

Vibrational excitations in H₂O in the framework of a local model

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Abstract

The vibrational description of H₂¹⁶O in terms of Morse local oscillators for both bending and stretching degrees of freedom is presented. Expansions of the kinetic and potential energies of the vibrational Hamiltonian are considered up to quartic terms. The local Morse coordinates y_i as well as the momenta p_i are thereafter expanded in terms of creation and annihilation operators of the Morse functions keeping terms up to order $1/\sqrt{\kappa}$ (up to quadratic terms in the operators), where κ is a parameter related with the depth of the potential. Only terms conserving the polyad are considered. The resulting Hamiltonian includes the known Darling–Dennison and Fermi-like interactions, but unlike the description in terms of a harmonic basis, all the force constants up to quartic order are involved. A tensorial formalism is developed to expand the Hamiltonian in powers of $1/\sqrt{\kappa}$ in terms of symmetry adapted operators. An energy fit is carried out for 72 experimental energies up to 23 000 cm⁻¹, obtaining an rms deviation of 5.00 cm⁻¹. The force constants are determined and predictions for the isotopes H₂¹⁷O, H₂¹⁸O, D₂¹⁶O, and T₂¹⁶O are presented.

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1. Introduction

In the last decades a diversity of approaches to describe the vibrational degrees of freedom of molecular systems has been proposed mainly due to the development of new spectroscopic methods which are able to characterize highly excited vibrational states, a region where chemical activation may take place [1–5]. It has been found that the appropriate approach to describe systems in such situations should be given in terms of local mode models [6–9]. In the framework of a local model the Hamiltonian as well as the basis are given in terms of internal variables. A remarkable result when using a local scheme is that the basis tends to approach the eigenstates at higher energies, usually associated to the local stretches of certain bonds. Although it is clear that a local mode scheme provides a better physical insight in the high energy regions of the spectra, it has two technical disadvantages with respect to the standard approach in terms of normal coordinates. On one hand the kinetic energy must be obtained through the calcu-

lation of the Wilson matrix, together with the momentum-independent contribution, and on the other hand redundant coordinates appear, which must be eliminated from both the Hamiltonian and the basis [3].

Once the expansion of the Hamiltonian in terms of local coordinates and momenta is obtained, the appropriate method to determine the structure constants greatly depends on the size of the molecular system. The appearance of fast computers in the last decades has allowed to use *ab initio* methods to calculate the force constants of small and some medium size molecules, and to carry out variational calculations using a discrete variable representation and exact kinetic energy operators [5]. This is not the case, however, for molecules with more than four atoms. In complex systems the potential surface is obtained from fittings to experimental energies. However, in both cases, the Wilson matrix together with the expansion of the Hamiltonian in terms of the local variables and momenta must be obtained in order to establish the correspondence with the structure constants, which may represent a formidable task for large molecules, a fact that constraints the applicability of this method. The conventional effective Hamiltonian approach provides a partial solution to this problem. It deals with the kinetic and potential energies

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simultaneously and consequently different spectroscopic parameters are needed for different isotopic species. This approach has been widely used to fit experimental data using a Hamiltonian in terms of creation and annihilation operators of harmonic functions [10]. It is possible, however, to establish a similar approach in the framework of a local model. In this work we present the vibrational Hamiltonian of the H₂O molecule as an expansion in terms of local creation and destruction Morse operators in the spirit to establish the connection between effective Hamiltonian approach and the standard local mode method in a basis of Morse functions. The analysis of this molecule will pave the way to the application of this approach to large molecules.

In the framework of a local mode approach the local oscillators may be approximated with harmonic potentials, but it is preferable to consider Morse oscillators because they more accurately reflect the main physical properties of a pure local bond [11]. Hence, in the zeroth-order approximation, independent Morse oscillators are considered. In a Morse oscillator basis, however, the interaction terms couple the whole space in the Hamiltonian matrix, not allowing to take advantage of the simplifications brought about by approximately conserved polyad numbers [12]. This problem is avoided by carrying out some approximations concerning the matrix elements of the interaction terms. The crudest approximation consists in considering the interaction between the Morse oscillators in a harmonic fashion (harmonically coupled anharmonic oscillator, HCAO model) [13]. This approximation has proved to be very useful to understand the structure of the spectra, and provides the same advantages existing when considering a harmonic basis. Although this model represents an attractive alternative for the description of complex molecules, it is possible to develop significant improvements by taking into account higher order corrections to the coupling matrix elements between Morse oscillators in such a way that polyads are still preserved. This goal can be achieved by expanding the interactions in terms of creation \hat{b}^\dagger and annihilation \hat{b} operators for the Morse functions [14,15]. An important property of these operators is that they are associated to an $su(2)$ algebra, which allows to establish the vibrational systems of a set Morse oscillators as an algebraic problem, in the same fashion as the harmonic oscillator description [16].

A remarkable feature of the expansions of the dynamical variables in terms of the operators $\{\hat{b}^\dagger, \hat{b}\}$ is that they are given in terms of powers of the parameter $1/\sqrt{\kappa}$, where κ is known as the Child's parameter [7] and is related to the depth of the Morse potential. In the limit $\kappa \rightarrow \infty$, the harmonic results are recovered. This property suggests to include terms in the expansion in successive form, an approach that breaks the polyad in natural form. This problem, however, can be avoided by

keeping only the terms which preserve the polyad. When only the leading terms ($(1/\sqrt{\kappa})^0$) are taken into account, the description is given in the framework of the vibron model approximation [17,18]. From the point of view of the general expansion mentioned previously the natural approach to go beyond the vibron model consists in taking the next terms of order $(1/\sqrt{\kappa})$. This can be done keeping again only the terms conserving the polyad. It can be shown however that a better convergence is obtained when the expansion of the Hamiltonian is carried out in terms of the Morse variable $y = 1 - e^{\beta x}$, instead of the variable x [8,9]. In this work we shall first proceed to obtain the Hamiltonian in terms of the Morse variables y_i and the momenta, and thereafter carry out their expansions in terms of the operators $\{\hat{b}_i^\dagger, \hat{b}_i\}$, keeping the terms preserving the polyad. For simplicity, we have chosen the water molecule to illustrate our approach, but the same procedure can be applied in more complex situations. In a future work we shall consider the polyad breaking effects provided by the method [19].

An important consequence of taking the terms of order $(1/\sqrt{\kappa})$ in the expansion in the Morse coordinate and momenta is that all the involved force constants up to quartic terms in the potential are well determined, even with the constraint of the polyad as a good quantum number. This is in contrast with the HCAO and vibron models, where only a subset of force constant can be obtained when the preservation of polyads are considered. In such cases only by breaking the polyad the potential surface can be determined in complete form (up to the approximation considered).

Because of its importance, the water molecule has been the subject of several studies since the early days of molecular quantum mechanics [20]. At first the vibrational description was focused on the stretching degrees of freedom [21], but later on the analysis was extended to the bending modes [22–24]. Nowadays very accurate methods based on ab initio calculations have been applied to describe in complete form the ro-vibrational spectroscopic properties of water [25]. Concerning the different approximations involved in the expansion of the coordinates and momenta, a detailed spectroscopic study of H₂O was carried out [26], where one of the objectives was the evaluation of the HCAO model by comparison with variational calculations. Later on an spectroscopic analysis of H₂O was carried out in the framework of the vibron model approximation [18], where both energies and intensities were studied and the potential energy surface was determined. Because of the approximation involved not all the force constant were able to be obtained.

In this work we develop a tensorial formalism in terms of the Morse operators $\{\hat{b}_i^\dagger, \hat{b}_i\}$ to express the expansion of Hamiltonian of water in terms powers of the parameter $1/\sqrt{\kappa}$. Both stretching and bending degrees of freedom are treated in the same fashion. An energy fit

is obtained and the force constants are determined. Prediction for different isotopic species are also presented.

This paper is organized as follows. The expansion of the vibrational Hamiltonian in terms of the Morse coordinate up to quartic terms is presented in Section 2. In Section 3 we present the expansion of the coordinates and momenta in the $su(2)$ space. In Section 4, a symmetry adapted tensorial formalism is introduced. Section 5 is devoted to the H_2O results for energies, determination of the force constants and isotopic predictions. Finally, our summary and conclusions are given in Section 6.

2. Description of water in terms of internal coordinates

The equilibrium structure of the water molecule is non-linear with structure parameters $r_{OH} = 0.9575 \text{ \AA}$ and $\angle HOH = 104.51^\circ$ [26]. The point symmetry is C_{2v} , but it is enough to consider the subgroup C_2 since all vibrations take place on a plane. This molecule has three degrees of freedom, two of them associated to the stretching modes ($A \oplus B$) and the other to the bending mode (A). The harmonic approximation provides a complete basis in terms of normal modes which can be used to diagonalize a general Hamiltonian. In the standard notation this basis is labeled by $|v_1 v_2 v_3\rangle$, where v_1 and v_3 are the number of quanta in the stretching A and B modes, respectively, while v_2 is associated with the bending A mode [27]. In our approach this basis will not be used, but we shall include this labeling scheme in the energy fits.

If we use internal displacement coordinates the quantum mechanical Hamiltonian that describes the vibrational excitations of the H_2O molecule takes the form [28,29]

$$H = \frac{1}{2} \hat{\mathbf{p}}^\dagger \mathbf{G}(\mathbf{q}) \hat{\mathbf{p}} + V(\mathbf{q}), \quad (1)$$

where \mathbf{q} and $\hat{\mathbf{p}}$ are three dimensional column vectors corresponding to the displacement internal coordinates and conjugate momenta, respectively. In (1) we have omitted the purely quantum mechanical term derived from the kinetic energy not involving momentum operators, since it has been proved that it is negligible for H_2O [24]. The components q_r and $q_{r'}$ will be assigned to displacements from equilibrium r_e of the two internal O–H stretching coordinates r and r' , while q_ϕ corresponds to the displacement from equilibrium of the $\angle HOH$ -bending coordinate $r_e \phi_e$:

$$q_r = \Delta r, \quad q_\phi = r_e \Delta \phi, \quad q_{r'} = \Delta r'. \quad (2)$$

In the kinetic energy contribution, the $\mathbf{G}(\mathbf{q})$ matrix depends on the internal coordinates and atomic masses, and is given explicitly by [30]

$$\mathbf{G}(\mathbf{q}) = \begin{bmatrix} \mu_H + \mu_O & -\mu_O \frac{r_e \sin \phi}{r_3} & \mu_O \cos \phi \\ -\mu_O \frac{r_e \sin \phi}{r_3} & \mu_H r_e^2 \left(\frac{1}{r_1^2} + \frac{1}{r_3^2} \right) + \mu_O r_e^2 \left(\frac{r_1^2 + r_3^2 - 2r_1 r_3 \cos \phi}{r_1^2 r_3^2} \right) & -\mu_O \frac{r_e \sin \phi}{r_1} \\ \mu_O \cos \phi & -\mu_O \frac{r_e \sin \phi}{r_1} & \mu_H + \mu_O \end{bmatrix}, \quad (3)$$

where we have introduced the variables $\mu_i = 1/m_i$, $i = O, H$, corresponding to the inverse of the masses. For semirigid molecules both the $\mathbf{G}(\mathbf{q})$ matrix and the potential $V(\mathbf{q})$ are expanded as a Taylor series about the equilibrium configuration. It has been pointed out, however, that these expansions do not have the correct asymptotic behavior, and an expansion in terms of the Morse variable $y = 1 - e^{-\beta q}$ is more appropriate for the stretches, because has a radius of convergence that extends all the way to dissociation [24,31–34]. Here we consider an expansion of the variables $\{y_i, i = r, r', \phi\}$ for both stretching and bending coordinates. In this spirit the elements g_{ij} of the $\mathbf{G}(\mathbf{q})$ matrix takes the form

$$g_{ij}(\mathbf{q}) = (g_{ij})_0 + \sum_{k=1}^3 \left(\frac{\partial g_{ij}}{\partial q_k} \right)_0 \beta_k^{-1} y_k + \frac{1}{2} \sum_{k=1}^3 \left[\left(\frac{\partial^2 g_{ij}}{\partial q_k^2} \right)_0 + \left(\frac{\partial g_{ij}}{\partial q_k} \right)_0 \beta_k \right] \beta_k^{-2} y_k^2 + \frac{1}{2!} \sum_{k \neq l=1}^3 \left(\frac{\partial^2 g_{ij}}{\partial q_k \partial q_l} \right)_0 \beta_k^{-1} \beta_l^{-1} y_k y_l, \quad (4)$$

where $i, j = r, r', \phi$. Here we have taken into account up to quadratic terms, since we intend to consider an expansion in the Hamiltonian up to quartic terms. Consequently an expansion up to quartic terms is carried out for the potential. It is worth noting the relevance of the ratio y_i/β_i . In the rigid limit this ratio tends to the variable q_i :

$$\lim_{q_i \rightarrow 0} \frac{y_i}{\beta_i} = q_i. \quad (5)$$

In a local mode picture the system is described as a set of interacting oscillators associated to the internal coordinates. For the stretching degrees of freedom each independent oscillator is usually described with a Morse potential, while for the bendings a harmonic oscillator is usually assumed. In this work we propose to use also a Morse oscillator to deal with the bending degree of freedom. This selection is based on the asymmetry of the potential and the fact that the oscillator can be made deep enough so that the dissociation limit is far away from the energies of interest. In case of tunneling effects a double Morse potential may be used, which has the advantage of being associated to an $su(2)$ algebra [35]. The identification with Morse oscillators is carried out in natural form through the quadratic terms in the potential expansion and the diagonal zeroth order terms in the expansion of $\mathbf{G}(\mathbf{q})$:

$$\hat{H}_i^M = \frac{1}{2} (g_{ii})_0 p_i^2 + \frac{1}{2} f_{ii} y_i^2, \quad i = r, r', \phi. \quad (6)$$

