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An Approach to Global Rovibrational Analysis Based on Anharmonic Ladder Operators: Application to Hydrogen Selenide ($H_2^{80}Se$)

O. Álvarez-Bajo*, M. Carvajal**, F. Pérez-Bernal

Dpto. Física Aplicada, Facultad de Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain

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Abstract

An algebraic approach to perform global rovibrational analysis of molecular spectra is presented. The approach combines the one-dimensional limit of the vibron model with rotational degrees of freedom. The model is based on the expression of the phase space Hamiltonian in terms of anharmonic ladder operators and the use of a symmetry-adapted basis set given by the linear combination of products of local vibrational and rotational wavefunctions. As an example we model the rovibrational spectra of a bent triatomic molecule, providing a global analysis for vibrational bands up to polyad 12 and J_{max}=5 of Hydrogen Selenide (H_2Se). Satisfactory fits of vibrational and rovibrational energies are obtained. A prediction of 2579 rovibrational energies up to $J \leq 5$ and polyad 12 for the 140 lowest vibrational bands is also obtained. A possible extension of the model to reach spectroscopic quality results in larger molecular systems is also given.

Keywords: H_2Se, Hydrogen Selenide, rovibrational spectra, variational calculation, algebraic model

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1. Introduction

The exploration of new theoretical procedures to ease the spectral analysis of medium and large size molecules can be undertaken either in a phenomenological way or by means of an *ab initio* Potential Energy Surface (PES). In this respect, the algebraic approach provides phenomenological models potentially suitable to perform global spectral analysis of various vibrational bands for large- and medium-size molecules. An important advantage of this approach is the simple way of selecting relevant interactions and their analytical expressions.

In particular, algebraic models based on the vibron model [1] have the advantage of taking into account anharmonicity from the outset, compared to alternative methods based on harmonic bases. The original vibron model includes the simultaneous treatment of vibrational and rotational degrees of freedom [2]. For the sake of simplicity and in order to cope with polyatomic molecular vibrations, the one dimensional limit of the vibron model (1DVM) was formulated, where only vibrational degrees of freedom are considered. This approach was first exclusively applied to stretching degrees of freedom [3], and later extended to comprise bending degrees of freedom [4].

The algebraic approach has been criticized due to its abstract character and the lack of a clear connection between the algebraic and the traditional approach in the phase space. The coherent or intrinsic state formalism provides a way

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*Present address: Instituto de Ciencias Físicas, UNAM, Av. Universidad s/n, Col. Chamilpa, Cuernavaca, Morelos, 62210, Mexico.

**E-mail: miguel.carvajal@dfa.uhu.es. Phone number: +34-959219792. Fax Number: +34-959219777

to obtain a Hamiltonian depending on momenta and coordinates from an algebraic model Hamiltonian [5]. The first application to this formalism to the vibron model can be found in Ref. [6].

An alternative approach to connect the traditional and algebraic approaches takes as a starting point the system Hamiltonian in coordinates and momenta and transform it into an algebraic Hamiltonian. This line of research has been active in a continuous effort that now lasts for more than twelve years. In the first place, a connection between the abstract algebraic space of the 1DVM and the phase space was established. In particular, it was proved that the 1DVM is equivalent to a model of local Morse or Pöschl-Teller potentials [7, 8, 9]. As a consequence of these efforts it has been possible to describe molecular systems in an algebraic fashion from a phase space Hamiltonian, obtaining an estimation of the system's force field constants. Recently, an interesting alternative to connect a Hamiltonian of interacting oscillators in the 1DVM with classical variables has been formulated [10].

The vibrational spectrum of several molecules have been studied algebraically exploiting the connection between spectroscopic parameters and force constants, e.g. bent and linear triatomic molecular species as H_2O [11, 12] and CO_2 [13], planar tetratomic as formaldehyde (H_2CO) [14, 15] and BF_3 [16], and pyramidal tetratomic molecules as arsine (AsH_3) and stibine (SbH_3) [17, 18, 19, 20, 21].

In this paper our aim is to extend the 1DVM to encompass rotational degrees of freedom in the analysis, achieving a complete rovibrational analysis of the spectra of polyatomic molecules, usually called spectral global analysis. The availability of models able to simultaneously consider rotations and vibrations is of special importance for molecular species with large amplitude degrees of freedom, e.g. to deal with internal CH_3 rotors in molecules of astrophysical interest [22, 23].

In principle, a full rovibrational treatment is possible within the original vibron model, though our aim is to present a simpler model, able to cope with polyatomic molecular rovibrational spectra in a computationally unexpensive way and with a clear connection with the phase space. As an example, we apply the approach to the modelling of the rovibrational spectrum of Hydrogen Selenide ($H_2^{80}Se$) in its ground electronic state.

The Hydrogen Selenide ($H_2^{80}Se$) infrared spectrum has been recorded for different vibrational bands up to polyad 27 [24, 25, 26, 27, 28, 29, 30, 31, 32, 33]. An extensive set of rovibrational term values is available for its analysis, making $H_2^{80}Se$ a suitable system to test new procedures for the study of molecular rovibrational structure. This molecule has also been the subject of several theoretical studies. In 1988 Senekowitsch *et al.* calculated an *ab initio* potential energy surface for the electronic ground state of the Hydrogen Selenide molecule [34]. Since then, some attempts to obtain an optimal PES for Hydrogen Selenide have been carried out with different theoretical models, making use of experimental data to improve the obtained results [35, 36, 37]. In particular, in 1993 Jensen & Kozin refined the Hydrogen Selenide *ab initio* potential energy surface using the MORBID approach [38] through a direct least-squares fitting to the available experimental data of different isotopologues, concluding that this molecule has a markedly local behaviour and presents fourfold clustering effects [37]. Ten years later, with a considerable increase in the number of available experimental rovibrational spacings, the potential energy surface for the Hydrogen Selenide was revisited, using again MORBID to improve the experimental data description [39].

It is worth to emphasize that the aim of the present paper is not to compete with the highly accurate recently published MORBID calculations for Hydrogen Selenide [39]. Instead of this, we propose a novel phenomenological approach to analyze rovibrational spectra able to cope with large molecular systems. Nevertheless, a brief comparison between Ref. [39] and our results has been included in Sect. 5.

The present paper is organized as follows. In Sect. 2 the rovibrational Hamiltonian for a triatomic molecule in the phase space is revised. Section 3 is devoted to set up the symmetrization procedure used in this work. In Sect. 4, the algebraic Hamiltonian is obtained from the rovibrational Hamiltonian in configuration space. The application of this approach to model Hydrogen Selenide rovibrational spectrum provides the results presented in Sect. 5. Finally, in Sect. 6, a summary of the work and some concluding remarks can be found.

