369	5039.327	0.042
6	0, 0, 3	1.	2, 1, 0, 0	0.752	6917.820^j	6918.150	-0.331
8	1, 4, 1	0.395	2, 0, 2, 2	0.395	5988.913^i	5988.617	0.296
8	3, 0, 1	0.585	4, 0, 0, 0	0.294	6122.713^i	6122.293	0.420
8	2, 2, 1	0.362	1, 0, 3, 3	0.346	6249.958^i	6250.672	-0.714
8	1, 4, 1	0.473	2, 0, 2, 2	0.473	6425.215^i	6425.509	-0.294
8	1, 0, 3	0.519	2, 1, 1, 1	0.361	8114.655^h	8114.525	0.130
8	0, 2, 3	0.519	2, 1, 1, 1	0.390	8216.041^h	8215.940	0.101
10	4, 0, 1	0.393	4, 1, 0, 0	0.220	7332.618^k	7331.878	0.740

Continued on next page

Table 10 – *Continued from previous page*

Polyad[a]	Normal state[b]	Normal coefficient[b]	Local state[c]	Local coefficient[c]	Experimental energy[d] [cm^{-1}]	Theoretical energy [cm^{-1}]	Δ [cm^{-1}]
10	4, 0, 1	0.478	4, 1, 0, 0	0.267	7459.013[k]	7459.952	-0.939
12	0, 2, 5	0.560	3, 2, 1, 1	0.351	12561.960[m]	12561.958	0.002
Symmetry Π_g							
3	0, 1, 1	1.	1, 0, 1, 0	1.	2980.285	2980.459	-0.174
Symmetry Π_u							
1	0, 1, 0	1.	0, 0, 1, 0	1.	662.0665[g]	662.6762	-0.610
3	1, 1, 0	0.604	0, 0, 2, 1	0.396	1900.254	1900.971	-0.717
3	0, 3, 0	0.604	0, 0, 2, 1	0.604	2048.123	2047.890	0.233
5	1, 3, 0	0.484	1, 0, 2, 1	0.484	3124.770	3125.700	-0.930
5	2, 1, 0	0.559	0, 0, 3, 2	0.399	3278.487[e]	3278.337	0.150
5	1, 3, 0	0.474	0, 0, 3, 2	0.405	3451.878[e]	3451.158	0.720
5	0, 1, 2	1.	1, 1, 1, 0	0.501	5273.873[f]	5273.590	0.284
9	4, 1, 0	0.398	0, 0, 5, 4	0.155	5714.589[l]	5714.330	0.258
Symmetry Δ_g							
4	0, 2, 1	1.	1, 0, 2, 0	1.	3630.395[e]	3630.199	0.196

[a] Polyad P_{212} of the state. [b] The second and third columns, with headings normal state and coefficient, assign normal-mode labels $(\nu_1\nu_2\nu_3)$ to the energy level according to the square value of the largest contribution in this basis. [c] The fourth and fifth columns, with headings local state and coefficient, assign local-mode labels $(1/\sqrt{2}[(v_1v_2n_+n_-)\pm(v_2v_1n_+n_-)])$ to the energy level and its squared maximum component in the local basis is shown. [d] Experimental vibrational energies are taken from Ref. [112], otherwise indicated. [e] Ref [113], [f] Ref [114] , [g] [115], [h] Ref. [116], [i] Ref. [117]. [j] Ref. [118], [k] Ref. [109], [l] Ref. [119], [m] Ref. [110].

Table 11: Predicted and experimental energies belonging to polyad 9 and symmetry Π_g for the isotopologue $^{12}C^{17}O_2$.

Polyad^a	Normal state^b	Normal coefficient^b	Local state^c	Local coefficient^c	Experimental energy [cm^{-1}]		Theoretical energy [cm^{-1}]	Δ [cm^{-1}]	
					Ref. [115]	Ref. [118]		Ref. [115]	Ref. [118]
					Symmetry Π_g				
9	3,1,1	0.504	1,0,4,3	0.277	6785.7152	6757.4405	6757.54	27.9752	-0.10
9	0,7,1	0.350	1,0,4,3	0.350	6912.8909	6922.6761	6923.75	-10.1291	-1.07
9	1,5,1	0.459	2,0,3,2	0.459	7091.7191	-	7118.74	-26.7509	-

^{a} Polyad P_{212} of the state. ^{b} The second and third columns, with headings normal state and coefficient, assign normal-mode labels $(\nu_1\nu_2\nu_3)$ the state according to the square value of the largest contribution in this basis. ^{c} The fourth and fifth columns, with headings local state and coefficient, assign local-mode labels $(1/\sqrt{2}[(v_1v_2n_+n_-)+(v_2v_1n_+n_-)])$ the state and its squared maximum component in the local basis is shown.