For the Morse potential the force constants have the explicit form

$$f_{ii} = 2D_i \beta_i^2, \quad (7)$$

where the parameters D_i and β_i are defined through the explicit expression of the potential

$$V_M(q_i) = D_i(1 - e^{-\beta_i q_i})^2. \quad (8)$$

The Morse Hamiltonians (6) have the eigenvalues [11]

$$\frac{E_M(v_i)}{hc} = \omega_e^i(v_i + 1/2) - \omega_e x_e^i(v_i + 1/2)^2, \quad (9)$$

where ω_e and $\omega_e x_e^i$ are the harmonic wave number and anharmonicity constants, respectively. In terms of the Morse parameters they have the form

$$hc\omega_e^i = \hbar\omega_i = \hbar\sqrt{\frac{f_{ii}}{\mu_i}} = 2\hbar\beta_i\sqrt{\frac{D_i}{2\mu_i}}, \quad hc\omega_e x_e^i = \frac{\hbar^2\beta_i^2}{2\mu_i}, \quad (10)$$

where $\mu_i = (g_{ii})^{-1}$, with $i = r, r', \phi$. Note that we used the same character for the inverse of the mass, but there should not be any confusion since the nature of the sub indices involved are different. The zeroth order Hamiltonian is then given by

$$\hat{H}_0 = \hat{H}_r^M + \hat{H}_{r'}^M + \hat{H}_\phi^M, \quad (11)$$

while the complete Hamiltonian up to quartic terms takes the form

$$\begin{aligned} \hat{H} = & \hat{H}_0 + (g_{rr'})_0 p_r p_{r'} + \frac{1}{2} \left(\frac{\partial g_{\phi\phi}}{\partial q_r} \right)_0 \beta_r^{-1} (y_r + y_{r'}) p_\phi^2 \\ & + \left(\frac{\partial g_{r\phi}}{\partial q_\phi} \right)_0 \beta_\phi^{-1} (p_r + p_{r'}) \frac{(y_\phi p_\phi + p_\phi y_\phi)}{2} \\ & + \frac{1}{4} \left[\left(\frac{\partial^2 g_{\phi\phi}}{\partial q_r^2} \right)_0 + \left(\frac{\partial g_{\phi\phi}}{\partial q_r} \right)_0 \beta_r \right] \beta_r^{-2} (y_r^2 + y_{r'}^2) p_\phi^2 \\ & - \frac{1}{2} \left(\frac{\partial^2 g_{\phi\phi}}{\partial q_\phi^2} \right)_0 \beta_r^{-2} y_r y_{r'} p_\phi^2 \\ & + \frac{1}{4} \left[\left(\frac{\partial^2 g_{\phi\phi}}{\partial q_\phi^2} \right)_0 + \left(\frac{\partial g_{\phi\phi}}{\partial q_\phi} \right)_0 \beta_\phi \right] \beta_\phi^{-2} p_\phi y_\phi^2 p_\phi \\ & + \frac{1}{2} \left[\left(\frac{\partial^2 g_{rr'}}{\partial q_\phi^2} \right)_0 + \left(\frac{\partial q_{rr'}}{\partial q_\phi} \right)_0 \beta_\phi \right] \beta_\phi^{-2} p_r p_{r'} y_\phi^2 \\ & + (g_{r\phi})_0 (p_r + p_{r'}) p_\phi \\ & + \frac{1}{2} \left(\frac{\partial g_{\phi\phi}}{\partial q_\phi} \right)_0 \beta_\phi^{-1} p_\phi y_\phi p_\phi \\ & + \left(\frac{\partial g_{rr'}}{\partial q_\phi} \right)_0 \beta_\phi^{-1} p_r y_\phi p_{r'} + \left(\frac{\partial g_{r\phi}}{\partial q_{r'}} \right)_0 \beta_r^{-1} (p_r y_{r'} + p_{r'} y_r) p_\phi \end{aligned}$$

$$\begin{aligned} & + \frac{1}{4} \left(\frac{\partial^2 g_{\phi\phi}}{\partial q_\phi^2} \right)_0 \beta_r^{-1} \beta_\phi^{-1} (p_r y_{r'} + p_{r'} y_r) (y_\phi p_\phi + p_\phi y_\phi) \\ & + \frac{1}{2} \left(\frac{\partial^2 g_{\phi\phi}}{\partial q_r \partial q_\phi} \right)_0 \beta_r^{-1} (y_r + y_{r'}) p_\phi y_\phi p_\phi \\ & + \frac{1}{2} \left[\left(\frac{\partial^2 q_{r\phi}}{\partial q_r^2} \right)_0 + \left(\frac{\partial^2 g_{r\phi}}{\partial q_r} \right)_0 \beta_r \right] \beta_r^{-2} (p_r y_{r'}^2 + p_{r'} y_r^2) p_\phi \\ & + \frac{1}{2} \left[\left(\frac{\partial^2 g_{r\phi}}{\partial q_\phi^2} \right)_0 + \left(\frac{\partial g_{r\phi}}{\partial q_\phi} \right)_0 \beta_\phi \right] \beta_\phi^{-2} (p_r + p_{r'}) \\ & \quad \times \frac{(y_\phi^2 p_\phi + p_\phi y_\phi^2)}{2} + f_{rr'} \beta_r^{-2} y_r y_{r'} \\ & + \frac{1}{2} (\beta_\phi f_{r\phi} + f_{r\phi\phi}) \beta_r^{-1} \beta_\phi^{-2} (y_r + y_{r'}) y_\phi^2 \\ & + \frac{1}{4!} (11\beta_\phi^2 f_{\phi\phi} + 6\beta_\phi f_{\phi\phi\phi} + f_{\phi\phi\phi\phi}) \beta_\phi^{-4} y_\phi^4 \\ & + \frac{1}{4!} (11\beta_r^2 f_{rr} + 6\beta_r f_{rrr} + f_{rrrr}) \beta_r^{-4} (y_r^4 + y_{r'}^4) \\ & + \frac{1}{4!} 6(\beta_r \beta_\phi f_{r\phi} + \beta_\phi f_{rr\phi} + \beta_r f_{r\phi\phi} + f_{rr\phi\phi}) \\ & \quad \times \beta_r^{-2} \beta_\phi^{-2} (y_r^2 + y_{r'}^2) y_\phi^2 \\ & + \frac{1}{4!} 12(\beta_\phi f_{rr'\phi} + f_{rr'\phi\phi}) \beta_r^{-2} \beta_\phi^{-2} y_r y_{r'} y_\phi^2 \\ & + \frac{1}{4!} 6(\beta_r^2 f_{rr'} + 2\beta_r f_{rr'\phi} + f_{rrr'\phi}) \beta_r^{-4} y_r^2 y_{r'}^2 \\ & + \frac{1}{4!} 4(2\beta_r^2 f_{rr'} + 3\beta_r f_{rrr'} + f_{rrr'r'}) \beta_r^{-4} (y_r^3 + y_{r'}^3) \\ & + f_{r\phi} \beta_r^{-1} \beta_\phi^{-1} (y_r + y_{r'}) y_\phi \\ & + \frac{1}{6} (3\beta_r f_{rr} + f_{rrr}) \beta_r^{-3} (y_r^3 + y_{r'}^3) \\ & + \frac{1}{6} (3\beta_\phi f_{\phi\phi} + f_{\phi\phi\phi}) \beta_\phi^{-3} y_\phi^3 \\ & + \frac{1}{2} (\beta_r f_{rr'} + f_{rrr'}) \beta_r^{-3} (y_r y_{r'}^2 + y_r^2 y_{r'}) \\ & + \frac{1}{2} (\beta_r f_{r\phi} + f_{rr\phi}) \beta_\phi^{-1} \beta_r^{-2} (y_r^2 + y_{r'}^2) y_\phi \\ & + f_{rr'\phi} \beta_r^{-2} \beta_\phi y_r y_{r'} y_\phi \\ & + \frac{1}{4!} 4(2\beta_r^2 f_{r\phi} + 3\beta_r f_{rr\phi} + f_{rrr\phi}) \beta_r^{-3} \beta_\phi^{-1} (y_r^3 + y_{r'}^3) y_\phi \\ & + \frac{1}{4!} 4(2\beta_\phi^2 f_{r\phi} + 3\beta_\phi f_{r\phi\phi} + f_{r\phi\phi\phi}) \beta_\phi^{-3} \beta_r^{-1} (y_r + y_{r'}) y_\phi^3 \\ & + \frac{1}{4!} 12(\beta_r f_{rr'\phi} + f_{rr'\phi\phi}) \beta_r^{-3} \beta_\phi^{-1} (y_r y_{r'}^2 + y_{r'} y_r^2) y_\phi. \end{aligned} \quad (12)$$

Since we consider non-interacting Morse oscillators as the zeroth-order Hamiltonian, the natural basis to diagonalize the Hamiltonian (12) consists in a set of products of Morse functions

$$|v_r v_\phi v_{r'}\rangle = |\Psi_{v_r}^{D_s}\rangle |\Psi_{v_\phi}^{D_b}\rangle |\Psi_{v_{r'}}^{D_s}\rangle, \quad (13)$$

where v_r and $v_{r'}$ stand for the number of quanta associated to q_r and $q_{r'}$, respectively, while v_ϕ corresponds to the bending q_ϕ coordinate. Here we have introduced the notation D_s and D_b for the stretches $\{q_r, q_{r'}\}$ and the bending q_ϕ , respectively. This approach, however,

presents the inconvenience of having to deal with the full space in the diagonalization procedure; the interaction terms mix the whole space. One way to bypass this problem is by using the concept of polyad, which implies simplifications in the Hamiltonian, allowing to reduce the Hamiltonian matrix to a block form. In general the polyad can be defined on the basis of the resonances of the first overtones with the fundamentals. For H₂O the energy of the symmetric mode is approximately twice the bending energy. Hence the appropriate polyad number is defined by

$$P = 2(v_r + v_{r'}) + v_\phi = 2(v_1 + v_3) + v_2, \quad (14)$$

where we remark that P is well defined in terms of either local or normal quantum numbers. The appearance of the number of quanta v_i in (14) implies that their corresponding operators should be well defined. This is the case in a harmonic basis, where the local number operators are given by

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i, \quad i = r, r', \phi, \quad (15)$$

where

$$\hat{a}_i^\dagger = \sqrt{\frac{\mu_i \omega_i}{2\hbar}} q_i - \frac{i}{\sqrt{2\hbar \mu_i \omega_i}} \hat{p}_i, \quad (16a)$$

$$\hat{a}_i = \sqrt{\frac{\mu_i \omega_i}{2\hbar}} q_i + \frac{i}{\sqrt{2\hbar \mu_i \omega_i}} \hat{p}_i, \quad (16b)$$

with the commutation relations

$$[\hat{a}_i, \hat{a}_j^\dagger] = \delta_{ij}, \quad [\hat{a}_i, \hat{a}_j] = [\hat{a}_i^\dagger, \hat{a}_j^\dagger] = 0, \quad (17)$$

and ω_i defined in (10). In a harmonic basis $|n_r n_\phi n_{r'}\rangle$ we thus have

$$\hat{n}_i |n_r n_\phi n_{r'}\rangle = n_i |n_r n_\phi n_{r'}\rangle, \quad (18)$$

whose relation with the basis (13) is given in the harmonic limit:

$$\lim_{D_i \rightarrow \infty} |v_r v_\phi v_{r'}\rangle = |n_r n_\phi n_{r'}\rangle. \quad (19)$$

The introduction of the operators \hat{a}_i^\dagger and \hat{a}_i , makes clear whether an interaction preserves the polyad. For example, an interaction of the form $(\hat{a}_r^\dagger + \hat{a}_{r'}^\dagger) \hat{a}_\phi \hat{a}_\phi$ conserves P , but $(\hat{a}_r + \hat{a}_{r'}) \hat{a}_\phi \hat{a}_\phi$ does not. It is important to note that this interpretation is valid only when a harmonic basis is considered. In the case of the basis (13) it is still possible to expand the Hamiltonian in terms of the operators (16a) and (16b), but they cease being creation and annihilation operators, and consequently the advantage of using such operators fades. Because of the evident advantages of expressing the Hamiltonian in terms of creation and annihilation operators, it is convenient to introduce such operators in the context of Morse oscillators. This will be done in the next section. For comparison, however, we next present the form of the Hamiltonian in terms of the operators (16a) and

(16b). Since the Hamiltonian has been expanded in terms of the Morse coordinates y_i , the direct substitution in terms of the operators $\{\hat{a}_i^\dagger, \hat{a}_i\}$ leads to an infinite expansion. To simplify the problem we must consider the rigid limit (5). When this is the case we obtain a Hamiltonian with both polyad conserving and non-conserving contributions. If we neglect the contributions that do not preserve the polyad, we obtain the simple Hamiltonian [18]

$$\begin{aligned} \lim_{q_i \rightarrow 0} \hat{H} = & \hat{H}_0 + \Omega_s \left(\frac{\hat{a}_r^\dagger \hat{a}_r + \hat{a}_{r'} \hat{a}_r^\dagger + \hat{a}_{r'}^\dagger \hat{a}_{r'} + \hat{a}_\phi \hat{a}_\phi^\dagger}{2} \right) \\ & + \Omega_b \left(\frac{\hat{a}_\phi^\dagger \hat{a}_\phi + \hat{a}_\phi \hat{a}_\phi^\dagger}{2} \right) + \lambda (\hat{a}_r^\dagger \hat{a}_{r'} + \hat{a}_{r'}^\dagger \hat{a}_r) \\ & + \omega x_r (\hat{a}_r^\dagger \hat{a}_r \hat{a}_r^\dagger \hat{a}_r + \hat{a}_{r'}^\dagger \hat{a}_{r'} \hat{a}_{r'}^\dagger \hat{a}_{r'}) \\ & + \omega x_\phi (\hat{a}_\phi^\dagger \hat{a}_\phi \hat{a}_\phi^\dagger \hat{a}_\phi) + \omega x_{rr} \hat{a}_r^\dagger \hat{a}_r \hat{a}_{r'}^\dagger \hat{a}_{r'} \\ & + \omega x_{r\phi} \frac{(\hat{a}_r^\dagger \hat{a}_r + \hat{a}_r \hat{a}_r^\dagger) + (\hat{a}_{r'}^\dagger \hat{a}_{r'} + \hat{a}_{r'} \hat{a}_{r'}^\dagger)}{2} \\ & \quad \times \frac{(\hat{a}_\phi^\dagger \hat{a}_\phi + \hat{a}_\phi \hat{a}_\phi^\dagger)}{2} \\ & + \lambda^{[2]} (\hat{a}_r^\dagger \hat{a}_r^\dagger \hat{a}_{r'} \hat{a}_{r'} + \hat{a}_{r'}^\dagger \hat{a}_{r'}^\dagger \hat{a}_r \hat{a}_r) \\ & + \beta_1 \left[\frac{(\hat{a}_r^\dagger \hat{a}_r + \hat{a}_r \hat{a}_r^\dagger) + (\hat{a}_{r'}^\dagger \hat{a}_{r'} + \hat{a}_{r'} \hat{a}_{r'}^\dagger)}{2} \right. \\ & \quad \left. \times (\hat{a}_{r'}^\dagger \hat{a}_{r'} + \hat{a}_{r'} \hat{a}_{r'}^\dagger) + hc \right] \\ & + \beta_2 (\hat{a}_r^\dagger \hat{a}_{r'} + \hat{a}_{r'}^\dagger \hat{a}_r) \frac{(\hat{a}_\phi^\dagger \hat{a}_\phi + \hat{a}_\phi \hat{a}_\phi^\dagger)}{2} \\ & + F \left[(\hat{a}_r^\dagger \hat{a}_\phi \hat{a}_\phi + \hat{a}_{r'}^\dagger \hat{a}_\phi \hat{a}_\phi) \right. \\ & \quad \left. + (\hat{a}_\phi^\dagger \hat{a}_\phi^\dagger \hat{a}_r + \hat{a}_\phi^\dagger \hat{a}_\phi^\dagger \hat{a}_{r'}) \right], \quad (20) \end{aligned}$$

where the spectroscopic parameters are given in terms of the structural and potential constants by

$$\lambda = \frac{\hbar \omega_r}{2} \left[\frac{f_{rr'}}{f_{rr}} + \frac{(G_{rr'})_0}{(G_{rr})_0} \right], \quad (21a)$$

$$\Omega_s = \frac{\hbar^2}{\mu_r^2 \omega_r^2} \frac{1}{8} [f_{rrrr} + 2f_{rrr'r'}], \quad (21b)$$

$$\Omega_b = \frac{\hbar^2}{8} \left(\frac{\partial^2 G_{\phi\phi}}{\partial q_\phi^2} \right)_0, \quad (21c)$$

$$\omega x_r = \frac{1}{16} \frac{\hbar^2}{\mu_r^2 \omega_r^2} f_{rrrr}, \quad (21d)$$

$$\omega x_\phi = \frac{\hbar^2}{16} \left[\frac{1}{\mu_\phi^2 \omega_\phi^2} f_{\phi\phi\phi\phi} + \frac{1}{2} \left(\frac{\partial^2 G_{\phi\phi}}{\partial q_\phi^2} \right)_0 \right], \quad (21e)$$

$$wx_{rr} = \frac{1}{4} \frac{\hbar^2}{\mu_r^2 \omega_r^2} f_{rrr'r'}, \quad (21f)$$

$$wx_{r\phi} = \frac{\hbar^2}{16} \left[\left(\frac{\partial^2 G_{\phi\phi}}{\partial q_r^2} \right)_0 \frac{\mu_\phi \omega_\phi}{\mu_r \omega_r} + \frac{1}{\mu_r \omega_r \mu_\phi \omega_\phi} f_{rr\phi\phi} \right], \quad (21g)$$

$$\lambda^{[2]} = \frac{1}{4} \omega x_{rr}, \quad (21h)$$

$$F = \frac{\hbar}{4} \sqrt{\frac{\hbar}{2\mu_r \omega_r}} \left[\frac{f_{r\phi\phi}}{\mu_\phi \omega_\phi} - \left(\frac{\partial G_{\phi\phi}}{\partial q_r} \right)_0 \mu_\phi \omega_\phi + 2 \left(\frac{\partial G_{r\phi}}{\partial q_\phi} \right)_0 \mu_r \omega_r \right], \quad (21i)$$

$$\beta_1 = \frac{1}{6} \frac{\hbar^2}{2\mu_r^2 \omega_r^2} f_{rrr'r'}, \quad (21j)$$

$$\beta_2 = -\frac{\hbar^2}{4} \left(\frac{\partial^2 G_{\phi\phi}}{\partial q_\phi^2} \right)_0 \left[\frac{\mu_\phi \omega_\phi}{\mu_r \omega_r} + \frac{1}{2} \frac{\mu_r \omega_r}{\mu_\phi \omega_\phi} \right] + \frac{\hbar^2}{4} \frac{f_{rr'\phi\phi}}{\mu_r \omega_r \mu_\phi \omega_\phi}. \quad (21k)$$