2. Rovibrational quantum Hamiltonian in the phase space

The modelling of the rovibrational molecular structure implies the consideration of the molecular Euler angles, $\{\theta, \phi, \chi\}$, that describe the overall rotation of the molecule. In addition to these angles, the necessary vibrational degrees of freedom should be considered. A possible option are internal valence coordinates, that for a triatomic ABA molecule can be selected as

$$\boldsymbol{q} = \{\Delta r_1, r_e\Delta\alpha, \Delta r_3\}. \tag{1}$$

In particular this option is specially suitable for molecules with local character (e.g. Hydrogen Selenide). The coordinates Δr_1 and Δr_3 denote the AB bond stretches, r_e is the AB bond equilibrium length, and $\Delta\alpha$ is the deviation of the ABA bending angle from its equilibrium value (Fig. 3.1). Hence, we consider six generalized coordinates and the corresponding conjugate generalized momenta are

$$\boldsymbol{\Pi} = \{\hat{J}_x, \hat{J}_y, \hat{J}_z, \hat{p}_k \;\; ; \; k = 1, 2, 3\}, \tag{2}$$

where $\{\hat{J}_x, \hat{J}_y, \hat{J}_z\}$ are the components of the molecule-fixed angular momentum [40, 41] and

$$\hat{p}_k = -i\hbar\frac{\partial}{\partial q_k} \;\; ; \; k = 1, 2, 3, \tag{3}$$

are the conjugate momenta of the vibrational internal valence coordinates.

The quantum-mechanical rovibrational kinetic energy may be expressed as [42, 43]

$$T = \frac{1}{2}\sum_{\alpha,\alpha'} \Pi_\alpha \, G_{\alpha,\alpha'} \, \Pi_{\alpha'} + U(\boldsymbol{q}); \tag{4}$$

where the G-matrix elements can be written in terms of the triatomic molecule internal coordinates and $U(\boldsymbol{q})$ is a mass-dependent potential term [35, 44]. A detailed Eckart-frame rovibrational kinetic operator in terms of valence coordinates and their conjugate momenta may be written in the form [45, 44]

$$\hat{T}_{vir} = \hat{T}_{rot-cent} + \hat{T}_{vib} + \hat{T}_{cor} + U(\boldsymbol{q}), \tag{5}$$

where $\hat{T}_{rot-cent}$ includes the rotational and centrifugal interactions

$$\begin{aligned} T_{rot-cent} \;&=\; \frac{1}{4}\left(G_{xx} + G_{yy}\right)\hat{J}^2 + \frac{1}{2}\left[G_{zz} - \frac{1}{2}\left(G_{xx} + G_{yy}\right)\right]\hat{J}_0^2 + \frac{1}{8}\left(G_{xx} - G_{yy}\right)\left[\hat{J}_+^2 + \hat{J}_-^2\right] \\ &+\; \frac{1}{4}\,G_{xz}\left[\hat{J}_-(2\hat{J}_0 + \hbar) + \hat{J}_+(2\hat{J}_0 - \hbar)\right], \end{aligned} \tag{6}$$

where $\{\hat{J}_0, \hat{J}_+, \hat{J}_-\}$ are the circular components of the angular momentum operator [40]. The pure vibrational term $\hat{T}_{vib}$ is

$$\begin{aligned} \hat{T}_{vib} \;&=\; \frac{1}{2}\,G_{11}\left[p_1^2 + p_3^2\right] + \frac{1}{2}\,p_2\,G_{22}\,p_2 + G_{13}\,p_1\,p_3 \\ &+\; \frac{1}{2}\left[p_1\,G_{12}\,p_2 + p_2 G_{12}\,p_1\right] + \frac{1}{2}\left[p_2\,G_{23}\,p_3 + p_3 G_{23}\,p_2\right], \end{aligned} \tag{7}$$

while the Coriolis interaction $\hat{T}_{cor}$ is as follows

$$\hat{T}_{cor} = \frac{1}{2}\sum_{k=1}^{3}\left(p_k\,G_{ky} + G_{ky}\,p_k\right)\hat{J}_y, \tag{8}$$

where the G_{ky} matrix elements depend on the local vibrational displacements (see Eq. (5) in Ref. [44]) and the sum of its product with the local conjugate momenta has the appropriate symmetry, which is B_2 in this case (see Table 1).

Finally, the explicit form of the pseudopotential $U(\boldsymbol{q})$ is given in Eq. (2.10) of Ref. [35].

The $\hat{T}_{rot-cent}$, $\hat{T}_{vib}$, and $\hat{T}_{cor}$ contributions to the kinetic energy are functions of the valence coordinates, which will be modeled with Morse potentials. Hence, any contribution of the Hamiltonian will be considered as part of a Taylor series expansion in terms of the q_k internal coordinates or the associated Morse variables

$$y_k = 1 - \exp(-a_k\, q_k); \quad k = 1, 2, 3, \tag{9}$$

where the a_k parameter defines the range of the Morse potential for the k-th oscillator.

The potential energy function may also be expanded either in terms of the q_k internal coordinates or in terms of Morse coordinates (9), keeping in mind that the interaction terms in the Hamiltonian must be totally-symmetric under the molecular symmetry group operations. The potential energy function, expanded up to fourth order in the Morse coordinates, takes the general form:

$$\begin{aligned} V(y_k) &= V_0 + \sum_j f_j\, y_j + \sum_{j\le k} f_{jk}\, y_j\, y_k \\ &+ \sum_{j\le k\le l} f_{jkl}\, y_j\, y_k\, y_l + \sum_{j\le k\le l\le m} f_{jklm}\, y_j\, y_k\, y_l\, y_m + \ldots \end{aligned} \tag{10}$$

The use of Morse coordinates has two advantages. On the one hand, it improves the calculations convergence and, on the other hand, quadratic terms can be identified with local Morse potentials, which implies a description of the system in terms of interacting Morse oscillators. The use of a Morse coordinate to model stretching degrees of freedom is standard. In this particular case, we also use a Morse variable to model the triatomic bending degree of freedom. This can be justified due to the asymmetric behaviour of the bending potential for large and small values of the bending coordinate as the excitation energy increases (being still far from the linearity). This conclusion is supported by the model potential energy functions for bending degrees of freedom obtained from an algebraic approach [46].

3. Basis set and symmetrization procedure

When solving the Schrödinger equation associated with a rovibrational Hamiltonian, the definition of a convenient basis set is a crucial step. It is convenient to consider a symmetry-adapted basis to simplify the diagonalization procedure and, if necessary, to get rid of spurious states. In this Section the basis set, as well as its corresponding symmetrization, are presented.