6. Algebraic Hamiltonian: polyad P_{214}

We now consider the Hamiltonian conserving the polyad (8c). According to the polyad analysis of Sect. 3, this polyad would be the preponderant and reflects the strong interaction between the stretching local oscillators. In this case the local polyad is broken and the interactions conserving the polyad do not necessarily coincide with the ones included in the fourth-order Hamiltonian (34). In this case it is convenient to start with the following Hamiltonian up to quartic order

$$\hat{H}'^{[4]}_{alg} = \sum_{i=1}^{3} \omega_i \hat{\nu}_i + \sum_{i\leq j} x_{ij}\{\hat{\nu}_i, \hat{\nu}_j\} + g_{22}\hat{\ell}^2 + \alpha_F \hat{F}, \tag{49}$$

which involves 11 parameters. In accordance with the discussion of the previous section we may add to (49) the sixth order contribution

$$\begin{aligned} \hat{V}'^{[6]}_{alg} =& \beta_s^{(1)}\{(\hat{n}_1+\hat{n}_2),(\hat{D}_L+2\hat{n}_1\hat{n}_2)\} + \beta_{sb}^{(1)}\{(\hat{n}_1+\hat{n}_2),\hat{F}\} && (50)\\ &+ \beta_{sb}^{(2)}\hat{n}(\hat{D}_L+2\hat{n}_1\hat{n}_2) + x_{123}\{\hat{\nu}_1,\hat{\nu}_3\}\hat{n} \quad , && (51)\end{aligned}$$

obtaining Hamiltonian

$$\hat{H}' = \hat{H}'^{[4]}_{alg} + \hat{V}'^{[6]}_{alg}, \tag{52}$$

with 15 parameters. It should be noted that the Hamiltonian (46) conserves polyad P_{212} and the fact that it contains the Darling-Dennison together with the independent operators $\hat{n}_1^2+\hat{n}_2^2$ and $\hat{n}_1\hat{n}_2$ makes this Hamiltonian characteristic of polyad P_{212}. On the other hand, Hamiltonian (52) conserves any polyad. If in the Hamiltonian (46) $\hat{D}_L$ is excluded and the interactions $\hat{n}_1^2+\hat{n}_2^2$ and $\hat{n}_1\hat{n}_2$ stop being independent we have basically the Hamiltonian (52). However, polyad P_{214} is characterized by the interaction

$$\hat{V}_{P_{214}} = f_{uu/gggg}[\hat{T}_u^{\dagger 2}\hat{T}_g^4 + H.c.] \quad , \tag{53}$$

and consequently a reasonable Hamiltonian is given by

$$\hat{H}_{P_{214}} = \hat{H}'^{[4]}_{alg} + \hat{V}'^{[6]}_{alg} + \hat{V}_{214}, \tag{54}$$

which involves 16 parameters as the one considered for polyad P_{212} (46). Since the energy levels are not so widely distributed over polyads as in P_{212} and P_{213} we carried out a fit up to polyad $P_{214} = 20$ involving 107 experimental energy levels for the isotopologue (636) considering the Hamiltonian (52). Each of the three missing energies belong individually to one different polyad. The deviation obtained was rms=0.12 cm^{-1}. Notice that this quality is similar to the fit with rms=0.093 cm^{-1} for polyad P_{212} with 15 parameters excluding the Darling-Dennison interaction but with a larger rms deviation. Hence we proceeded to add the interaction $\hat{V}_{214}$, but a convergence was not reached. Hence this interaction does not provide the stability obtained by the Darling-Dennison interaction, which resulted in a rms=0.06 cm^{-1} (See Sect.5). We even explored different fits of Hamiltonian (54) starting with different set of parameters but either the interaction does not converge or it converges to a null interaction. This means that the provided experimental energies are not enough to determine the interaction $\hat{V}_{214}$. This conclusion is also the same even when the missing three experimental energies are taken into account to complete the 110 energies. The stability of the interaction $\hat{V}_{214}$ strongly depends of the available experimental energies associated with the states mixed by the effect of this interaction. Unfortunately the isotopologues (828) and (727) do not present enough energies to determine this interaction and consequently we were unable to explore them in the framework of polyad P_{214}.