From these expressions we notice that only 8 force constants remain, namely, $\{f_{rr'}, f_{rrrr}, f_{rrr'r'}, f_{rrr'r'}, f_{\phi\phi\phi\phi}, f_{rr\phi\phi}, f_{r\phi\phi\phi}, f_{rr'\phi\phi}\}$, which together with the Morse parameters $\{D_s, D_b, \beta_s, \beta_b\}$, constitute the set of parameters to be fitted. The number of force constant in the Hamiltonian (12), however, is 17, which means that 9 of the force constants cannot be determined in this approximation. It is then necessary either to break the polyad or go beyond the approximation (5) in order to determine the parameters. We should remark upon the constraint (21f). This equation arises as a consequence of our approximations and it is expected to be relaxed in a more general description. This situation will be considered in Section 4.

In practice all matrix elements of the interactions in (12) may be computed in a harmonic basis, while for the diagonal part a Morse oscillator basis must be considered. This approximation makes plausible the application of the polyad concept. The use of a full Morse basis to compute the interaction matrix elements breaks the polyad and there is no obvious method similar to the one leading to (20) in order to generate a polyad preserving Hamiltonian. In the next section, we establish an approach where the interaction matrix elements with respect to the Morse basis are calculated in an systematic fashion in such a way that the polyad is still preserved.

3. The $su(2)$ representation

In this section, we introduce algebraic representations of the Morse coordinate and momentum, which are based on the connection between the Morse oscillator and the $u(2)$ algebra [36]. We start by establishing the bound solutions for the Morse Potential. Choosing the

separated atoms limit as the zero of energy, the Morse potential has the following form:

$$V(x) = D(e^{-2\beta x} - 2e^{-\beta x}), \quad (22)$$

where $D > 0$ corresponds to its depth, β is related with the range of the potential, and x gives the relative distance from the equilibrium position of the atoms.

The solution of the Schrödinger equation associated to the potential (22) is given by [11]

$$\Psi_v^j(z) = N_v^j e^{-z/2} z^s L_v^{2s}(z), \quad (23)$$

where $L_v^{2s}(z)$ are the associated Laguerre functions, the argument z is related with the physical displacement coordinate x by $z = (2j+1)e^{-\beta x}$, N_v^j is the normalization constant

$$N_v^j = \sqrt{\frac{\beta(2j-2v)\Gamma(v+1)}{\Gamma(2j-v+1)}}, \quad (24)$$

and the variables j and s are related with the potential and the energy, respectively, through

$$\kappa = 2j+1 = \sqrt{\frac{8\mu D}{\beta^2 \hbar^2}}, \quad s = \sqrt{\frac{-2\mu E}{\beta^2 \hbar^2}}, \quad (25)$$

with the constraint condition

$$s = j - v, \quad (26)$$

where μ is the reduced mass of the molecule. The variable $\kappa = 2j+1$ has been introduced in order to simplify subsequent results and because it turns out to be the relevant parameter in the expansions. This variable corresponds to the Child's parameter introduced in [7]. The constraint (26) gives rise to the energy spectrum

$$E_v = -\hbar\omega_0(v-j)^2, \quad (27)$$

where

$$\omega_0 = \frac{\hbar\beta^2}{2\mu}. \quad (28)$$

It is possible to obtain an algebraic representation of the solutions (23) by introducing creation \hat{b}^\dagger and annihilation \hat{b} operators, which have the following action on the Morse functions:

$$\hat{b}^\dagger \Psi_v^j(z) = \sqrt{(v+1)(1-(v+1)/\kappa)} \Psi_{v+1}^j(z), \quad (29a)$$

$$\hat{b} \Psi_v^j(z) = \sqrt{v(1-v/\kappa)} \Psi_{v-1}^j(z), \quad (29b)$$

with

$$\hat{v} \Psi_v^j(z) = v \Psi_v^j(z). \quad (30)$$

The explicit form of these operators are obtained in [37]. We must note, however, that they are functions of the operator \hat{v} , which means that are defined in the space of solutions (23). The operators $\{b^\dagger, b\}$, together with the number operator \hat{v} , satisfy the commutation relations

$$[\hat{b}, \hat{b}^\dagger] = 1 - \frac{2\hat{v}+1}{\kappa}, \quad [\hat{v}, \hat{b}^\dagger] = \hat{b}^\dagger, \quad [\hat{v}, \hat{b}] = -\hat{b}, \quad (31)$$

which can be identified with the usual $su(2)$ commutation relations by introducing the set of transformations $\{\hat{b}^\dagger = \hat{J}_-/\sqrt{\kappa}, \hat{b} = \hat{J}_+/\sqrt{\kappa}, \hat{v} = j - \hat{J}_0\}$, where J_μ satisfy the usual “angular momentum” commutation relations [38]. The $su(2)$ group is the dynamical symmetry for the bound states for the Morse potential and any dynamical variable can be expanded in terms of the generators [16]

$$G_{su(2)} = \{\hat{b}^\dagger, \hat{b}, \hat{v}\}. \quad (32)$$

From the group theoretical point of view the parameter j labels the irreducible representations of the $su(2)$ group. The projection of the angular momentum m is related with v by [16]

$$m = v - j. \quad (33)$$

From this relation we see that the ground state ($v = 0$) corresponds to $m = -j$, while from the dissociation condition in (27)

$$j - v = 0, \quad (34)$$

the expected maximum number of quanta is $v = j$ ($m = 0$). The state corresponding to $v = j$, however, is not normalizable, and consequently

$$v_{\max} = [j], \quad (35)$$

where the notation $[j]$ stands for the closest integer to j that is smaller than j . We shall thus consider Morse potentials with $[j] + 1$ bound states. In the algebraic space the functions (23) acquire the simple form

$$|\Psi_v^j\rangle = \mathcal{N}_v^j (\hat{b}^\dagger)^v |\Psi_0^j\rangle, \quad (36)$$

with normalization constant

$$\mathcal{N}_v^j = \sqrt{\kappa^v \frac{(2j - v)!}{v!(2j)!}}. \quad (37)$$

The Morse functions are then associated to one brach (in this case to $m \leq -1$) of the $su(2)$ representations. The bound solutions (23), however, do not form a complete set of states in the Hilbert space. A complete set is obtained when the continuum part of the spectrum is taken into account [39]. Since in the present analysis the vibrational excitations are far from the dissociation limit, it is a reasonable approximation to consider the bound states as a complete space.

The realization of the Morse Hamiltonian in terms of the $su(2)$ algebra is given by

$$\hat{H} = \frac{\hbar\tilde{\omega}}{2} (\hat{b}^\dagger \hat{b} + \hat{b} \hat{b}^\dagger). \quad (38)$$

From (29a) and (29b) we obtain the corresponding eigenvalues

$$E_M(v) = \hbar\tilde{\omega} \frac{(\kappa - 1)}{\kappa} (v + 1/2) - \frac{\hbar\tilde{\omega}}{\kappa} (v + 1/2)^2, \quad (39)$$

which can now be compared with the Morse eigenvalues (9) to establish the identification

$$\hbar c \omega_e = \hbar\omega = \hbar\tilde{\omega} \frac{(\kappa - 1)}{\kappa}, \quad \hbar c \omega_e x_e = \frac{\hbar\tilde{\omega}}{\kappa}. \quad (40)$$

The values of κ and $\tilde{\omega}$ are then fixed by the potential shape.

The harmonic limit is obtained by taking the limit $\kappa \rightarrow \infty$:

$$\lim_{\kappa \rightarrow \infty} \hat{b} = \hat{a}, \quad (41a)$$

$$\lim_{\kappa \rightarrow \infty} \hat{b}^\dagger = \hat{a}^\dagger, \quad (41b)$$

while for the Morse Hamiltonian

$$\lim_{\kappa \rightarrow \infty} \hat{H} = \lim_{\kappa \rightarrow \infty} \frac{\hbar\tilde{\omega}}{2} (\hat{b}^\dagger \hat{b} + \hat{b} \hat{b}^\dagger) = \frac{\hbar\tilde{\omega}}{2} (\hat{a}^\dagger \hat{a} + \hat{a} \hat{a}^\dagger), \quad (42)$$

with eigenstates given by the harmonic functions

$$|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}} |0\rangle. \quad (43)$$

Since the set of operators (32) constitutes the dynamical algebra for the Morse potential, any dynamical variable can be expanded in terms of them. In particular we are interested in the expansion of the momenta and Morse coordinates. For the momenta the following second order expansion is obtained [14]

$$\hat{p} = \frac{i}{2} \sqrt{2\hbar\omega\mu} \left[h_v \hat{b}^\dagger - \hat{b} h_v + \frac{1}{\sqrt{\kappa}} (\hat{b} \hat{b} q_v - q_v \hat{b}^\dagger \hat{b}^\dagger) + O(1/\kappa) \right], \quad (44)$$

where h_v and q_v are functions of the operator \hat{v} . Since this operator is diagonal we can substitute \hat{v} by v , so that

$$h_v = 1 - \frac{v}{(\kappa - v)}, \quad (45a)$$

$$q_v = r_v + s_v, \quad (45b)$$

with the definitions

$$r_v = \left(\frac{3\kappa - 2(2v - 1)}{4\kappa(1 - (v - 1)/\kappa)(1 - v/\kappa)} \right), \quad (46a)$$

$$s_v = \left(\frac{\kappa - 2(2v - 1)}{4\kappa(1 - (v - 1)/\kappa)(1 - v/\kappa)} \right), \quad (46b)$$

For the Morse variable the expansion takes the form [15]

$$\frac{y}{\beta} = \sqrt{\frac{\hbar}{2\omega\mu}} \left[f_v \hat{b}^\dagger + \hat{b} f_v + \frac{1}{\sqrt{\kappa}} (f_v^d + g_v \hat{b}^\dagger \hat{b}^\dagger + \hat{b} \hat{b} g_v) + O(1/\kappa) \right], \quad (47)$$

where

$$f_v^d = 1 + 2v, \quad (48a)$$

$$f_v = \sqrt{\frac{(\kappa - 2v - 1)(\kappa - 2v + 1)}{(\kappa - v)^2}}, \quad (48b)$$

$$g_v = -\sqrt{\frac{\kappa^2(\kappa - 2v - 1)(\kappa - 2v + 3)}{(\kappa - v + 1)^2(\kappa - v)^2}}, \quad (48c)$$

On the other hand, for the x variable the expansion is given by [14]

$$x = \frac{1}{2} \sqrt{\frac{2\hbar}{\omega\mu}} \left[(2 - h_v) \hat{b}^\dagger + \hat{b}(2 - h_v) + \frac{1}{\sqrt{\kappa}} (g_v^d + q_v^d \hat{b}^\dagger \hat{b}^\dagger + \hat{b} \hat{b} q_v^d) + O(1/\kappa) \right], \quad (49)$$

where

$$\hat{q}_v^d = s_v - r_v, \quad (50)$$

with the diagonal contribution given by

$$\hat{g}_v^d = \kappa \left\{ \ln \kappa - \Phi(\kappa - 2v - 1) + \sum_{j=1}^v \frac{1}{(\kappa - v - j)} (1 - \delta_{v,0}) \right\}, \quad (51)$$

where Φ is the digamma function [40]. Combining the expressions (44) and (51) we can also obtain the expansion of the operators

$$\hat{c}_i^\dagger = \sqrt{\frac{\mu_i \omega_i}{2\hbar}} q_i - \frac{i}{\sqrt{2\hbar\mu_i\omega_i}} \hat{p}_i, \quad (52a)$$

$$\hat{c}_i = \sqrt{\frac{\mu_i \omega_i}{2\hbar}} q_i + \frac{i}{\sqrt{2\hbar\mu_i\omega_i}} \hat{p}_i. \quad (52b)$$

Although these operators have the same definition as $\{\hat{a}^\dagger, \hat{a}\}$ in (16a) and (16b), the difference between them rely on the basis upon which they act. While the operators (16a) and (16b) are intended to act over harmonic functions, the operators (54a) and (54b) are general, and their action is determined by the operators $\{q, \hat{p}\}$. We can thus substitute (44) and (49) into (52a) and (52b) in order to obtain the their representation in the $su(2)$ space. For \hat{c}^\dagger we have

$$\hat{c}^\dagger = \hat{b}^\dagger + \hat{b}(1 - \hat{h}_v) + \frac{1}{\sqrt{\kappa}} \left[\frac{g_v^d}{2} + \hat{b} \hat{b} \hat{s}_v - r_v \hat{b}^\dagger \hat{b}^\dagger \right] + O(1/\kappa), \quad (53)$$

while \hat{c} is obtained by taking its hermitian conjugate. From this result it is clear that in the Morse basis the operators are not ladder operators, although by definition are bosons. The expressions (44), (47), (49), and (53) are given in terms of a expansion of powers of the parameter $1/\sqrt{\kappa}$. Since in the harmonic limit $\kappa \rightarrow \infty$, the form of the expansions makes particularly clear the relevance of the different terms and consequently allows to carry out the harmonic limit in a straightforward way as well as to establish successive approximations. In order to achieve this task we first present the harmonic limit of the diagonal operators

$$\lim_{\kappa \rightarrow \infty} h_v = \lim_{\kappa \rightarrow \infty} f_v = \lim_{\kappa \rightarrow \infty} g_v = 1, \quad (54a)$$

$$\lim_{\kappa \rightarrow \infty} q_v = \frac{1}{2}, \quad \lim_{\kappa \rightarrow \infty} q_v' = -\frac{1}{2}. \quad (54b)$$

These results lead to the harmonic limit

$$\lim_{\kappa \rightarrow \infty} \hat{p} = \frac{i}{2} \sqrt{2\hbar\omega\mu} [\hat{a}^\dagger - \hat{a}], \quad (55a)$$

$$\lim_{\kappa \rightarrow \infty} \frac{y}{\beta} = \lim_{\kappa \rightarrow \infty} x = \sqrt{\frac{\hbar}{2\omega\mu}} [\hat{a}^\dagger + \hat{a}], \quad (55b)$$

$$\lim_{\kappa \rightarrow \infty} \hat{c}^\dagger = \hat{a}^\dagger. \quad (55c)$$

The importance of the expansions we have presented is that they provide different approximations, which may be useful depending of the parameter κ . Let us suppose that κ is large but finite. In this case the anharmonic effect can be taken into account through

$$\hat{c}^\dagger \simeq \hat{b}^\dagger \quad (56)$$

and consequently

$$p \simeq \frac{i}{2} \sqrt{2\hbar\omega\mu} [\hat{b}^\dagger - \hat{b}] \quad (57a)$$

$$\frac{y}{\beta} = x \simeq \sqrt{\frac{\hbar}{2\omega\mu}} [\hat{b}^\dagger + \hat{b}]. \quad (57b)$$

This is the simplest approximation beyond the harmonic limit, and takes into account the anharmonic effects through the leading terms in the Morse matrix elements [14]. This approximation is equivalent to carry out the substitution $\hat{a}^\dagger \rightarrow \hat{b}^\dagger$ in (20). We could thus work in the harmonic scheme and at the end the above substitution allows to take into account the effect of the Morse basis in the interactions, which represent an improvement to the Child's model.