3.1. Basis set

The rovibrational basis is defined as a direct product of a vibrational and a rotational basis. Since the Hamiltonian of Hydrogen Selenide is written in terms of internal coordinates, the vibrational basis set is provided by the direct product of three Morse oscillators, associated with local coordinates

$$|\mathrm{v}_1\,,\ \mathrm{v}_2\,,\ \mathrm{v}_3\,\rangle \equiv |\mathrm{v}_1\,\rangle \otimes |\mathrm{v}_2\,\rangle \otimes |\mathrm{v}_3\,\rangle\,, \tag{11}$$

where v_1 and v_3 are quantum numbers for the local stretching H-Se modes, and v_2 is the quantum number associated with the bending angle $\angle$(HSeH).

The symmetric top basis is employed for the description of the rotational degrees of freedom. The rotational functions, $|J, k_a, m\rangle$, depend on the rotational quantum numbers: the total angular momentum (J), its projection in the a axis of the molecule-fixed system of reference k_a, and its projection in the Z axis of the laboratory-fixed system of reference (m); assuming the I^r convention [$abc = zxy$] for the axis system (see Figure 3.1). From now on, the Z-component of the angular momentum in the laboratory system is not explicitly considered since the problem is rotationally invariant and no external field is considered.

Hence, the rovibrational basis set can be expressed as follows

$$|\mathrm{v}_1\,,\ \mathrm{v}_2\,,\ \mathrm{v}_3\,;\ J\,,\ k_a\rangle = |\mathrm{v}_1\,,\ \mathrm{v}_2\,,\ \mathrm{v}_3\rangle\, |J\,,\ k_a\rangle\,. \tag{12}$$

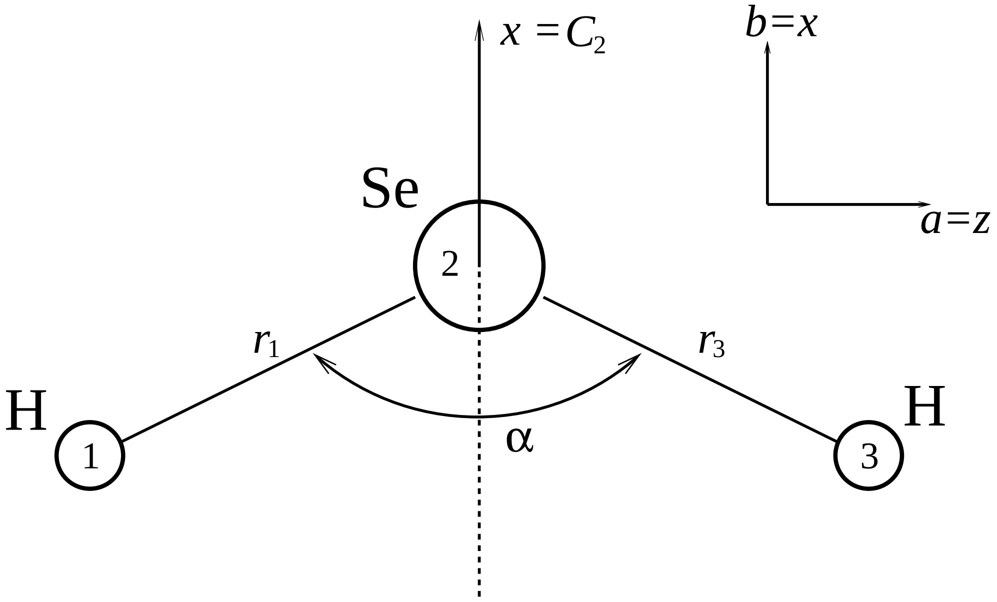

Figure 1. Schematic diagram of a bent triatomic ABA molecule, depicting the selected atom numbering, and molecular axis system.

Table 1. Character table for the MS group $C_{2v}(M)$ in terms of the group classes [40].

$C_{2v}(M)$	K_1	K_2	K_3	K_4	
A_1	1	1	1	1	$\frac{1}{\sqrt{2}}(r_1 + r_3)$, α
A_2	1	1	-1	-1	$J_b \equiv J_x$
B_1	1	-1	-1	1	$J_a \equiv J_z$
B_2	1	-1	1	-1	$\frac{1}{\sqrt{2}}(r_1 - r_3)$, $J_c \equiv J_y$

The $C_{2v}(M)$ group classes are the following:
$K_1 = E$; $K_2 = (13)$; $K_3 = E^*$; $K_4 = (13)^*$

3.2. Symmetrization procedure

The rovibrational basis set (12) is symmetry-projected using a method that has already been presented in detail elsewhere [47, 48, 49]. Hence, only the basic steps of the approach are included.

The symmetry projection is accomplished using the eigenfunction method, whose basic idea consists in defining an operator that is a linear of combination of the classes of equivalence of the symmetry group. The diagonalization of this operator in the basis under projection allows to assign symmetry labels to the resulting eigenvectors. If the irreducible representations (irreps) of the symmetry group are one-dimensional and the reducible representation space presents no multiplicity, it is possible to distinguish the irreps through one operator, called a type I Complete Set of Commuting Operators (CSCO-I). The diagonalization of the matrix representation of the CSCO-I operator provides symmetry-adapted eigenvectors whose associated irrep is determined by the eigenvalues [50].

The molecular symmetry group of the H_2Se molecule is $C_{2v}(M)$, whose character table is given in Table 1. Each element of the $C_{2v}(M)$ group can be decomposed as a product of their actions upon the rotational, the vibrational, and the nuclear spin subspaces, as displayed in Table 2 [40]. In the following we only consider the first two subspaces.

In order to define the CSCO-I operator we proceed to construct the table of possible λ eigenvalues, defined by the equation

Table 2. Equivalent rotations, elements of the molecular point group and nuclear spin permutations associated with the elements of $C_{2v}(M)$ group. The notation used for the equivalent rotations is standard and is defined, for example, in Ref. [40].

$O(M)$	O_r	O_v	O_s
E	R_z^0	E	p_0
(13)	R_0^π	C_{2x}	p_{13}
E^*	$R_{\pi/2}^\pi$	σ_{xz}	p_0
$(13)^*$	R_z^π	σ_{xy}	p_{13}

Table 3. Table of λ's for the MS group $C_{2v}(M)$.

Γ	λ_1^Γ	λ_2^Γ	λ_3^Γ	λ_4^Γ	$\nu = \lambda_2^\Gamma + 3\lambda_4^\Gamma$
A_1	1	1	1	1	+4
A_2	1	1	-1	-1	-2
B_1	1	-1	-1	1	+2
B_2	1	-1	1	-1	-4

$$\lambda_i^\Gamma = \frac{|K_i|\chi_i^{(\Gamma)*}}{n_\Gamma} \ , \tag{13}$$

where $|K_i|$ stands for the number of elements belonging to the i-th class, n_Γ corresponds to the dimension of the Γ-th irrep, while $\chi_i^{(\Gamma)}$ is its character. The possible values of λ can be found in Table 3, where the combination $\lambda_2^\Gamma + 3\lambda_4^\Gamma$ distinguishes among the possible cases. Thus a suitable CSCO-I may be defined as

$$C_I = (13) + 3(13)^* \ , \tag{14}$$

with eigenvalues $\nu = \lambda_2^\Gamma + 3\lambda_4^\Gamma$ that provide the symmetry label Γ. In the following subsections this symmetrization procedure is applied in the first place to the rotational subspace and then to the full rovibrational basis set.