7. Conclusions

In this contribution we have extended our study of the main isotopologue of carbon dioxide ($^{12}C^{16}O_2$) to the symmetric isotopologues $^{13}C^{16}O_2$, $^{12}C^{18}O_2$ and $^{12}C^{17}O_2$. Based on our previous work on the principal isotopologue we have developed our study in the framework of a polyad-conserving Hamiltonian associated with polyad P_{212}, although we have also explored polyad P_{214}. Polyad P_{213} was not considered in the light of the results given in Ref. [33], where polyad P_{213} did not provide a notable improvement with respect to P_{212} and P_{214}.

The complete available experimental data of the isotopologue $^{13}C^{16}O_2$ was described taking into account 110 vibrational energy terms up to 25864 cm^{-1} corresponding to polyad $P_{212} = 24$. The full Hamiltonian (46) conserving the polyad P_{212} provided us a fit with rms of 0.06 cm^{-1}. The description of the interactions was set up in the framework of a local mode scheme to show the advantage of considering the polyad P_{212} where both normal and local polyads are equivalent. It was shown that the only term characterizing the polyad P_{212} is the Darling-Dennison interaction. A fit involving 15 interactions common to the three polyads provides an rms=0.093 cm^{-1}, which means that the effect of the Darling-Dennison interaction has the impact of reducing the deviation from 0.093 cm^{-1} to 0.06 cm^{-1}. On the other hand, when the polyad P_{214} was considered, the interaction characterizing this polyad became unstable during the fit procedure. This is a consequence of not enough available experimental energies to stabilize the interaction. We have also explored excluding parameters to identify possible redundancies but the interaction $\hat{V}_{P_{214}}$ was unstable nevertheless.

Regarding the isotopologue $^{12}C^{18}O_2$, we have analyzed the vibrational spectrum including the 42 available experimental energies. In this case we carried out consecutive fits increasing the number of parameters from 12 to 16. We found the best fit corresponding to rms=0.05 cm^{-1} with 15 parameters. The description does not improve if the interaction associated with the parameter $\beta_{sb}^{(2)}$ is included. The isotopologue $^{12}C^{17}O_2$ was also studied in the framework of the Hamiltonian (46). Three fits were explored to describe the available

28 experimental energies. Two fits including 11 parameters providing an rms=0.55 cm^{-1}. When $\alpha_{sb}^{(2)}$ was substituted for the Darling-Dennison interaction the fit did not improve, but including the 16 parameters the deviation reduced to rms=0.17 cm^{-1}. Although three more experimental energies were available, when they are included unexpected large deviations manifested increasing the root mean square deviation from 0.17 cm^{-1} to 8.2 cm^{-1}. A more recent report [118], of two of those energies coincide with our predictions.

In general our descriptions for the three isotopologues can be considered of spectroscopic quality. Although our descriptions are comparable to variational calculations we should remark that our model has been set up in a polyad-conserving Hamiltonian which implies that the wave functions are expected to be different. However this difference was proven not to be of high importance due to the fact that it was possible to simulate the Raman spectrum accurately with these functions for the principal isotopologue. In addition, in view of the predictive power of this approach in the study of vibrational structure of carbon dioxide, these results could be helpful in the verification of the assignments of experimental energies and used as complement to comprehensive databases [22, 120] as well as they could give some support to the Raman observations [3, 121, 122]. In the near future, the simulation of the Raman spectra will be carried out for the additional isotopologues based on the new predictions reported in this study. In addition, new non symmetric isotopologues of carbon dioxide will be addressed to help the experimentalists in the assignment of new spectral data.

8. Author Contribution

Conceptualization, all authors. Methodology, M.B.M., M.R.A, M.C., and R.L. Formal analysis M.C., and R.L. Software, M.B.M. and R.L. Writing – Original Draft, M.B.M., M.C., and R.L. Writing –Review and Editing, all authors; Supervision, M.C., C.O.H, and R.L.

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