As the parameter κ diminishes, the anharmonic effects becomes more important and eventually the diagonal operators as well as the terms of order $1/\sqrt{\kappa}$ become relevant. This fact can be established by analyzing the behavior of the diagonal functions. In Figs. 1–3 we display the different diagonal operators as a function of the number of quanta for different values of the parameter κ . We have included the results for the values $\kappa = 83, 43,$ and 23 . Except for f_v^d , which is independent of κ , the curves approach the harmonic limit as the parameter κ increases. For high number of quanta, however, the anharmonic effects become patent, which makes clear the need to include the second order terms in the expansions. Remarkable differences between the functions involved in the expansion of x and y/β should be appreciated. While the absolute value of g_v^d and q_v^d (involved in x) increases exponentially as the number of quanta approach to the dissociation limit, the deviation with respect to the harmonic limit of the functions f_v^d and g_v are moderate. This difference reflects the better convergence of the Morse variable y , in

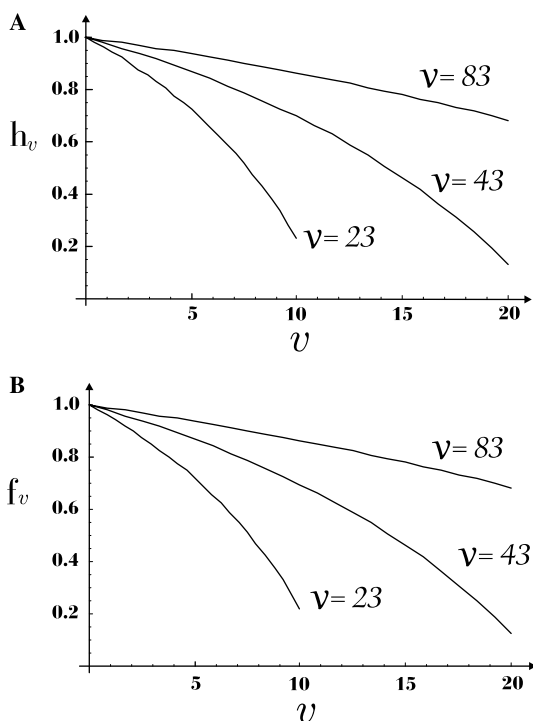


Fig. 1. Diagonal contributions h_v and f_v involved in the linear terms of the expansions (44) and (47), respectively.

contrast to the coordinate x . We next establish a tensorial formalism to express the Hamiltonian (12) in terms of the expansions (44) and (47).

4. Symmetry adapted scheme

The diagonalization of the Hamiltonian (12) gives rise to the set of eigenfunctions carrying irreducible representations of the symmetry group, as established by Wigner's theorem [41]. In our case the eigenstates are linear combinations of the local functions (13). In practice, however, in order to optimize the procedure as well as to facilitate the identification of the functions with the normal mode scheme, a change of basis before the diagonalization is required. The new basis should carry quantum numbers isomorphic to the normal quanta, as well as irreducible representations of the symmetry group. A basis with these characteristics can be constructed in several ways, but the most efficient approach consists in a combination of the eigenfunction method developed by Chen [42] and the diagonalization of the symmetry adapted number operators in a harmonic basis. This approach is explained in detail in [43,44]. Here we shall only present the relevant aspects concerning the symmetry adapted basis.

The generation of a symmetry adapted functions carrying labels isomorphic to the normal labels represents a simple task in the harmonic limit. To show this we define the symmetry adapted operators

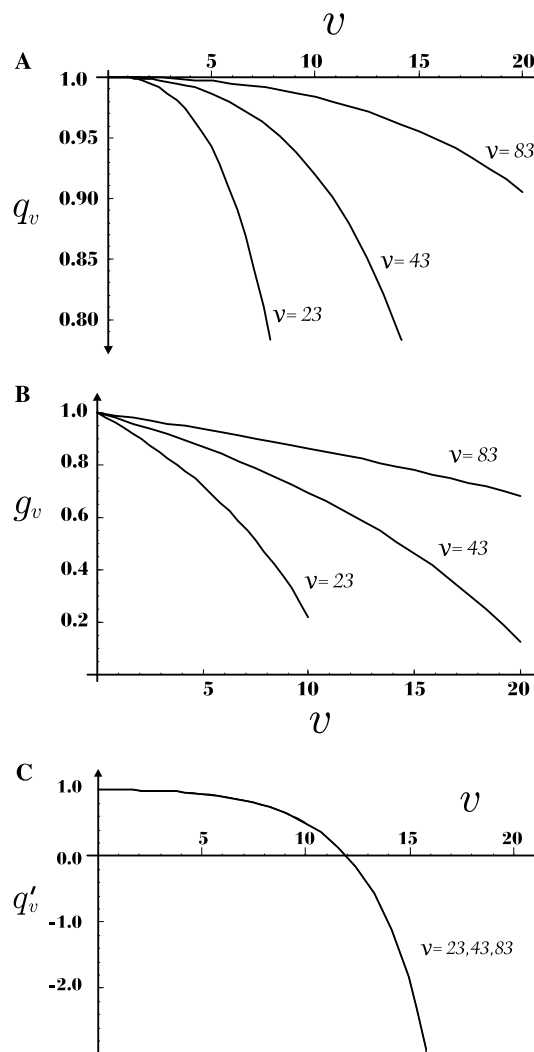


Fig. 2. Diagonal contributions q_v , g_v , and q'_v involved in the quadratic terms of the expansions (44), (47), and (49), respectively.

$$\hat{a}_{A,s}^\dagger = \frac{1}{\sqrt{2}} (\hat{a}_r^\dagger + \hat{a}_\nu^\dagger), \quad (58a)$$

$$\hat{a}_{A,b}^\dagger = \hat{a}_\phi^\dagger, \quad (58b)$$

$$\hat{a}_{B,s}^\dagger = \frac{1}{\sqrt{2}} (\hat{a}_r^\dagger - \hat{a}_\nu^\dagger), \quad (58c)$$

where the set $\{\hat{a}_r^\dagger, \hat{a}_\nu^\dagger, \hat{a}_\phi^\dagger\}$ is defined by (16a) and (16b) and the subindices s, b stand for stretching and bending, respectively. The transformation (58a)–(58c) is canonical, and consequently the symmetry adapted operators together with their hermitian conjugates satisfy the commutation relations for bosons. The harmonic basis for any number of quanta in terms of such operators is then given by

$$|\bar{n}_1 \bar{n}_2 \bar{n}_3\rangle^r = \frac{1}{\sqrt{\bar{n}_1! \bar{n}_2! \bar{n}_3!}} (\hat{a}_{A,s}^\dagger)^{\bar{n}_1} (\hat{a}_{A,b}^\dagger)^{\bar{n}_2} (\hat{a}_{B,s}^\dagger)^{\bar{n}_3} |0\rangle, \quad (59)$$

where $\{\bar{n}_1, \bar{n}_2, \bar{n}_3\}$ correspond to the eigenvalues of the operators

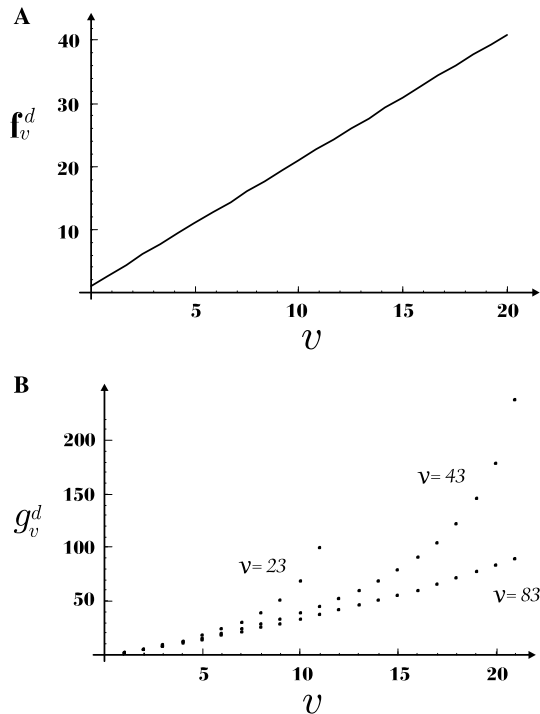


Fig. 3. Diagonal contributions f_v^d and g_v^d involved in the expansions (47) and (49), respectively.

$$\hat{n}_1 = a_{A,s}^\dagger a_{A,s}; \quad \hat{n}_2 = a_{A,b}^\dagger a_{A,b}; \quad \hat{n}_3 = a_{B,s}^\dagger a_{B,s}. \quad (60)$$

The irrep Γ in (59) is obtained by simple direct products. It is then clear that the basis (60) is isomorphic to the normal basis

$$|v_1 v_2 v_3\rangle \approx |\bar{n}_1 \bar{n}_2 \bar{n}_3\rangle. \quad (61)$$

In terms of the harmonic local basis, the states (59) take the general form

$$|\bar{n}_1 \bar{n}_2 \bar{n}_3\rangle^\Gamma = \sum_{\{n_i\}} A_{\{\bar{n}_i\}}^{\{n_i\}} |\{n_i\}\rangle, \quad (62)$$

where $|\{n_i\}\rangle$ are defined by (18) and the coefficients $A_{\{\bar{n}_i\}}^{\{n_i\}}$ are obtained either by expanding the operators (58a)–(58c) in (59) or through group theoretical techniques [43].

We can construct an orthonormal symmetry adapted basis in terms of the local anharmonic set (13) by simply applying the correspondence $\hat{a}^\dagger \rightarrow \hat{b}^\dagger$:

$$|[\kappa_s, \kappa_b]; \bar{v}_1 \bar{v}_2 \bar{v}_3\rangle = \sum_{\{\bar{v}_i\}} A_{\{\bar{v}_i\}}^{\{v_i\}} |[\kappa_i]\{v_i\}\rangle, \quad (63)$$

where the labels $\{\bar{v}_i\}$ have the same association as the harmonic labels $\{n_i\}$ and $|[\kappa_i]\{v_i\}\rangle$ is a shorthand notation for (13). The coefficients satisfy

$$A_{\{\bar{v}_i\}}^{\{v_i\}} = A_{\{\bar{n}_i\}}^{\{n_i\}}, \quad (64)$$

a simple result which is a consequence of the correspondence

$$\lim_{\kappa \rightarrow \infty} |[\kappa_i]\{v_i\}\rangle = |\{n_i\}\rangle, \quad (65)$$

and the orthonormality of both (13) and $|\{n_i\}\rangle$. The states (63) do not correspond to the normal basis, but are isomorphic to it. The eigenfunctions of the Hamiltonian (12) can thus be expressed in terms of an expansion of the form

$$\psi_\alpha = \sum_{\{\bar{v}_i\}} C_{\{\bar{v}_i\}}^j |[\kappa_s, \kappa_b] \bar{v}_1 \bar{v}_2 \bar{v}_3\rangle, \quad (66)$$

which are labeled by the state associated to the maximum contribution in (66). The substitution of (63) into (66) provides the eigenstates in terms of the local basis (13).

In any system the symmetrization comprises both the basis and the operators. In particular, the Hamiltonian by definition is totally symmetric. Although by construction this is the case for (12), we can make it explicit by expressing the Hamiltonian in terms of symmetry adapted tensors coupled to the totally symmetric irreducible representation. Since we intend to express the Hamiltonian in the $su(2)$ representation, it is convenient to introduce symmetry adapted tensors in terms of the different contributions to the expansions (44) and (47). For tensors related to the Morse coordinates we define

$$\hat{Y}_{0,x}^\Gamma = \sum_i \alpha_{x,i}^\Gamma f_{v,i}^d, \quad (67a)$$

$$\hat{Y}_{1,x}^{\Gamma\dagger} = \sum_i \alpha_{x,i}^\Gamma f_{v,i}^d \hat{b}_i^\dagger, \quad (67b)$$

$$\hat{Y}_{2,x}^{\Gamma\dagger} = \sum_i \alpha_{x,i}^\Gamma g_{v,i}^d \hat{b}_i^\dagger \hat{b}_i^\dagger, \quad (67c)$$

while for the momenta

$$\hat{P}_{1,x}^{\Gamma\dagger} = \sum_i \alpha_{x,i}^\Gamma h_{v,i} \hat{b}_i^\dagger, \quad (68a)$$

$$\hat{P}_{2,x}^{\Gamma\dagger} = \sum_i \alpha_{x,i}^\Gamma q_{v,i} \hat{b}_i^\dagger \hat{b}_i^\dagger, \quad (68b)$$

where the subindex $x = s, b$ was included in order to distinguish tensors arising from the stretching and bending degrees of freedom, respectively, and the coefficients $\alpha_{x,i}^\Gamma$ are obtained using projection techniques [45]. In general they coincide with the factors appearing in the symmetry adapted functions for one quantum, e.g., in this case the coefficients are obtained directly from (58a)–(58c). Note that the same coefficients are assigned to all tensors, independently of their order and nature (coordinate or momenta). Because of the limits (54a) the tensors $\hat{Y}_{1,x}^{\Gamma\dagger}$ and $\hat{P}_{1,x}^{\Gamma\dagger}$ coincide in the approximation (57a) and (57b):

$$\lim_{\kappa \rightarrow \text{large}} \hat{Y}_{1,x}^{\Gamma\dagger} = \lim_{\kappa \rightarrow \text{large}} \hat{P}_{1,x}^{\Gamma\dagger} = \hat{T}_x^{\Gamma\dagger}, \quad (69)$$

where

$$\hat{T}_s^{\Gamma\dagger} = \frac{1}{\sqrt{2}} (\hat{b}_r^\dagger + \hat{b}_r^\dagger), \quad (70a)$$

$$\hat{T}_b^{\Gamma\dagger} = \hat{b}_\phi^\dagger, \quad (70b)$$

$$\hat{T}_s^{B\dagger} = \frac{1}{\sqrt{2}} (\hat{b}_r^\dagger - \hat{b}_r^\dagger). \quad (70c)$$

Similar expressions are obtained for the hermitian conjugate operators. Note that the tensors (67a) are hermitian and consequently their adjoint are not needed. The tensors (70a)–(70c) correspond to the same tensors introduced in the symmetry adapted version of the vibron model [45].