3.2.1. Symmetrization of the rotational basis set

When dealing with the rotational subspace, Eq. (14) should be written in terms of the equivalent rotations (see Table 2)

$$C_I = R_0^\pi + 3R_z^\pi \ . \tag{15}$$

The rotational basis $\{|J,K\rangle, |J,-K\rangle\}$ is defined for a given J and $K = |k_a|$. In this basis the representation of the operator C_I takes the form

$$\mathbf{\Delta}(C_I) = \begin{pmatrix} 3e^{-iK\pi} & (-1)^J \\ (-1)^J & 3e^{iK\pi} \end{pmatrix} \ , \tag{16}$$

with eigenvalues

$$\lambda_\pm = (-1)^K(3 \pm 1) \tag{17}$$

and eigenvectors (Wang basis functions)

Table 4. $C_{2v}(M)$ group symmetry labeling of H_2Se rotational wave functions.

K	Γ	ν	eigenvector
K =even			
	A_1	4	$\frac{1}{\sqrt{2}}\left[(-1)^{-J}\|J,K\rangle + \|J,-K\rangle\right]$
	B_1	2	$\frac{1}{\sqrt{2}}\left[(-1)^{-J+1}\|J,K\rangle + \|J,-K\rangle\right]$
K =odd			
	A_2	-2	$\frac{1}{\sqrt{2}}\left[(-1)^{-J}\|J,K\rangle + \|J,-K\rangle\right]$
	B_2	-4	$\frac{1}{\sqrt{2}}\left[(-1)^{-J+1}\|J,K\rangle + \|J,-K\rangle\right]$

$$\Psi_+ = \frac{1}{\sqrt{2}}\left[(-1)^{-J-K}|J,K\rangle + |J,-K\rangle\right] , \tag{18}$$

$$\Psi_- = \frac{1}{\sqrt{2}}\left[-(-1)^{-J-K}|J,K\rangle + |J,-K\rangle\right] . \tag{19}$$

The correspondence of this eigensystem with the eigenvalues ν given in Table 3 is shown in Table 4.

3.2.2. Projection of the rovibrational basis set

With respect to the rotation-vibration degrees of freedom, we should note that each group element of the CSCO-I in the Molecular Symmetry Group is given as a direct product of an equivalent rotation and a point group operation, as it happens for their representations. Thus, the C_I representation is the following

$$\mathbf{\Delta}(C_I) = \mathbf{\Delta}(R_0^{\pi}) \otimes \mathbf{\Delta}(C_{2x}) + 3\mathbf{\Delta}(R_z^{\pi}) \otimes \mathbf{\Delta}(\sigma_{xy}) \ , \tag{20}$$

where $\mathbf{\Delta}(C_I)$ stands for the C_I operator representation, $\mathbf{\Delta}(R_0^{\pi})$ is the equivalent rotation R_0^{π} representation, $\mathbf{\Delta}(C_{2x})$ is the point group operation C_{2x} representation, etc.

The rovibrational subspace may be expressed in the following form

$$\phi_1 = |J,K\rangle \otimes |\mathrm{v}', \mathrm{v}_2, \mathrm{v}''\rangle \ , \tag{21}$$

$$\phi_2 = |J,K\rangle \otimes |\mathrm{v}'', \mathrm{v}_2, \mathrm{v}'\rangle \ , \tag{22}$$

$$\phi_3 = |J,-K\rangle \otimes |\mathrm{v}', \mathrm{v}_2, \mathrm{v}''\rangle \ , \tag{23}$$

$$\phi_4 = |J,-K\rangle \otimes |\mathrm{v}'', \mathrm{v}_2, \mathrm{v}'\rangle \ , \tag{24}$$

where v_2 is the bending quantum number and v' and v'' stand for the stretching local quantum numbers, which are equivalent under symmetry operations. In this basis the reducible matrix representation of C_I takes the explicit form

$$\mathbf{\Delta}(C_I) = \begin{pmatrix} 0 & 3e^{-iK\pi} & 0 & (-1)^J \\ 3e^{-iK\pi} & 0 & (-1)^J & 0 \\ 0 & (-1)^J & 0 & 3e^{iK\pi} \\ (-1)^J & 0 & 3e^{iK\pi} & 0 \end{pmatrix} . \tag{25}$$

In Table 5 the corresponding eigensystem is displayed, where eigenvectors correspond to (not normalized) symmetry-projected functions and eigenvalues determine the associated irrep in accordance to Table 3. In the particular case $\mathrm{v}' = \mathrm{v}''$ the rovibrational subspace has dimension two and half the eigenvectors in Table 5 are exactly zero.

Table 5. $C_{2v}(M)$ molecular group symmetry labeling of the rovibrational wavefunctions subspace spanned by Eqs. (21-24) for H_2Se.

Γ	ν	eigenvector
$C_{2v}(M)$	$\lambda_2 + 3\lambda_4$	
K =even		
A_2	-2	$(-1)^J\phi_1 - (-1)^J\phi_2 - \phi_3 + \phi_4$
B_1	2	$-(-1)^J\phi_1 - (-1)^J\phi_2 + \phi_3 + \phi_4$
B_2	-4	$-(-1)^J\phi_1 + (-1)^J\phi_2 - \phi_3 + \phi_4$
A_1	4	$(-1)^J\phi_1 + (-1)^J\phi_2 + \phi_3 + \phi_4$
K =odd		
B_1	2	$-(-1)^J\phi_1 + (-1)^J\phi_2 - \phi_3 + \phi_4$
A_2	-2	$(-1)^J\phi_1 + (-1)^J\phi_2 + \phi_3 + \phi_4$
A_1	4	$(-1)^J\phi_1 - (-1)^J\phi_2 - \phi_3 + \phi_4$
B_2	-4	$-(-1)^J\phi_1 - (-1)^J\phi_2 + \phi_3 + \phi_4$

4. Algebraic Hamiltonian

In this section an algebraic realization of the rovibrational Hamiltonian presented in Section 2 is established. To this end, ladder operators associated with one dimensional Morse wave functions are introduced. Since such ladder operators satisfy $U(2)$ commutation relations, this is the dynamical algebra of the one-dimensional Morse potential. One of the advantages of the algebraic representation is that the relevant interactions can be easily distinguished and constructed, and their matrix elements are analytical. This greatly facilitates the selection of convenient higher-order interactions.

The dynamical algebra for the vibrational subspace corresponds to the direct product $G_v \equiv U_1(2) \times U_2(2) \times U_3(2)$, where each of the $U(2)$ Lie algebras is associated to a particular local mode of the Hydrogen Selenide. The dynamical algebra for the rovibrational space is then built combining the direct product of the vibrational and rotational groups $G_v \times SO^{(rot)}(3)$. A suitable rovibrational basis to diagonalize the Hamiltonian is provided by the chain [51]

$$\begin{array}{ccccccccccccccc}
U_1^{(s)}(2) & \times & U_2^{(b)}(2) & \times & U_3^{(s)}(2) & \times & SO^{(rot)}(3) & \supset & SO_1^{(s)}(2) & \times & SO_2^{(b)}(2) & \times & SO_3^{(s)}(2) & \times & SO^{(rot)}(2) \\
\downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\
| N_s & & N_b & & N_s & & J & ; & v_1 & & v_2 & & v_3 & & K\rangle
\end{array}$$

where the associated quantum number is indicated under each algebra. The superscripts s, b, and rot stand for stretching, bending, and rotational degrees of freedom, respectively. The total number of boson in $U^{(s)}(2)$ and $U^{(b)}(2)$, N_s and N_b, indicate the maximum number of quanta of excitation in each local degree of freedom, and they are related to the stretching and bending Morse potential parameters by

$$N_k + 1 = \sqrt{\frac{8D_k\mu}{\hbar^2 a_k^2}}, \tag{26}$$

where D_k is the depth of the Morse potential for the k-th local vibrational degree of freedom, μ is the reduced mass, given by the diagonal contribution of the vibrational G-matrix elements, and a_k is the range of the local Morse potential, already defined in Sect. 2.

The mapping of the phase-space Hamiltonian, defined in Section 2, with an algebraic Hamiltonian, expressed in terms of Morse variables, is carried out as follows: internal bond coordinates, associated with Morse oscillators, and their conjugate momenta are expressed in terms of $U(2)$ generators in the linear approximation [7, 8]

$$\hat{p}_k \simeq \frac{i}{2}\sqrt{2\,\hbar\,\omega_k\,\mu}\,(b_k^\dagger - b_k), \tag{27}$$

$$\frac{\hat{y}_k}{a_k} \simeq \sqrt{\frac{\hbar}{2\,\omega_k\,\mu}}\,(b_k^\dagger + b_k), \tag{28}$$

where $b_k^\dagger$ and b_k are creation and annihilation operators for the Morse functions [7, 8]

$$\begin{aligned} b_k^\dagger\, |\mathrm{v}_k\rangle &= \sqrt{(\mathrm{v}_k+1)\,(1-\frac{\mathrm{v}_k}{N_k})}\, |\mathrm{v}_k+1\rangle, & (29)\\ b_k\, |\mathrm{v}_k\rangle &= \sqrt{\mathrm{v}_k\,(1-\frac{\mathrm{v}_k-1}{N_k})}\, |\mathrm{v}_k-1\rangle. & (30)\end{aligned}$$

In this algebraic space, the Morse energies for the k-th degree of freedom are given by

$$\hat{H}_k^{(Morse)} = \hbar\omega_k(b_k^\dagger b_k + b_k b_k^\dagger)/2, \tag{31}$$

plus a neglected constant energy shift.

It is worth to note that the results in Eqs. (27-31) are the same in the case of a Pöschl-Teller potential. This is due to the isomorphism that exists between the one dimensional limit of the vibron model and the one dimensional Morse and Pöschl-Teller potentials [9].

The substitution of internal coordinates and their corresponding conjugate momenta by ladder $U(2)$ operators provides the algebraic representation of the vibrational part of the Hamiltonian. To complete this step it is necessary, however, to expand in a Taylor series the vibrational G-matrix elements expressed in terms of internal coordinates. In this way the substitution of the kinetic (5) and potential (10) energy operators can be done in a straightforward way. The G-matrix elements for the rovibrational description have been taken from Refs. [35, 44].

4.1. Rotational matrix elements

In this subsection we present the matrix elements of the Hamiltonian in the rotational basis $|JK\rangle$. From this result, the matrix elements in the symmetrized rotational basis can be obtained, making the corresponding linear transformation.

The matrix elements of the rotational and centrifugal kinetic energy (6) have a diagonal part

$$\langle JK|\hat{T}_{rot-cent}|JK\rangle = \frac{1}{4}(G_{xx}+G_{yy})\,\hbar^2 J(J+1) - \left[\frac{1}{4}(G_{xx}+G_{yy}) - \frac{1}{2}G_{zz}\right]\hbar^2 K^2, \tag{32}$$

and a nondiagonal contribution

$$\begin{aligned} \langle JK\pm 1|\hat{T}_{rot-cent}|JK\rangle &= \frac{\hbar^2}{4}\, G_{xz}\, \sqrt{J(J+1)-K(K\pm 1)}\,(2K\pm 1), & (33)\\ \langle JK\pm 2|\hat{T}_{rot-cent}|JK\rangle &= \frac{\hbar^2}{8}\left(G_{xx}-G_{yy}\right)\,\sqrt{J(J+1)-K(K\pm 1)} & \\ &\times\ \sqrt{J(J+1)-(K\pm 1)(K\pm 2)}. & (34)\end{aligned}$$

The Coriolis kinetic energy matrix elements are

$$\begin{aligned} \langle JK\pm 1|\hat{T}_{cor}|JK\rangle &= \pm i\frac{\hbar}{4}\sum_k (p_k\, G_{ky} + G_{ky}\, p_k) & \\ &\times\ \sqrt{J(J+1)-K(K\pm 1)}. & (35)\end{aligned}$$

The matrix representation of each component of the angular momentum were taken from Refs. [40, 41].

4.2. The rovibrational Hamiltonian

The expansion of kinetic and potential energy terms is undertaken up to eighth-order inclusive. Although the present formalism has been conceived to establish a link between spectroscopic parameters and structure and force constants [11, 12, 13, 15, 18, 19, 20, 21], in the present case it is used in a purely phenomenological way. Our aim is to show the power and simplicity of this approach providing a fit of spectroscopic quality for a particular case. A substantial improvement is expected including higher orders of the rotational angular momentum components in the kinetic operator expansion, akin to what happens in the Watson Hamiltonian [52]. This latter implementation is currently under study.

Hence, from the correspondence between phase space and the anharmonic ladder operators, an algebraic representation of the rovibrational Hamiltonian is obtained [7, 8, 9]. This approach to construct an algebraic Hamiltonian has the advantage of providing an estimation of the PES force constants from the algebraic spectroscopic parameters.