When the expressions (44) and (47) are substituted into (12), each term of the Hamiltonian will be given in terms of an expansion in powers of the parameter $1/\sqrt{\kappa}$, which according to the approximation, range from $(1/\sqrt{\kappa})^0$ to $1/\kappa^2$. If we restrict ourselves to keep only the polyad conserving terms, not all these powers appear. Concerning the interactions leading to the Hamiltonian

(20) there is always a contribution of zeroth-order, but for interactions which do not contribute to (20), only some terms ranging from $(1/\sqrt{\kappa})$ to $1/\kappa^2$ appear. This situation is best reflected in the tensorial formalism.

As mentioned above, we could introduced directly the expansions (44) and (47) into (12), and express the Hamiltonian in term of the $su(2)$ generators for each oscillator, in similar form to the procedure followed to obtain the Hamiltonian (20). Instead we shall invoke the symmetry adapted tensors (67a)–(67c) and (68a) and (68b), in order to make clear the invariance of the Hamiltonian as well as the order of the interactions. To simplify the Hamiltonian we shall keep only terms up to order $(1/\sqrt{\kappa})$, or up to $(1/\kappa)$ when necessary. Hence in terms of symmetry adapted tensors, the Hamiltonian (12) takes the form

$$\begin{aligned} \hat{H} = & \hat{H}_0 - x_1 \left[(\mathcal{P}_{1,s}^{A\dagger} \mathcal{P}_{1,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{P}_{1,s}^B) \right] - x_2 \sqrt{2} \left[\mathcal{Y}_{1,s}^{A\dagger} \mathcal{P}_{1,b}^A \mathcal{P}_{1,b}^A + \frac{1}{\sqrt{\kappa}} \mathcal{Y}_{0,s}^A \mathcal{P}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^A + hc \right] - x_3 \left[\mathcal{P}_{1,s}^{A\dagger} (\mathcal{Y}_{1,b}^A \mathcal{P}_{1,b}^A + \mathcal{P}_{1,b}^A \mathcal{Y}_{1,b}^A) + hc \right] \\ & - x_4 \left[(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B) \mathcal{P}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^A - \frac{1}{\sqrt{\kappa}} \left\{ (\mathcal{Y}_{0,s}^A \mathcal{Y}_{1,s}^{A\dagger} + \mathcal{Y}_{0,s}^B \mathcal{Y}_{1,s}^{B\dagger}) \mathcal{P}_{1,b}^A \mathcal{P}_{1,b}^A + (\mathcal{Y}_{0,s}^A \mathcal{Y}_{1,s}^A + \mathcal{Y}_{0,s}^B \mathcal{Y}_{1,s}^B) \mathcal{P}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^{A\dagger} \right. \right. \\ & \left. \left. + (\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{2,s}^A + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{2,s}^B) \mathcal{P}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^{A\dagger} + (\mathcal{Y}_{1,s}^A \mathcal{Y}_{2,s}^{A\dagger} + \mathcal{Y}_{1,s}^B \mathcal{Y}_{2,s}^{B\dagger}) \mathcal{P}_{1,b}^A \mathcal{P}_{1,b}^A + hc \right\} \right] \\ & - x_5 \left[(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A - \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B) (\mathcal{P}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^A + \mathcal{P}_{1,b}^A \mathcal{P}_{1,b}^{A\dagger}) - \frac{1}{\sqrt{\kappa}} \left\{ (\mathcal{Y}_{0,s}^A \mathcal{Y}_{1,s}^{A\dagger} - \mathcal{Y}_{0,s}^B \mathcal{Y}_{1,s}^{B\dagger}) \mathcal{P}_{1,b}^A \mathcal{P}_{1,b}^A \right. \right. \\ & \left. \left. + (\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{2,s}^A - \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{2,s}^B) \mathcal{P}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^{A\dagger} + hc \right\} \right] \\ & + x_6 \left[\left\{ \mathcal{P}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^A \mathcal{Y}_{1,b}^A \mathcal{P}_{1,b}^{A\dagger} + hc \right\} - \mathcal{P}_{1,b}^{A\dagger} (\mathcal{Y}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^A + \mathcal{Y}_{1,b}^A \mathcal{Y}_{1,b}^{A\dagger}) \mathcal{P}_{1,b}^A - \mathcal{P}_{1,b}^A (\mathcal{Y}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^A + \mathcal{Y}_{1,b}^A \mathcal{Y}_{1,b}^{A\dagger}) \mathcal{P}_{1,b}^{A\dagger} \right] \\ & - x_7 \left[(\mathcal{P}_{1,s}^{A\dagger} \mathcal{P}_{1,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{P}_{1,s}^B) (\mathcal{Y}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^A - \mathcal{Y}_{1,b}^A \mathcal{Y}_{1,b}^{A\dagger}) - \frac{1}{\sqrt{\kappa}} \left\{ \mathcal{P}_{1,s}^{A\dagger} \mathcal{P}_{2,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{P}_{2,s}^B \right\} \mathcal{Y}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^A + hc \right] \\ & + x_8 \sqrt{2} \left[\frac{1}{\sqrt{\kappa}} (\mathcal{P}_{1,s}^{A\dagger} \mathcal{P}_{2,b}^A + \mathcal{P}_{1,s}^A \mathcal{P}_{2,b}^{A\dagger}) \right] \\ & - x_9 \left[\frac{1}{\sqrt{\kappa}} \left\{ \mathcal{P}_{1,b}^{A\dagger} \mathcal{Y}_{0,b}^A \mathcal{P}_{1,b}^A + \mathcal{P}_{1,b}^A \mathcal{Y}_{0,b}^A \mathcal{P}_{1,b}^{A\dagger} - \left[\mathcal{P}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^{A\dagger} \mathcal{P}_{2,b}^A + \mathcal{P}_{1,b}^{A\dagger} \mathcal{Y}_{2,b}^A \mathcal{P}_{1,b}^{A\dagger} + \mathcal{P}_{1,b}^A \mathcal{Y}_{1,b}^A \mathcal{P}_{2,b}^{A\dagger} + hc \right] \right\} \right] \\ & + x_{10} \left[\frac{1}{\sqrt{\kappa}} (\mathcal{P}_{1,s}^{A\dagger} \mathcal{P}_{1,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{P}_{1,s}^B) \mathcal{Y}_{0,b}^A \right] \\ & + x_{11} \left[\frac{1}{\kappa} \left\{ (\mathcal{P}_{1,s}^{A\dagger} \mathcal{Y}_{0,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{Y}_{0,s}^B) \mathcal{P}_{2,b}^A + (\mathcal{P}_{1,s}^{A\dagger} \mathcal{Y}_{2,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{Y}_{2,s}^B) \mathcal{P}_{2,b}^{A\dagger} + (\mathcal{P}_{2,s}^{A\dagger} \mathcal{Y}_{1,s}^A - \mathcal{P}_{2,s}^{B\dagger} \mathcal{Y}_{1,s}^B) \mathcal{P}_{2,b}^A + hc \right\} \right] \\ & + x_{12} \left[(\mathcal{P}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B) \left[(\mathcal{P}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^A + \mathcal{Y}_{1,b}^A \mathcal{P}_{1,b}^{A\dagger}) - (\mathcal{Y}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^A - \mathcal{P}_{1,b}^A \mathcal{Y}_{1,b}^{A\dagger}) \right] + \frac{1}{\sqrt{\kappa}} \left\{ (\mathcal{P}_{2,s}^{A\dagger} \mathcal{Y}_{1,s}^A - \mathcal{P}_{2,s}^{B\dagger} \mathcal{Y}_{1,s}^B) \right. \right. \\ & \left. \left. + (\mathcal{P}_{1,s}^A \mathcal{Y}_{2,s}^{A\dagger} - \mathcal{P}_{1,s}^B \mathcal{Y}_{2,s}^{B\dagger}) - (\mathcal{P}_{1,s}^{A\dagger} \mathcal{Y}_{0,s}^A - \mathcal{P}_{1,s}^{B\dagger} \mathcal{Y}_{0,s}^B) \right\} (\mathcal{Y}_{1,b}^A \mathcal{P}_{1,b}^A + \mathcal{P}_{1,b}^A \mathcal{Y}_{1,b}^A) + hc \right] \\ & + x_{13} \sqrt{2} \left[\frac{1}{\sqrt{\kappa}} \left\{ \mathcal{Y}_{1,s}^{A\dagger} \left[(\mathcal{P}_{1,b}^{A\dagger} \mathcal{Y}_{1,b}^A \mathcal{P}_{2,b}^A + \mathcal{P}_{2,b}^A \mathcal{Y}_{1,b}^A \mathcal{P}_{1,b}^{A\dagger}) - (\mathcal{P}_{1,b}^A \mathcal{Y}_{2,b}^A \mathcal{P}_{1,b}^{A\dagger} + \mathcal{P}_{1,b}^{A\dagger} \mathcal{Y}_{2,b}^A \mathcal{P}_{1,b}^A) \right. \right. \right. \\ & \left. \left. - (\mathcal{P}_{1,b}^A \mathcal{Y}_{1,b}^{A\dagger} \mathcal{P}_{2,b}^A + \mathcal{P}_{2,b}^A \mathcal{Y}_{1,b}^{A\dagger} \mathcal{P}_{1,b}^A) + \mathcal{P}_{1,b}^A \mathcal{Y}_{0,b}^A \mathcal{P}_{1,b}^A \right] + hc \right\} \right] \\ & + x_{14} \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{\kappa}} \left\{ \mathcal{P}_{1,s}^{A\dagger} (\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B) \mathcal{P}_{2,b}^A - \mathcal{P}_{1,s}^{B\dagger} (\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^A) \mathcal{P}_{2,b}^A + \mathcal{P}_{1,s}^A (\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^{A\dagger} + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^{B\dagger}) \mathcal{P}_{2,b}^{A\dagger} \right. \right. \\ & \left. \left. - \mathcal{P}_{1,s}^B (\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^{B\dagger} + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^{A\dagger}) \mathcal{P}_{2,b}^{A\dagger} + \mathcal{P}_{1,s}^{B\dagger} (\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^A) \mathcal{P}_{2,b}^{A\dagger} - \mathcal{P}_{1,s}^{A\dagger} (\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^B) \mathcal{P}_{2,b}^{A\dagger} + hc \right\} \right] \end{aligned}$$

$$\begin{aligned}
 & - \mathcal{Y}_{1,s}^B \left(\mathcal{Y}_{0,s}^A \mathcal{Y}_{1,s}^{B\dagger} + \mathcal{Y}_{0,s}^B \mathcal{Y}_{1,s}^{A\dagger} \right) + \mathcal{Y}_{1,s}^{A\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{2,s}^A + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{2,s}^B \right) - \mathcal{Y}_{1,s}^{B\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{2,s}^B + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{2,s}^A \right) + \mathcal{Y}_{1,s}^{A\dagger} \left(\mathcal{Y}_{2,s}^A \mathcal{Y}_{1,s}^{A\dagger} + \mathcal{Y}_{2,s}^B \mathcal{Y}_{1,s}^{B\dagger} \right) \\
 & - \mathcal{Y}_{1,s}^{B\dagger} \left(\mathcal{Y}_{2,s}^A \mathcal{Y}_{1,s}^{B\dagger} + \mathcal{Y}_{2,s}^B \mathcal{Y}_{1,s}^{A\dagger} \right) + \mathcal{Y}_{2,s}^{A\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^B \right) - \mathcal{Y}_{2,s}^{B\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^A \right) + hc \left. \right\} \\
 & + z_{13} \left[\frac{1}{\sqrt{K}} \left(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^{A\dagger} + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^{B\dagger} \right) \mathcal{Y}_{0,b}^A \right] \\
 & + z_{14} \left[\frac{1}{\sqrt{K}} \left(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A - \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B \right) \mathcal{Y}_{0,b}^A \right] \\
 & + z_{15} \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{K}} \left\{ \mathcal{Y}_{1,s}^{A\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^{A\dagger} + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^{B\dagger} \right) \mathcal{Y}_{2,b}^A + \mathcal{Y}_{1,s}^{B\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^{B\dagger} + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^{A\dagger} \right) \mathcal{Y}_{2,b}^B \right. \right. \\
 & \quad \left. \left. + \mathcal{Y}_{1,s}^A \left(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B \right) \mathcal{Y}_{2,b}^A + \mathcal{Y}_{1,s}^B \left(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^A \right) \mathcal{Y}_{2,b}^B + hc \right\} \right] \\
 & + z_{16} \sqrt{2} \left[\frac{1}{\sqrt{K}} \left\{ \mathcal{Y}_{1,s}^{A\dagger} \left[\mathcal{Y}_{1,b}^A \left(\mathcal{Y}_{1,b}^A \mathcal{Y}_{2,b}^A + \mathcal{Y}_{2,b}^A \mathcal{Y}_{1,b}^A \right) + \mathcal{Y}_{2,b}^A \left(\mathcal{Y}_{1,b}^A \mathcal{Y}_{1,b}^A + \mathcal{Y}_{1,b}^A \mathcal{Y}_{1,b}^{A\dagger} \right) \right. \right. \right. \\
 & \quad \left. \left. + \mathcal{Y}_{1,b}^A \left(\mathcal{Y}_{1,b}^{A\dagger} \mathcal{Y}_{2,b}^A + \mathcal{Y}_{2,b}^A \mathcal{Y}_{1,b}^{A\dagger} + \mathcal{Y}_{0,b}^A \mathcal{Y}_{1,b}^A + \mathcal{Y}_{1,b}^A \mathcal{Y}_{0,b}^A \right) + \mathcal{Y}_{0,b}^A \mathcal{Y}_{1,b}^A \mathcal{Y}_{1,b}^A \right] + hc \right\} \right] \\
 & + z_{17} \frac{1}{\sqrt{2}} \left[\frac{1}{\sqrt{K}} \left\{ \mathcal{Y}_{1,s}^{A\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^{A\dagger} + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^{B\dagger} \right) - \mathcal{Y}_{1,s}^{B\dagger} \left(\mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^B \mathcal{Y}_{1,s}^{A\dagger} + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^A \mathcal{Y}_{1,s}^{B\dagger} \right) \right. \right. \\
 & \quad \left. \left. + \mathcal{Y}_{1,s}^A \left(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^A + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^B \right) - \mathcal{Y}_{1,s}^B \left(\mathcal{Y}_{1,s}^{A\dagger} \mathcal{Y}_{1,s}^B + \mathcal{Y}_{1,s}^{B\dagger} \mathcal{Y}_{1,s}^A \right) \right\} \mathcal{Y}_{2,b}^A + hc \right]. \tag{71}
 \end{aligned}$$

In Tables 1 and 2 are given the coefficients with their the associated interactions. In spite of the apparent complexity of the Hamiltonian (71), the form of the tensorial expansion is very enlightening. On one hand it makes clear the order of the interaction involved in each

term, and on the other hand provides the type of the additional interactions which are taken into account when the polyad is conserved. Concerning the potential

Table 1
Coefficients involved in the Hamiltonian (71) associated to the interactions of the kinetic energy

Interaction	Coefficient
$P_r P_r$	$x_1 = -\frac{\hbar}{2} (g_{rr'})_0 \omega_r \mu_r$
$(Y_r + Y_r') P_\phi^2$	$x_2 = -\frac{\hbar}{4} \left(\frac{\partial g_{\phi\phi}}{\partial q_r} \right)_0 \omega_\phi \mu_\phi \sqrt{\frac{\hbar}{2\mu_r \omega_r}}$
$(P_r + P_r') \frac{(Y_\phi P_\phi + P_\phi Y_\phi)}{2}$	$x_3 = -\frac{\hbar}{4} \left(\frac{\partial g_{r\phi}}{\partial q_\phi} \right)_0 \sqrt{\frac{\hbar \omega_r \mu_r}{2}}$
$(Y_r^2 + Y_r'^2) P_\phi^2$	$x_4 = -\frac{\hbar^2}{16} \left[\left(\frac{\partial^2 g_{\phi\phi}}{\partial q_r^2} \right)_0 + \left(\frac{\partial g_{\phi\phi}}{\partial q_r} \right)_0 \beta_r \right] \frac{\omega_\phi \mu_\phi}{\omega_r \mu_r}$
$Y_r Y_r' P_\phi^2$	$x_5 = \frac{\hbar^2}{8} \left(\frac{\partial^2 g_{\phi\phi}}{\partial q_r^2} \right)_0 \frac{\omega_\phi \mu_\phi}{\omega_r \mu_r}$
$P_\phi Y_\phi^2 P_\phi$	$x_6 = -\frac{\hbar^2}{16} \left[\left(\frac{\partial^2 g_{\phi\phi}}{\partial q_\phi^2} \right)_0 + \left(\frac{\partial g_{\phi\phi}}{\partial q_\phi} \right) \beta_\phi \right]$
$P_r P_r' Y_\phi^2$	$x_7 = \frac{\hbar^2}{8} \left[\left(\frac{\partial^2 g_{r\phi}}{\partial q_\phi^2} \right)_0 + \left(\frac{\partial g_{r\phi}}{\partial q_\phi} \right) \beta_\phi \right] \frac{\omega_r \mu_r}{\omega_\phi \mu_\phi}$
$(P_r + P_r') P_\phi$	$x_8 = -\frac{\hbar}{2} (g_{r\phi})_0 \sqrt{\omega_r \mu_r \omega_\phi \mu_\phi}$
$P_\phi Y_\phi P_\phi$	$x_9 = -\frac{\hbar}{2} \left(\frac{\partial g_{\phi\phi}}{\partial q_\phi} \right) \sqrt{\frac{\hbar \omega_\phi \mu_\phi}{2}}$
$P_r Y_\phi P_r$	$x_{10} = -\frac{\hbar}{2} \left(\frac{\partial g_{rr'}}{\partial q_\phi} \right)_0 \omega_r \mu_r \sqrt{\frac{\hbar}{2\omega_\phi \mu_\phi}}$
$(P_r Y_r + P_r' Y_r') P_\phi$	$x_{11} = -\frac{\hbar}{4} \left(\frac{\partial g_{r\phi}}{\partial q_r} \right)_0 \sqrt{2\hbar \omega_\phi \mu_\phi}$
$(P_r Y_r + P_r' Y_r') (Y_\phi P_\phi + P_\phi Y_\phi)$	$x_{12} = -\frac{\hbar^2}{16} \left(\frac{\partial^2 g_{\phi\phi}}{\partial q_\phi^2} \right)_0$
$(Y_r + Y_r') P_\phi Y_\phi P_\phi$	$x_{13} = -\frac{\hbar^2}{8} \left(\frac{\partial^2 g_{\phi\phi}}{\partial q_r \partial q_\phi} \right)_0 \sqrt{\frac{\omega_\phi \mu_\phi}{\omega_r \mu_r}}$
$(P_r Y_r^2 + P_r' Y_r'^2) P_\phi$	$x_{14} = -\frac{\hbar^2}{8} \left[\left(\frac{\partial^2 g_{r\phi}}{\partial q_r^2} \right)_0 + \left(\frac{\partial g_{r\phi}}{\partial q_r} \right)_0 \beta_r \right] \sqrt{\frac{\omega_\phi \mu_\phi}{\omega_r \mu_r}}$
$(P_r + P_r') \frac{(Y_\phi P_\phi + P_\phi Y_\phi)}{2}$	$x_{15} = -\frac{\hbar^2}{16} \left[\left(\frac{\partial^2 g_{r\phi}}{\partial q_r^2} \right)_0 + \left(\frac{\partial g_{r\phi}}{\partial q_r} \right) \beta_r \right] \sqrt{\frac{\omega_r \mu_r}{\omega_\phi \mu_\phi}}$

Table 2
Coefficients involved in the Hamiltonian (71) associated to the interactions of the potential energy

Interaction	Coefficient
$Y_r Y_r'$	$z_1 = \frac{\hbar}{2} f_{rr'} \frac{1}{\omega_r \mu_r}$
$(Y_r + Y_r') Y_\phi^2$	$z_2 = \frac{\hbar}{4} (\beta_\phi f_{r\phi} + f_{r\phi\phi}) \frac{1}{\omega_\phi \mu_\phi} \sqrt{\frac{\hbar}{\omega_r \mu_r}}$
Y_ϕ^4	$z_3 = \frac{\hbar^2}{4!} (11\beta_\phi^2 f_{\phi\phi\phi} + 6\beta_\phi f_{\phi\phi\phi\phi} + f_{\phi\phi\phi\phi\phi}) \frac{1}{4\omega_\phi^3 \mu_\phi^3}$
$(Y_r^A + Y_r'^A)$	$z_4 = \frac{\hbar^2}{4!} (11\beta_r^2 f_{rrr} + 6\beta_r f_{rrr'} + f_{rrrr'}) \frac{1}{4\omega_r^3 \mu_r^3}$
$(Y_r^2 + Y_r'^2) Y_\phi^2$	$z_5 = \frac{\hbar^2}{16} (\beta_r \beta_\phi f_{r\phi} + \beta_\phi f_{rr\phi} + \beta_r f_{r\phi\phi} + f_{rr\phi\phi}) \frac{1}{\omega_r \mu_r \omega_\phi \mu_\phi}$
$Y_r Y_r' Y_\phi^2$	$z_6 = \frac{\hbar^2}{8} (\beta_\phi f_{rr'\phi} + f_{rr'\phi\phi}) \frac{1}{\omega_r \mu_r \omega_\phi \mu_\phi}$
$Y_r^2 Y_r'^2$	$z_7 = \frac{\hbar^2}{16} (\beta_r^2 f_{rrr} + 2\beta_r f_{rrr'} + f_{rrr'r'}) \frac{1}{\omega_r^3 \mu_r^3}$
$(Y_r Y_r^3 + Y_r' Y_r'^3)$	$z_8 = \frac{\hbar^2}{4!} (2\beta_r^2 f_{rrr} + 3\beta_r f_{rrr'} + f_{rrr'r'}) \frac{1}{\omega_r^3 \mu_r^3}$
$(Y_r + Y_r') Y_\phi$	$z_9 = \frac{1}{2} f_{r\phi} \frac{\hbar}{\sqrt{\omega_r \mu_r \omega_\phi \mu_\phi}}$
$(Y_r^3 + Y_r'^3)$	$z_{10} = \frac{\hbar}{12} (3\beta_r f_{rrr} + f_{rrr'}) \frac{1}{\omega_r \mu_r} \sqrt{\frac{\hbar}{2\omega_r \mu_r}}$
Y_ϕ^3	$z_{11} = \frac{\hbar}{12} (3\beta_\phi f_{\phi\phi\phi} + f_{\phi\phi\phi\phi}) \frac{1}{\omega_\phi \mu_\phi} \sqrt{\frac{\hbar}{2\omega_\phi \mu_\phi}}$
$(Y_r Y_r^2 + Y_r' Y_r'^2)$	$z_{12} = \frac{\hbar}{4} (\beta_r f_{rrr} + f_{rrr'}) \frac{1}{\omega_r \mu_r} \sqrt{\frac{\hbar}{2\omega_r \mu_r}}$
$(Y_r^2 + Y_r'^2) Y_\phi$	$z_{13} = \frac{\hbar}{4} (\beta_r f_{r\phi} + f_{rr\phi}) \frac{1}{\omega_r \mu_r} \sqrt{\frac{\hbar}{2\omega_\phi \mu_\phi}}$
$Y_r Y_r' Y_\phi$	$z_{14} = f_{rr'\phi} \frac{\hbar}{2\omega_r \mu_r} \sqrt{\frac{\hbar}{2\omega_\phi \mu_\phi}}$
$(Y_r^3 + Y_r'^3) Y_\phi$	$z_{15} = \frac{1}{4!} (2\beta_r^2 f_{r\phi} + 3\beta_r f_{rr\phi} + f_{rrr\phi}) \frac{\hbar^2}{\omega_r \mu_r} \sqrt{\frac{1}{\omega_r \mu_r \omega_\phi \mu_\phi}}$
$(Y_r + Y_r') Y_\phi^3$	$z_{16} = \frac{\hbar}{4!} (2\beta_\phi f_{r\phi\phi} + 3\beta_\phi f_{r\phi\phi\phi} + f_{r\phi\phi\phi\phi}) \frac{\hbar^2}{\omega_\phi \mu_\phi} \sqrt{\frac{1}{\omega_r \mu_r \omega_\phi \mu_\phi}}$
$(Y_r Y_r^2 + Y_r' Y_r'^2) Y_\phi$	$z_{17} = \frac{1}{8} (\beta_r f_{rrr'\phi} + f_{rr'r'\phi}) \frac{\hbar^2}{\omega_r \mu_r} \sqrt{\frac{1}{\omega_r \mu_r \omega_\phi \mu_\phi}}$

expansion, the interactions associated with the parameters $\{z_1, z_3, z_4, z_7, z_8\}$ do not present additional contributions of order $1/\sqrt{\kappa}$, although they do of higher order. They are not included because we are writing the interactions only up to order $1/\sqrt{\kappa}$. The interaction for z_2 , which gives rise to a Fermi interaction in zeroth order, presents a bending one-quantum transfer term of order $1/\sqrt{\kappa}$. The interactions for z_5 and z_6 , which present stretching-bending anharmonic interactions, include Fermi interactions of order $1/\sqrt{\kappa}$. The interactions associated to $\{z_9, z_{15}, z_{16}, z_{17}\}$ give rise to Fermi interactions of order $1/\sqrt{\kappa}$. On the other hand the interactions associated to $\{z_{10}, z_{11}, z_{12}\}$ present Darling–Dennison interactions, in addition to the one-quantum transfer interactions, all of them of order $1/\sqrt{\kappa}$.

If in this Hamiltonian we carry out the limit $\kappa \rightarrow \infty$, the Hamiltonian (20) is recovered. If we keep the approximation (57a) and (57b) we obtain the same Hamiltonian from the functional point of view, but with the change $\hat{a}^\dagger \rightarrow \hat{b}^\dagger$. Another advantage of having rewritten the Hamiltonian (12) in the form (71) is that it becomes clear up to which order the force constants are determined. In practice, however, it is more convenient to carry out the calculations from (12). In principle, using the $su(2)$ commutation relations the Hamiltonian (71) can be rearranged to obtain a simple expression, but it does not provide additional physical insight to the problem.

In the same spirit we could break the polyad taking terms up to order $1/\sqrt{\kappa}$, or any order we decide by means of the expansions (44) and (47). This analysis we be presented in future publication [19]. In the next section we shall present the results when the Hamiltonian (71) is used to describe the vibrational energy spectrum of H_2O .

5. Results

In this section we start by considering the Hamiltonian (71) to describe the vibrational spectrum of the most abundant isotopic species of water, H_2^{16}O , including data up to $22\,500\text{ cm}^{-1}$. The Hamiltonian (71) includes 17 force constants, the Morse parameters β_r and β_ϕ , plus the Child's parameters κ_s and κ_b . Since the latter parameters are connected with the anharmonicity of the oscillators, we can estimate their values by considering the energy levels for one and two quanta. Although this approach provides both sets of parameters $\{\beta_r, \beta_\phi\}$ and $\{\kappa_r, \kappa_\phi\}$, it is possible to extract from the data only the Child's parameters. This procedure is explained in [18] and gives rise to the parameters

$$\kappa_s = 47, \quad \kappa_b = 86. \quad (72)$$

These values reflect the anharmonic character of the stretching modes, compared with the more harmonic-like behavior of the bending mode. Since the parameters

$\{\beta_r, \beta_\phi\}$ and $\{\kappa_r, \kappa_\phi\}$ are involved in the zeroth-order Hamiltonian (11) as well as in the parameters $\{x_i, z_i\}$ through ω_r and ω_ϕ , the strategy to follow in the fitting procedure must be a self consistent approach. We start by taking an initial set of parameters $\{\beta_r, \beta_\phi\}$. Such values can be taken from the previous fit given in [18]:

$$\beta_r = 2.1542; \quad \beta_\phi = 0.7296. \quad (73)$$

These parameters, together with the equilibrium geometry of the molecule allows to fix the constants x_i . We then proceed to carry out an energy fit varying the linear parameters z_i and the Morse frequencies $\tilde{\omega}_i$, $i = r, \phi$. The fitting provides a set of force constants, but also a new values for β_r and β_ϕ through the $\tilde{\omega}'_i$ s. The new parameters together with (72) are then used as initial parameters to start a new fit. This procedure is repeated until the input and output values of the β' s parameters are the same. We should note that during this procedure the Child's parameters remain fixed. In order to obtain the best possible set we vary the κ' s parameters and repeat the approach described above. The quality of the fit is expressed in terms of the rms deviation

$$\text{rms} = \left[\sum_{i=1}^{N_{\text{exp}}} \left(E_{\text{exp}}^i - E_{\text{cal}}^i \right)^2 / (N_{\text{exp}} - N_{\text{par}}) \right]^{1/2}, \quad (74)$$

where N_{exp} is the total number of experimental energies and N_{par} the number of parameters used in the fit.

We now present the results of the least-square fit to the vibrational spectrum of H_2^{16}O , including 72 experimental energies with equal weights. In this analysis we have taken into account the same experimental energies considered in [18], plus 14 energies taken from [47]. In Table 3 we present the theoretical and experimental energies, where an rms deviation of 5.0 cm^{-1} was obtained with the parameters $\kappa_s = 47$ and $\kappa_b = 66$. In Table 4, we display the parameters z_i provided by the fitting procedure. From this set of parameters and their explicit expressions given in Table 2 we derive the force constants displayed in Table 5. In Table 3 we have also included predicted levels up to polyad $P = 14$. As explained before, the quantum number assignment of the states corresponds to the maximum component in the symmetry adapted basis. Since the basis is isomorphic to the normal basis, there is a full coincidence with standard labeling.