In this work, the relevant physical interactions chosen for the algebraic Hamiltonian stem from the phase space Hamiltonian (5,10)[1] and they are restricted to those that preserve the polyad number

$$P = 2(\mathrm{v}_1 + \mathrm{v}_3) + \mathrm{v}_2 \ , \tag{36}$$

where v_k stands for the number of quanta in the k-th vibrational local mode. Therefore, the rovibrational Hamiltonian in the local anharmonic representation is given by

$$\begin{aligned}
\hat{H}_{rv} &= \hat{H}_{vib} \\
&+ B_J \hat{J}^2 \\
&+ B_K \hat{J}_z^2 \\
&+ B_{xy}(\hat{J}_+^2 + \hat{J}_-^2) \\
&+ D_{J\omega_1} \hat{J}^2 (b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2 \\
&+ D_{J\lambda} \hat{J}^2 (b_1^\dagger b_3 + b_3^\dagger b_1) \\
&+ D_{J\omega_2} \hat{J}^2 (b_2^\dagger b_2 + b_2 b_2^\dagger)/2 \\
&+ D_{J\omega x_1} \hat{J}^2 (b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3) \\
&+ D_{J\omega x_{11}} \hat{J}^2 b_1^\dagger b_1 b_3^\dagger b_3 \\
&+ D_{J\omega x_{12}} \hat{J}^2 \, (b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)(b_2^\dagger b_2 + b_2 b_2^\dagger)/4 \\
&+ D_{J\beta_1} \hat{J}^2 \, [(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)(b_1^\dagger b_3 + b_3^\dagger b_1)/2 + h.c.] \\
&+ D_{JF} \hat{J}^2 \, \hat{F}_m \\
&+ D_{J\gamma_2} \hat{J}^2 \, [(b_1^\dagger b_3 + b_3^\dagger b_1)\,(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)] \\
&+ D_{K\omega_1} \hat{J}_z^2 (b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2 \\
&+ D_{K\lambda} \hat{J}_z^2 (b_1^\dagger b_3 + b_3^\dagger b_1) \\
&+ D_{K\omega_2} \hat{J}_z^2 (b_2^\dagger b_2 + b_2 b_2^\dagger)/2 \\
&+ D_{K\omega x_1} \hat{J}_z^2 (b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3) \\
&+ D_{K\omega x_2} \hat{J}_z^2 (b_2^\dagger b_2 b_2^\dagger b_2) \\
&+ D_{K\beta_2} \hat{J}_z^2 \, (b_1^\dagger b_3 + b_3^\dagger b_1)(b_2^\dagger b_2 + b_2 b_2^\dagger)/2 \\
&+ D_{K\gamma_1} \hat{J}_z^2 \, [(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)] \\
&+ D_{K\delta_1} \hat{J}_z^2 \, [(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)
\end{aligned}$$

---

[1] Interaction terms could also be determined by the coupling of tensorial operators [53] or with the help of the eigenfunction method (See Sec. 3), without a direct connection with the phase space Hamiltonian.

$$\begin{aligned}
&\quad - 2\,(b_1^\dagger b_1 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_3^\dagger b_3)] \\
&+ \; D_{K\delta_3}\hat{J}_z^2\,[(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_3^\dagger b_3)] \\
&+ \; D_{xy\omega_1}(\hat{J}_+^2 + \hat{J}_-^2)(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2 \\
&+ \; D_{xy\lambda}(\hat{J}_+^2 + \hat{J}_-^2)(b_1^\dagger b_3 + b_3^\dagger b_1) \\
&+ \; D_{xy\omega_2}(\hat{J}_+^2 + \hat{J}_-^2)(b_2^\dagger b_2 + b_2 b_2^\dagger)/2 \\
&+ \; D_{xy\omega x_1}(\hat{J}_+^2 + \hat{J}_-^2)(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3) \\
&+ \; D_{xy\omega x_2}(\hat{J}_+^2 + \hat{J}_-^2)(b_2^\dagger b_2 b_2^\dagger b_2) \\
&+ \; D_{xy\omega x_{11}}(\hat{J}_+^2 + \hat{J}_-^2)b_1^\dagger b_1 b_3^\dagger b_3 \\
&+ \; D_{xy\gamma_1}(\hat{J}_+^2 + \hat{J}_-^2)\,[(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)] \\
&+ \; D_{xy\gamma_4}(\hat{J}_+^2 + \hat{J}_-^2)\,[(b_1^\dagger b_1 b_3^\dagger b_3)\,(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2] \\
&+ \; D_{xy\delta_1}(\hat{J}_+^2 + \hat{J}_-^2)\,[(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3) \\
&\quad - 2\,(b_1^\dagger b_1 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_3^\dagger b_3)] \\
&+ \; D_{xy\delta_3}(\hat{J}_+^2 + \hat{J}_-^2)\,[(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_3^\dagger b_3)] \\
&+ \; C_\lambda(\hat{J}_+ - \hat{J}_-)\,(b_1^\dagger b_3 - b_3^\dagger b_1) \\
&+ \; C_{\lambda^{[2]}}(\hat{J}_+ - \hat{J}_-)\,(b_1^\dagger b_1^\dagger b_3 b_3 - b_3^\dagger b_3^\dagger b_1 b_1) \\
&+ \; C_F(\hat{J}_+ - \hat{J}_-)\,(b_2^\dagger b_2^\dagger b_1 - b_2^\dagger b_2^\dagger b_3 - b_1^\dagger b_2 b_2 + b_3^\dagger b_2 b_2) \\
&+ \; D_{xz\omega_1}[\hat{J}_-(2\hat{J}_0 + 1) + \hat{J}_+(2\hat{J}_0 - 1)]\,(b_1^\dagger b_1 - b_3^\dagger b_3) + \ldots \;\; ,
\end{aligned} \tag{37}$$

where *h.c.* stands for hermitian conjugate, the *B* parameters refer to equilibrium rotational constants, the *D* parameters correspond to centrifugal terms, and the *C* parameters stems from the Coriolis interaction. In this expression we have introduced the notation $\hat{F}_m$ for the Fermi interaction, given by

$$\hat{F}_m = [(b_1^\dagger b_2 b_2 + b_3^\dagger b_2 b_2) + (b_2^\dagger b_2^\dagger b_1 + b_2^\dagger b_2^\dagger b_3)] \;\; . \tag{38}$$