In order to determine the significance of the fits, a statistical error analysis for the parameters was carried out [48]. Two types of uncertainty measures were defined and computed for the parameters z_i : the delta-error (δz_i) and the epsilon-error (ϵz_i). They are defined in such a way that the value of the quadratic energy deviation Q^2 , defined by

$$Q^2 = \sum_{i=1}^{N_{\text{exp}}} \left(E_{\text{exp}}^i - E_{\text{cal}}^i \right)^2, \quad (75)$$

Table 3
Energies (in cm^{-1}) provided by the fit using the Hamiltonian (71)

Polyad	State ($v_1 v_2 v_3$)	Energies		
		Exp. ^a	Theor.	ΔE_{o-c}
<i>Symmetry A</i>				
1	(0, 1, 0)	1594.75	1591.55	3.20
2	(0, 2, 0)	3151.63	3152.42	-0.79
2	(1, 0, 0)	3657.05	3658.13	-1.1
3	(0, 3, 0)	4666.8	4669.52	-2.7
3	(1, 1, 0)	5235.	5234.45	0.5
4	(0, 4, 0)	6134.03	6133.06	0.97
4	(1, 2, 0)	6775.1	6780.47	-5.37
4	(2, 0, 0)	7201.54	7200.73	0.8
4	(0, 0, 2)	7445.07	7449.74	-4.7
5	(0, 5, 0)	7542.39	7535.94	6.45
5	(1, 3, 0)	8273.98	8278.81	-4.8
5	(2, 1, 0)	8761.59	8760.7	0.89
5	(0, 1, 2)	9000.14	8996.45	3.69
6	(0, 6, 0)	8870.5	8872.85	-2.35
6	(1, 4, 0)	0	9721.96	—
6	(2, 2, 0)	10284.4	10289.1	-4.8
6	(0, 2, 2)	10524.3	10523.7	0.6
6	(3, 0, 0)	10599.7	10597.9	1.77
6	(1, 0, 2)	10868.9	10870.8	-1.9
7	(0, 7, 0)	0	10140.2	—
7	(1, 5, 0)	0	11104.7	—
7	(2, 3, 0)	0	11768.7	—
7	(0, 3, 2)	0	12014.	—
7	(1, 1, 2)	12139.2	12136.	3.2
7	(1, 1, 2)	12407.6	12404.5	3.1
8	(0, 8, 0)	0	11336.2	—
8	(1, 6, 0)	0	12423.	—
8	(2, 4, 0)	13205.1	13193.9	11.21
8	(0, 4, 2)	13448.	13457.	-9.0
8	(1, 2, 2)	13642.2	13643.4	-1.16
8	(2, 0, 2)	13828.3	13826.9	1.4
8	(1, 2, 2)	13910.9	13914.5	-3.6
8	(4, 0, 0)	14221.2	14221.7	-0.5
8	(0, 0, 4)	14536.5	14532.5	3.96
9	(0, 9, 0)	0	12460.7	—
9	(1, 7, 0)	13661.3	13674.1	-12.81
9	(2, 5, 0)	0	14560.	—
9	(0, 5, 2)	0	14844.8	—
9	(1, 3, 2)	15107.	15104.9	2.14
9	(2, 1, 2)	15344.5	15341.6	2.9
9	(1, 3, 2)	0	15381.6	—
9	(4, 1, 0)	15742.8	15740.4	2.4
9	(0, 1, 4)	0	16035.3	—
10	(1, 10, 0)	0	13515.	—
10	(1, 8, 0)	0	14857.	—
10	(2, 6, 0)	0	15863.3	—
10	(0, 6, 2)	0	16171.7	—
10	(3, 4, 0)	0	16516.5	—
10	(1, 4, 2)	0	16793.4	—
10	(2, 2, 2)	16825.2	16824.6	0.6
10	(3, 0, 2)	16898.4	16898.7	-0.3
10	(4, 2, 0)	17227.7	17231.2	-3.5
10	(5, 0, 0)	17458.3	17455.8	2.5
10	(0, 2, 4)	0	17527.7	—
10	(1, 0, 4)	17748.1	17748.1	0.0
11	(0, 11, 0)	0	14501.5	—
11	(1, 9, 0)	0	15972.1	—
11	(2, 7, 0)	0	17101.6	—
11	(0, 7, 2)	0	17433.6	—
11	(3, 5, 0)	0	17872.2	—

Table 3 (continued)

Polyad	State ($v_1 v_2 v_3$)	Energies		
		Exp. ^a	Theor.	ΔE_{o-c}
11	(1, 5, 2)	0	18156.4	—
11	(2, 3, 2)	0	18265.	—
11	(3, 1, 2)	18393.	18394.	-1.00
11	(4, 3, 0)	0	18674.9	—
11	(5, 1, 0)	0	18950.6	—
11	(0, 3, 4)	0	18992.	—
11	(1, 1, 4)	0	19232.9	—
12	(0, 12, 0)	0	15423.1	—
12	(1, 10, 0)	0	17021.3	—
12	(2, 8, 0)	0	18274.2	—
12	(0, 8, 2)	0	18628.5	—
12	(3, 6, 0)	0	19167.3	—
12	(1, 6, 2)	0	19459.5	—
12	(2, 4, 2)	0	19664.1	—
12	(4, 0, 2)	0	19781.9	—
12	(3, 2, 2)	0	19871.5	—
12	(4, 4, 0)	0	20068.6	—
12	(0, 4, 4)	0	20400.5	—
12	(1, 2, 4)	0	20430.3	—
12	(6, 0, 0)	0	20532.4	—
12	(1, 2, 4)	0	20703.6	—
12	(6, 0, 0)	0	20913.4	—
12	(0, 0, 6)	0	21262.1	—
13	(0, 13, 0)	0	16283.4	—
13	(1, 11, 0)	0	18007.5	—
13	(2, 9, 0)	0	19382.3	—
13	(0, 9, 2)	0	19756.3	—
13	(3, 7, 0)	0	20398.9	—
13	(1, 7, 2)	0	20701.3	—
13	(2, 5, 2)	0	21012.8	—
13	(4, 1, 2)	0	21225.2	—
13	(3, 3, 2)	0	21321.2	—
13	(4, 5, 0)	0	21409.9	—
13	(0, 5, 4)	0	21774.6	—
13	(5, 3, 0)	0	21850.6	—
13	(2, 1, 4)	0	22004.5	—
13	(1, 3, 4)	0	22138.9	—
13	(6, 1, 0)	0	22383.8	—
13	(0, 1, 6)	0	22720.6	—
14	(0, 14, 0)	0	17086.	—
14	(1, 12, 0)	0	18934.2	—
14	(2, 10, 0)	0	20428.1	—
14	(0, 10, 2)	0	20818.4	—
14	(3, 8, 0)	0	21566.6	—
14	(1, 8, 2)	0	21880.5	—
14	(2, 6, 2)	0	22303.8	—
14	(3, 0, 4)	0	22525.9	—
14	(4, 2, 2)	0	22634.	—
14	(4, 6, 0)	0	22690.2	—
14	(3, 4, 2)	0	22755.4	—
14	(0, 6, 4)	0	23087.9	—
14	(5, 4, 0)	0	23229.7	—
14	(5, 0, 2)	0	23418.8	—
14	(6, 2, 0)	0	23466.2	—
14	(1, 4, 4)	0	23534.7	—
14	(6, 2, 0)	0	23833.4	—
14	(7, 0, 0)	0	23980.9	—
14	(0, 2, 6)	0	24175.3	—
14	(1, 0, 6)	0	24294.1	—
<i>Symmetry B</i>				
2	(0, 0, 1)	3755.93	3762.48	-6.55
3	(0, 1, 1)	5331.27	5329.2	2.07

Table 3 (continued)

Polyad	State ($v_1 v_2 v_3$)	Energies		
		Exp. ^a	Theor.	ΔE_{o-c}
4	(0, 2, 1)	6871.51	6873.16	-1.65
4	(1, 0, 1)	7249.81	7253.5	-3.7
5	(0, 3, 1)	8373.85	8377.65	-3.8
5	(1, 1, 1)	8807.	8804.8	2.2
6	(0, 4, 1)	9833.58	9832.29	1.29
6	(1, 2, 1)	10328.7	10331.3	-2.6
6	(2, 0, 1)	10613.4	10615.4	-2.07
6	(0, 0, 3)	11032.4	11032.8	-0.40
7	(0, 5, 1)	0	11229.4	—
7	(1, 3, 1)	11813.2	11815.2	-2.0
7	(2, 1, 1)	12151.3	12149.2	2.1
7	(0, 1, 3)	12565.	12557.1	7.93
8	(0, 6, 1)	0	12563.1	—
8	(1, 4, 1)	13256.2	13248.9	7.3
8	(2, 2, 1)	13652.7	13655.7	-3.0
8	(3, 0, 1)	13830.9	13831.4	-0.5
8	(0, 2, 3)	14066.2	14066.8	-0.6
8	(1, 0, 3)	14318.8	14319.7	-0.9
9	(0, 7, 1)	13835.4	13829.5	5.9
9	(1, 5, 1)	14640.	14626.2	13.83
9	(2, 3, 1)	15119.	15118.9	0.1
9	(3, 1, 1)	15348.	15345.9	2.1
9	(0, 3, 3)	15534.7	15543.9	-9.22
9	(1, 1, 3)	15832.8	15825.2	7.56
10	(0, 8, 1)	0	15026.6	—
10	(1, 6, 1)	0	15942.2	—
10	(2, 4, 1)	0	16534.1	—
10	(3, 2, 1)	16821.6	16824.4	-2.80
10	(2, 0, 3)	16898.8	16899.2	-0.4
10	(0, 4, 3)	0	16977.1	—
10	(1, 2, 3)	17312.5	17314.3	-1.80
10	(4, 0, 1)	17495.5	17500.	-4.52
10	(0, 0, 5)	0	17938.6	—
11	(0, 9, 1)	0	16154.3	—
11	(1, 7, 1)	0	17193.5	—
11	(2, 5, 1)	0	17895.2	—
11	(3, 3, 1)	18265.8	18265.8	0.07
11	(0, 5, 3)	0	18356.7	—
11	(2, 1, 3)	18393.3	18395.5	-2.18
11	(1, 3, 3)	0	18767.5	—
11	(4, 1, 1)	18990.	18987.8	2.17
11	(0, 1, 5)	0	19418.9	—
12	(0, 10, 1)	0	17213.8	—
12	(1, 8, 1)	0	18378.9	—
12	(2, 6, 1)	0	19197.2	—
12	(0, 6, 3)	0	19656.3	—
12	(0, 6, 3)	0	19687.6	—
12	(3, 0, 3)	19781.1	19782.4	-1.2
12	(2, 2, 3)	0	19872.1	—
12	(1, 4, 3)	0	20176.7	—
12	(4, 2, 1)	0	20454.8	—
12	(5, 0, 1)	20543.1	20545.8	-2.7
12	(0, 2, 5)	0	20892.2	—
12	(1, 0, 5)	0	21039.9	—
13	(0, 11, 1)	0	18207.5	—
13	(1, 9, 1)	0	19498.5	—
13	(2, 7, 1)	0	20436.9	—
13	(0, 7, 3)	0	20930.4	—
13	(3, 5, 1)	0	21021.3	—
13	(3, 1, 3)	21221.8	21225.8	-4.02
13	(2, 3, 3)	0	21322.7	—
13	(1, 5, 3)	0	21535.8	—

Table 3 (continued)

Polyad	State ($v_1 v_2 v_3$)	Energies		
		Exp. ^a	Theor.	ΔE_{o-c}
13	(4, 3, 1)	0	21884.5	—
13	(5, 1, 1)	0	22015.1	—
13	(0, 3, 5)	0	22339.7	—
13	(1, 1, 5)	0	22497.3	—
14	(0, 12, 1)	0	19138.7	—
14	(1, 10, 1)	0	20554.3	—
14	(2, 8, 1)	0	21613.2	—
14	(0, 8, 3)	0	22124.2	—
14	(3, 6, 1)	0	22313.	—
14	(4, 0, 3)	22529.4	22526.	3.41
14	(3, 2, 3)	0	22638.3	—
14	(3, 2, 3)	0	22748.	—
14	(1, 6, 3)	0	22841.6	—
14	(4, 4, 1)	0	23273.3	—
14	(6, 0, 1)	0	23425.3	—
14	(5, 2, 1)	0	23476.	—
14	(0, 4, 5)	0	23748.4	—
14	(1, 2, 5)	0	23947.6	—
14	(4, 0, 3)	0	24049.8	—
14	(0, 0, 7)	0	24498.	—

^a Experimental energies were taken from [26,47].

Table 4

Parameters of the Hamiltonian (71) in cm^{-1} obtained in the fit to 72 vibrational energies of H_2^{16}O

Parameter	Fit	Errors	
		Delta	Epsilon
ω_r	3889.69	0.146	5.917
ω_ϕ	1633.01	0.197	6.052
z_1	-36.95	0.417	3.250
z_2	-145.85	0.272	28.353
z_3	-15.39	0.007	0.821
z_4	3.69	0.006	0.326
z_5	-9.15	0.016	2.333
z_6	-0.18	0.10	0.861
z_7	-3.33	0.043	0.344
z_8	0.74	0.037	0.323
z_9	-569.56	1.795	236.577
z_{10}	44.20	0.076	4.421
z_{11}	-221.09	0.090	11.421
z_{12}	-5.61	0.405	1.792
z_{13}	352.52	1.011	112.992
z_{14}	-114.00	5.142	33.42
z_{15}	11.71	0.234	10.48
z_{16}	3.04	0.109	1.832
z_{17}	-3.93	0.762	4.509

The Child's parameters are taken to be $k_s = 47$ and $k_b = 66$. The statistical error analysis has been included in the last two columns, where the Epsilon and Delta errors are shown.

does not increase more than a fraction Δ of the minimum value Q_{\min}^2 . Specifically, the delta-error for the parameter z_i is defined through the condition that Q^2 remains smaller than $(1 + \Delta)Q^2$ when z_i is chosen in the interval $[z_i - \delta z_i, z_i + \delta z_i]$ around its optimum value z_i . In this case all other parameters are kept fixed at their optimized values. On the other hand, ϵz_i determines the

Table 5
Force constants provided by the fit displayed in Table 3

Order	Force constant	This work	Jensen ^a	Halonen–Carrington ^b	Lemus et al. ^c	Ab initio ^d
1	$\beta_s/\text{\AA}^{-1}$	2.1573		2.053	2.1542	
1	D_s/aJ	0.8694		0.999	0.9050	
1	$\beta_b/\text{\AA}^{-1}$	0.8279			0.7296	
1	D_b/aJ	0.5190			0.7055	
1	$f_{rr}/aJ \text{\AA}^{-2}$	8.093	8.4393	8.428	8.401	8.443
1	$r_e^2 f_{\phi\phi}/aJ$	0.652	0.7070	0.699	0.688	0.7921
1	$f_{rr'}/aJ \text{\AA}^{-2}$	-0.1571	-0.1051	-0.101	-0.11	-0.100
$1/\sqrt{\kappa}$	$r_e f_{r\phi}/aJ \text{\AA}^{-1}$	-1.0578	0.3064	0.219		0.2743
$1/\sqrt{\kappa}$	$f_{rrr}/aJ \text{\AA}^{-3}$	-35.880	-55.40	-51.91		-56.400
$1/\sqrt{\kappa}$	$r_e f_{rr'\phi}/aJ \text{\AA}^{-2}$	-3.098	-0.447	0.414		-0.505
$1/\sqrt{\kappa}$	$f_{rrr'}/aJ \text{\AA}^{-3}$	-0.358	-0.318	0.645		-0.076
1	$r_e^2 f_{r\phi\phi}/aJ \text{\AA}^{-1}$	-2.6243	-0.3383	-0.314	-0.51	-0.3210
$1/\sqrt{\kappa}$	$r_e f_{rr'\phi}/aJ \text{\AA}^{-2}$	21.442	-0.252	1.341		-0.084
$1/\sqrt{\kappa}$	$f_{rrr''}/aJ \text{\AA}^{-3}$	-8.4312	-0.7332	-0.918		-0.7482
1	$f_{rrrr}/aJ \text{\AA}^{-4}$	130.87	306.0	248.7	275.39	338
1	$r_e^2 f_{rr\phi\phi}/aJ \text{\AA}^{-2}$	-15.89	-0.950	-2.0	-15.699	-0.28
1	$f_{rrrr'}/aJ \text{\AA}^{-4}$	7.861	2.57		3.728	-0.30
1	$r_e^2 f_{rr'\phi\phi}/aJ \text{\AA}^{-2}$	2.3910	0.1150		-0.632	0.62
1	$f_{rrr'r'}/aJ \text{\AA}^{-4}$	-9.843	1.93		-12.68	0.52
1	$r_e^4 f_{\phi\phi\phi\phi}/aJ$	23.349	-0.238	-0.1	2.32	-0.74
$1/\sqrt{\kappa}$	$r_e f_{rrr'\phi}/aJ \text{\AA}^{-3}$	-100.98	-6.14			-1.2
$1/\sqrt{\kappa}$	$r_e f_{rrr''\phi}/aJ \text{\AA}^{-3}$	3.5584	-3.22			0.2
$1/\sqrt{\kappa}$	$r_e^3 f_{r\phi\phi\phi}/aJ \text{\AA}^{-1}$	8.955	0.87			0.648

^a From [25].

^b From [24].

^c From [18].

^d From [53].

range in which z_i varies when all other parameters are optimized again. The epsilon error is generally much larger than the delta-error, as can be seen in Table 4, where the fraction Δ was chosen to be 0.05.

From Table 4, we identify z_6 as the only parameter displaying an error comparable to the parameter itself, but this situation appears only for the epsilon error, the delta error being significantly smaller. In addition to the delta and epsilon errors we have also calculated the correlation matrix for the parameters. From this point of view the set of parameters are well determined since for all cases the matrix correlation values are not greater than 0.94, to be compared with the value of 0.99 estimated to be typical for correlation [49].

In this work the relation between the spectroscopic parameters and the structure and force constants has been established in the framework of $su(2)$ representation. Using the relations (72) of Table 2 we have derived the force constants displayed in Table 5. We have included for comparison the force constants obtained by other approaches. While the Morse parameters for the stretches are quite similar, the rest of the constants display significant differences, in particular $f_{r\phi}$, $f_{rr\phi}$, $f_{rrr'}$, and $f_{\phi\phi\phi\phi}$, whose signs differ from the ab initio results. These differences can be attributed to a renormalization of the constants, owing to the different con-

tributions which are taken into account in the Hamiltonian and the approximations involved. We remark that the approach presented here establishes a method to determine all the force constants when the polyads are preserved and only the leading Morse matrix elements are taken into account. Here we have considered up to quartic order terms, but the method can be applied to higher order expansions. This approach represents the extension to the algebraic approach developed in [10], whose corresponding force constants are displayed in the sixth column of Table 5. There are three main differences between the description of Halonen and Carrington [24] and this work. First, the Hamiltonians are different, as indicated by the absence of some constants in Table 5. Second, the expansion in [24] is given in terms of the Morse variables for the stretches and the coordinate for the bending, while we are using in both cases the Morse variables. Finally, the approximation involved in [24] is concerned only with the use of a limited basis set, but the interactions connect the whole basis. In contrast, in our description only the leading matrix elements $\Delta v = 0, \pm 1, \pm 2$ are considered, in such a way that the polyad number (14) is exactly conserved. On the other hand, the description of Jensen [25] is based on the Morse oscillator rigid bender internal dynamics (MORBID) approach [50], which is

designed to describe the rotations and vibrations for non rigid molecules. The potential energy function is expanded in terms of the Morse variable for the stretches, where the coefficients are in turn functions of the bending variable [50,51]. The ro-vibrational energies and wave functions are obtained by diagonalization of a matrix representation of the Hamiltonian. The basis functions used are products of rotation–contortion functions for the bending coordinate and Morse oscillators for the stretches. On the basis of the above discussion we remark that our description represents a way to include in a systematic fashion the Morse matrix elements in an algebraic framework, which represents a simpler approach to carry out the calculations as well as to establish the relevant interactions involved in the conservation of the polyad. The use of the $su(2)$ representation may be particularly relevant for more complex molecules, where other models are more difficult to apply. In this work we have taken the approximation (44) and (47) up to second order, but the next order terms may be included. We believe, however, that a more promising approach to improve the description is the breaking of the polyad pseudoquantum number and/or increasing the order of the expansions in the kinetic and potential energies.

From Table 3 we identify two sets of states with particularly large deviations. The states (2, 4, 0), (0, 4, 2), (1, 7, 0), with symmetry *A*, and (1, 5, 1), (0, 3, 3), with symmetry *B*. The deviation of these states are of the order of 9–14 cm^{-1} , which is in contrast to the deviation of 5 cm^{-1} obtained in the fit. Most of these states have a large number of bending quanta, which at first suggests that either the Morse potential for the bending mode is not appropriate to describe the spectrum or that additional interactions involving pure bending and bending–stretching interactions should be included. We note, however, that the energies of these states are similar to the energies of adjacent polyads. In the subspace with symmetry *A*, the state (1, 7, 0) of polyad 9 overlaps with the states (0, 4, 2), (2, 4, 0), and (1, 2, 2) of polyad 8. A similar situation occurs in the *B* subspace, where the energy of the state (0,7,1) of polyad 9 resembles the energy of the state (3,0,1) of polyad 8. Same situation is present in the case of the states (1, 1, 3) and (1, 6, 1). It is thus clear that an interaction among these states must be present, since the overlap of polyads increases for higher energy regions of the spectrum. We are currently exploring polyad-mixing by taking into account all the terms involved in the expansions (44) and (47). The states discussed above may be an interesting test for this approach.

In order to test the reliability of the force constants, we have obtained the kinetic energy constants x_i predicted for the isotopes H_2^{17}O , H_2^{18}O , D_2^{16}O , and T_2^{16}O . In Table 6 we present the predicted energies as well as their comparison with the observed energies.

Table 6
Predicted vibrational levels for different isotopic species

Polyad	State ($v_1 v_2 v_3$)	Energies		
		Exp. ^a	Theor.	$\Delta E_{\theta-c}$
H_2^{17}O				
Symmetry <i>A</i>				
1	(0, 1, 0)	1591.32	1588.35	3.0
2	(1, 0, 0)	3653.15	3653.46	−0.31
2	(0, 2, 0)	3144.98	3145.85	−0.87
3	(1, 1, 0)	5227.75	5226.7	1.0
Symmetry <i>B</i>				
2	(0, 0, 1)	3748.32	3754.65	−6.33
3	(0, 1, 1)	5320.26	5318.12	2.1
4	(1, 0, 1)	7238.73	7241.08	−2.35
H_2^{18}O				
Symmetry <i>A</i>				
1	(0, 1, 0)	1588.28	1585.5	2.78
2	(1, 0, 0)	3649.69	3649.3	0.39
2	(0, 2, 0)	3139.05	3140.	−0.95
3	(1, 1, 0)	5221.25	5219.81	1.44
3	(0, 3, 0)	4648.46	4650.79	−2.33
4	(0, 0, 2)	7418.72	7421.54	−2.82
4	(2, 0, 0)	7185.9	7181.78	4.12
4	(1, 2, 0)	6755.51	6759.61	−4.10
Symmetry <i>B</i>				
2	(0, 0, 1)	3741.57	3747.68	−6.1
3	(0, 1, 1)	5310.46	5308.25	2.21
4	(1, 0, 1)	7228.9	7230.04	−1.1
4	(0, 2, 1)	6844.6	6845.98	−1.4
D_2^{16}O				
Symmetry <i>A</i>				
1	(0, 1, 0)	1178.38	1170.15	8.23
2	(1, 0, 0)	2669.40	2651.81	19.84
2	(0, 2, 0)	2336.84	2314.54	22.30
4	(2, 0, 0)	5291.6	5225.73	65.9
5	(2, 1, 0)	6452.	6382.89	69.1
6	(3, 0, 0)	7853.	7710.12	142.88
7	(1, 1, 2)	9205.86	9043.54	162.32
Symmetry <i>B</i>				
2	(0, 0, 1)	2787.92	2767.01	20.9
3	(0, 1, 1)	3956.21	3912.58	43.6
4	(1, 0, 1)	5373.98	5296.17	77.8
4	(0, 2, 1)	5105.44	5041.08	64.36
5	(1, 1, 1)	6533.37	6434.97	98.4
6	(2, 0, 1)	7899.8	7740.21	159.6
7	(0, 1, 3)	9376.05	9194.14	181.9
T_2^{16}O				
Symmetry <i>A</i>				
1	(0, 1, 0)	995.37	987.4	8.0
2	(1, 0, 0)	2233.9	2213.22	23.93
2	(0, 2, 0)	1977.9	1947.87	30.03
3	(1, 1, 0)	3223.3	3204.46	18.84
3	(0, 3, 0)	2946.2	2880.18	66.02
4	(0, 0, 2)	0	4607.84	—
4	(2, 0, 0)	0	4364.42	—
4	(1, 2, 0)	4199.2	4146.06	53.14
4	(0, 4, 0)	3899.3	3783.65	115.65
Symmetry <i>B</i>				
2	(0, 0, 1)	2366.61	2335.3	31.31
3	(0, 1, 1)	3354.3	3298.37	55.93
4	(1, 0, 1)	0	4444.86	—
4	(0, 2, 1)	4330.2	4244.07	86.13

^aThe experimental values were taken from [24,25].

From the general quality of the predictions we are led to believe that the potential surface defined by the constants in Table 5, provides a reliable physical description of the systems H_2^{17}O , H_2^{18}O , consistent with the approximations involved. In contrast, for the isotopes D_2^{16}O , T_2^{16}O , where a large percent of change in mass is involved, the predictions are poor. The approximations considered in the description are too strong to take into account large mass changes. To improve the description is clear that polyad mixing must be taken into account, although another ingredients, like adding terms in the Hamiltonian expansion and taking into account rotation–vibration interactions, must be eventually considered [25].

6. Conclusions

In this work, we have presented a local mode description of the vibrational excitations of H_2^{16}O . The model we consider uses a local Morse basis for both stretching and bending degrees of freedom, and is based on the expansion of the momenta and Morse coordinates in terms of creation and annihilation operators of the Morse functions. This approach represents a considerable improvement to both the Child Lawton Model and the vibron model approximation.

Using an expansion of the Hamiltonian up to fourth order terms in the coordinates and momenta we have carried out a polyad conserving fit to 72 experimental levels with an rms deviation of 5.0 cm^{-1} . In contrast to the harmonic and vibron model approximation where the preservation of polyads restricts the number of computed force constants, we have calculated the whole set of force constants associated to the potential up to fourth order. This is possible because the expansions (44) and (47) take into account in the Hamiltonian higher order terms, which are a consequence of considering the $\Delta v = 0, \pm 2$ Morse matrix elements in addition to the leading term $\Delta v = \pm 1$. In order to make clear the order of approximation which is needed to determine the force constants, an expansion of the Hamiltonian in terms of symmetry adapted tensors has been developed. These tensors, in addition to the irreducible representations, are characterized by their order, nature (coordinates or momenta), and type of degree of freedom (stretching or bending). For small oscillations the tensors associated to the coordinates and momenta reduce to the tensors previously introduced in the context of the vibron model approximation [46].

An important ingredient of our description is the expansion of the Hamiltonian in terms of the Morse variable $y = 1 - e^{-\beta q}$, which allows to establish a one to one correspondence with the traditional local models in configuration space [15]. The algebraic framework, however, has the advantage of simplifying the compu-

tation of matrix elements, establishing a specific way to approximate the results of the exact Morse matrix elements. In this manner we are able to determine a natural order for polyad mixing, thus improving precision while maintaining the simplifications that arise from the algebraic approach, which can be readily extended to more complex molecules. In the latter situation, however, further work is needed to assess the relevance of these methods.

The physical content of the generated potential surface was tested by comparing the predicted energies for the isotopes H_2^{17}O , H_2^{18}O , D_2^{16}O , and T_2^{16}O with their experimental spectrum. With the exception of D_2^{16}O and T_2^{16}O , where a large percentage of change in mass is involved, the surface is reliable. It seems that in this case a higher order potential surface is needed or the rotation vibration interaction must be taken into account, although additional effect may be important.

Several improvements to the model can be considered. According to the discussion concerning the overlap of polyads, the natural step to improve the description is to proceed to break the polyads. The algebraic approach presented here is particularly suitable to investigate the effects because it allows to carry out the polyad breaking in a systematic fashion. A problem which arises is concerned with the dimension of the space. A limited space must be considered, whose criteria to establish its dimensions is the convergence of the description. A work dealing with this situation is in progress [19]. A fact that should be kept in mind is that the states which are expected to interact by breaking the polyads involve high number of bending quanta. Two effects may thus be important to improve the description, on one hand the polyad breaking, but on the other hand the use of a Morse potential for the bending coordinate may not provide the best description. Both effects must be investigated simultaneously. Finally, one could also calculate infrared absorption intensities and compare the results with experiment, similarly to the case of the vibron model approximation [18]. This analysis will be included in the work on polyad breaking [19].

This analysis involve only the vibrational degrees of freedom, but in a more complete study, the rotation–vibration interactions should be included. A rotation–vibration description, however, represent a project by itself. A Hamiltonian including the most important interactions must be proposed and a new code must be written to carry out the diagonalization. This work is in progress.

The present approach is completely general. Once we have constructed the Hamiltonian in configuration space in terms of local coordinates and momenta, the substitution of the expansions (44) and (47) gives rise to an algebraic representation that allows to carry out successive approximations for the Morse matrix elements. The physical interpretation of the interactions is

carried out with the help of the tensorial formalism introduced in Section 4.

Finally, we should remark that the goal of this contribution is to analyze the consequences and perspectives of using the expansions (44) and (47) in the framework of a local model based on interacting Morse oscillators. This approach does not intend to improve the accuracy of previous descriptions. The importance of this work is based on the possibility to be applied to complex situations where the existing numerical methods are not effective. For example, the vibron model approximation has been applied to triatomic molecules, but also to medium size molecules like methane [52]. This analysis could not have been possible without previous studies of simple systems [46]. In the present case, the Hamiltonian (71), which is impossible to write down in more complex situations, is fundamental to interpret the different interactions derived from the use of the expansions (44) and (47). In the latter case the program should be adapted to interpret the interactions according to the tensorial formalism of Section 4.

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