The pure vibrational Hamiltonian $\hat{H}_{vib}$ is

$$\begin{aligned}
\hat{H}_{vib} \;\; = \;\; & \omega_1(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2 \\
+ \;\; & \lambda(b_1^\dagger b_3 + b_3^\dagger b_1) \\
+ \;\; & \omega_2(b_2^\dagger b_2 + b_2 b_2^\dagger)/2 \\
+ \;\; & \omega x_1(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3) \\
+ \;\; & \omega x_2(b_2^\dagger b_2 b_2^\dagger b_2) \\
+ \;\; & \omega x_{11}\, b_1^\dagger b_1 b_3^\dagger b_3 \\
+ \;\; & \omega x_{12}\,(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)(b_2^\dagger b_2 + b_2 b_2^\dagger)/4 \\
+ \;\; & \lambda^{[2]}(b_1^\dagger b_1^\dagger b_3 b_3 + h.c.) \\
+ \;\; & \beta_1\,[(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)(b_1^\dagger b_3 + b_3^\dagger b_1)/2 + h.c.] \\
+ \;\; & \beta_2\,(b_1^\dagger b_3 + b_3^\dagger b_1)(b_2^\dagger b_2 + b_2 b_2^\dagger)/2 \\
+ \;\; & F[(b_1^\dagger b_2 b_2 + b_3^\dagger b_2 b_2) + (b_2^\dagger b_2^\dagger b_1 + b_2^\dagger b_2^\dagger b_3)] \\
+ \;\; & \frac{1}{2}\,F\omega_1\left[\hat{F}_m\,(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2 + h.c.\right] \\
+ \;\; & \frac{1}{2}\,F\lambda[\hat{F}_m\,(b_1^\dagger b_3 + b_3^\dagger b_1) + h.c.]
\end{aligned}$$

$$
\begin{aligned}
&+ \quad \frac{1}{2}\, F\omega_2[\hat{F}_m\,(b_2^\dagger b_2 + b_2 b_2^\dagger)/2 + h.c.]\\
&+ \quad \gamma_1[(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2\,(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\\
&\qquad - (b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2\,(b_1^\dagger b_1 b_3^\dagger b_3)]\\
&+ \quad \gamma_2[(b_1^\dagger b_3 + b_3^\dagger b_1)\,(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)]\\
&+ \quad \gamma_3[(b_2^\dagger b_2 + b_2 b_2^\dagger)/2\,(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)]\\
&+ \quad \gamma_4[(b_1^\dagger b_1 b_3^\dagger b_3)\,(b_1^\dagger b_1 + b_1 b_1^\dagger + b_3^\dagger b_3 + b_3 b_3^\dagger)/2]\\
&+ \quad \delta_1[(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\\
&\qquad - 2\,(b_1^\dagger b_1 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_3^\dagger b_3)]\\
&+ \quad \delta_2\,(b_1^\dagger b_1 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_3^\dagger b_3)\\
&+ \quad \delta_3\,[(b_1^\dagger b_1 b_1^\dagger b_1 + b_3^\dagger b_3 b_3^\dagger b_3)\,(b_1^\dagger b_1 b_3^\dagger b_3)]\\
&+ \quad F^{[2]}\hat{F}_m\,\hat{F}_m \;\; . \qquad (39)
\end{aligned}
$$

The matrix elements of the rovibrational Hamiltonian can be obtained in a straightforward way in the local basis set (12). However, in practice, it is more convenient to use the symmetry-projected basis set

$$|\nu_{vr}, \Gamma_{vr}\rangle = |\nu_{vib}, \Gamma_{vib}\rangle\, |J, K, \Gamma_{rot}\rangle \;\; , \qquad (40)$$

obtained with the approach presented in Section 3. The Γ_{vr} symmetry can also be obtained as the direct product $\Gamma_{vib} \otimes \Gamma_{rot}$ [40]. The quantum numbers ν_{vr} of the complete basis set gather the vibrational and rotational quantum numbers. In the framework of this approach it is possible to work either in a local or in a normal scheme. The latter one is obtained through the diagonalization of the symmetrized number operators defined in terms of bosonic operators [47].

In case that the polyad number is not a good quantum number, the polyad scheme has to be broken with the inclusion of additional interactions, leaving aside the restriction in Eq. (36). The polyad breaking may be treated perturbatively [54].

5. Application to Hydrogen Selenide ($H_2^{80}Se$)

As an application of the presented approach, a fit to the experimental rovibrational spectrum of Hydrogen Selenide ($H_2^{80}Se$) in its ground electronic state [24, 25, 26, 27, 28, 29, 30, 31, 32, 33] has been performed, including levels up to angular momentum $J_{max} = 5$ and up to polyad $P_{max} = 10$. In the pure vibrational case energies up to polyad $P_{max} = 12$ were considered.

The number of bosons (26) were adjusted to $N_s = 56$ and $N_b = 234$, for stretching and bending degrees of freedom. An initial estimate of the N value for a particular mode of vibration can be made using the fundamental (E_1) and first overtone (E_2) energies and the formula $N = \omega_e/\omega_e x_e - 1 \simeq (4E_1 - E_2)/(2E_1 - E_2)$ [2]. In the triatomic stretching case, two values can be obtained, one for the symmetric and another for the antisymmetric vibrational degrees of freedom; the initial N value in this case is the average of the former two values. This initial value is manually varied to optimize the agreement with experimental data. The dependence on this parameter of the *rms* is usually quite smooth.

The fitting procedure, a non-linear least square fit, was carried out as follows. In first place, pure vibrational term values were calculated for the 140 lowest vibrational states, up to polyad 12, through the fit of the available 24 experimental term values. In this step, the theoretical vibrational energies were replaced within the experimental accuracy by the corresponding experimental band centers, using the empirical basis set correction (EBSC) applied in the spectral simulation of ammonia [55, 56]. The obtained vibrational rms was 0.0016 cm^{-1}. Once the pure vibrational parameters were determined, they were kept fixed to fit the rovibrational parameters. The final value of the complete Hamiltonian parameters was obtained gradually, by increasing the number of experimental data polyad by polyad and increasing the total angular momentum value step by step. A total number of 3324 rovibrational energies was calculated through the fit of 745 available experimental levels, with an rms of 0.117 cm^{-1}. Therefore, 2579

Table 6. Parameters of the vibrational Hamiltonian (39) used in the global fit up to polyad 12 and J up to 5 in the analysis of $H_2^{80}Se$. All parameters are given in cm^{-1} units with one standard deviation statistical uncertainties for final significant digits.

Parameter	Values	Parameter	Values
ω_1	2393.65686(1)	$F\omega_1$	0.155478(5)
λ	-9.52086(1)	$F\lambda$	-0.38570(2)
ω_2	1037.145816(6)	$F\omega_2$	-0.376478(4)
ω_{x_1}	-1.095555(6)	γ_1	0.556735(4)
ω_{x_2}	1.457815(4)	γ_2	-0.23644(1)
$\omega_{x_{11}}$	-29.615626(6)	γ_3	-1.070584(7)
$\omega_{x_{12}}$	-19.436396(9)	γ_4	28.029001(4)
$\lambda^{[2]}$	-0.33035(1)	δ_1	-0.071699(3)
β_1	1.219793(9)	δ_2	-12.9510250(9)
β_2	-0.041515(3)	δ_3	-6.3920624(6)
F	-11.13182(2)	$F^{[2]}$	-0.118708(4)

rovibrational energies have been predicted for the 140 lowest vibrational bands and this is the first time that some levels up to a maximum angular momentum $J_{max}= 5$ and polyad number $P_{max}=10$ are reported.

The total number of fitted parameters is 57: 22 of them are associated with pure vibrational interactions and the remaining 35 affect rotation-vibration interactions. In Tables 6 and 7, the values and uncertainties of Hamiltonian (37) fitted parameters are shown. From this set of optimized algebraic spectroscopic parameters is possible to obtain an estimation of the canonical force, Coriolis, and centrifugal distortion coupling constants (see, e.g. [13]).

In the provided supplementary material we include a calculated spectrum up to angular momentum $J = 5$ and polyad $P = 10$, and up to polyad $P = 12$ for the pure vibrational term values. The available experimental rovibrational energy terms have been included to assess the goodness of fit. The obtention of results of spectroscopic accuracy including levels with a larger angular momentum implies the extension of the model, including higher order operators in the Hamiltonian expansion. This extension of the model, in the spirit of a Watson Hamiltonian, is currently being under research.

As noted in the introduction, the aim of the present work is not to compete with the calculations published in Ref. [39]. However, a comparison of the present results with theirs is mandatory. In Ref. [39], 1723 rovibrational energies were reproduced for the isotopologue $H_2^{80}Se$, with an rms of 0.16 cm^{-1}, up to polyad $P = 12$ and $J = 8$. In this work, the number of rovibrational energy spacings is smaller, because included levels go up to $J = 5$. The calculated 72 vibrational term values, up to polyad $P = 12$, of Ref. [39] are in good agreement with our results for the lower polyads. For the highest polyads, differences increase between the predictions in Ref. [39] and ours. An experimental recording in this energy range would be a great help in the obtention of an appropriate theoretical description of the coupling between highly-excited states. Also, due to differences between the models, there are some discrepancies in the labeling of some vibrational term values between Ref. [39] and our results; e.g. in the bands $3\nu_1$ and $\nu_1 + 2\nu_3$. In this case, our labeling agrees with the labels suggested in the paper which provides the experimental vibrational band centers [30].

To finish, a last remark in favour of the anharmonic interactions built with the ladder operators $\hat{b}_k^\dagger$ and $\hat{b}_k$. In the harmonic limit (large number of bosons N) of the Hamiltonian, the vibrational standard deviation increases from 0.0003 cm^{-1} to 0.007 cm^{-1}. Therefore, the inclusion of anharmonic terms in the Hamiltonian seems reasonable when the aim of an spectral analysis is to reach experimental accuracy.

6. Summary and conclusions

The approach presented has been devised as an alternative methodology of spectral analysis, that offers the possibility of carrying out global analysis of rovibrational data, taking into account vibrational anharmonicities from the outset, and without a high computational cost. In our opinion, the theoretical method proposed in this paper could

Table 7. Parameters of the rotation-vibration interactions used in the global fit up to polyad 10 and J up to 5 with Hamiltonian (37) in the analysis of $H_2{}^{80}Se$. All parameters are given in cm^{-1} units with one standard deviation statistical uncertainties for final significant digits.

Parameter	Values	Parameter	Values	Parameter	Values
B_J	5.80839(3)	$D_{K\omega_2}$	0.1635(7)	$D_{K\gamma_1}$	-0.01899(7)
$D_{J\omega_1}$	-0.07243(5)	$D_{K\omega x_1}$	0.028(1)	$D_{K\delta_1}$	0.0022(5)
$D_{J\lambda}$	0.0129(8)	$D_{K\omega x_2}$	0.0083(6)	$D_{K\delta_3}$	-0.00521(1)
$D_{J\omega_2}$	0.0690(1)	$D_{K\beta_2}$	0.0110(7)	$D_{xy\gamma_1}$	0.0101(1)
$D_{J\omega x_1}$	0.004(1)	B_{xy}	0.953(2)	$D_{xy\gamma_4}$	0.4635(4)
$D_{J\omega x_{11}}$	0.009(1)	$D_{xy\omega_1}$	0.0016(3)	$D_{xy\delta_1}$	-0.0013(7)
$D_{J\omega x_{12}}$	0.004(1)	$D_{xy\lambda}$	-0.0091(3)	$D_{xy\delta_3}$	-0.1570(1)
$D_{J\beta_1}$	-0.008(1)	$D_{xy\omega_2}$	0.0523(1)	C_λ	-0.3346(1)
D_{JF}	0.0289(7)	$D_{xy\omega x_1}$	-0.0196(4)	$C_{\lambda^{[2]}}$	-0.0170(2)
B_K	2.341(1)	$D_{xy\omega x_2}$	0.0024(1)	C_F	0.248(1)
$D_{K\omega_1}$	-0.0839(3)	$D_{xy\omega x_{11}}$	-0.594(1)	$D_{xz\omega_1}$	0.0613(6)
$D_{K\lambda}$	0.008(2)	$D_{J\gamma_2}$	0.0116(2)		

be of help in the assignment of experimentally recorded term values in when a large set of vibrational bands are considered in the global analysis.

The novelty of this method is the combination of the 1DVM with rotational degrees of freedom to achieve a global rovibrational analysis. Most other spectral assignment procedures describe, for the sake of simplicity, vibrational bands using harmonic oscillators bases.

The present method starts building a rovibrational Hamiltonian in terms of angular momentum components and anharmonic Morse ladder operators, associated with rotational and vibrational degrees of freedom, respectively. The Hamiltonian interactions are chosen according to their relevance in the description of the molecular spectra, which could be assessed, in first order, enforcing the polyad number conservation. The resulting Hamiltonian is diagonalized in a symmetry-adapted basis set given by the product of rotational states and three Morse wavefunctions, one for each local vibrational degree of freedom.

As an application of the present method, the rovibrational energies of the main Hydrogen Selenide isotopologue have been computed theoretically and compared to the available experimental data up to a maximum polyad number $P_{max} = 10$, and a maximum angular momentum $J_{max} = 5$. A total number of 745 rovibrational energies have been fitted using 57 parameters (22 vibrational plus 35 rovibrational parameters) with a standard deviation of 0.115 cm^{-1}.

With this Hamiltonian, 2579 new rovibrational energies were predicted for the 140 lowest vibrational bands and they can be found in the supplementary material associated with this manuscript. It is interesting to note that from the 140 vibrational bands that exist up to polyad 12, only 24 of them have been measured experimentally [32]. Therefore, apart from the new methodology presented in the rovibrational study of a triatomic molecule, new clues are provided to the spectroscopists for the assignment of unidentified H_2Se spectral lines.

This work can be considered a first step towards an extension of the algebraic model to obtain spectroscopic parameters comparable to those in the Watson Hamiltonian [52]. This topic will be the object of a future work.

Besides, we expect that the present procedure will be particularly useful to deal with large systems, where some vibrational modes could be considered more relevant and supposing that the rest are rigid modes. In fact, the application of this model to molecules involving more than six atoms is also the aim of future works.

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