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Algebraic description of stretching and bending modes in non-linear triatomic molecules

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ABSTRACT. We extend the U(2) model of n–coupled anharmonic oscillators, originally proposed to describe stretching vibrations, to include bending modes. The model describes the infrared spectrum of the molecules $H_2{}^{16}O$, $H_2{}^{32}S$, $^{32}S^{16}O_2$, and $^{16}O_3$ with rms deviations ranging from 13.42 to 1.05 cm^{-1}. In addition, we present a calculation of the dipole transition intensities for the $H_2^{16}O$ molecule.

RESUMEN. En este trabajo extendemos el modelo algebraico U(2) de osciladores anarmónicos acoplados con el objeto de incluir los modos vibracionales de flexión. Mediante este modelo se describe el espectro infrarrojo de las moléculas $H_2{}^{16}O$, $H_2{}^{32}S$, $^{32}S^{16}O_2$ y $^{16}O_3$ con desviaciones en las energías vibracionales que van de 13.42 a 1.05 cm^{-1}. Además se presenta un cálculo de intensidades de transición dipolares para la molécula de $H_2^{16}O$.

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I. INTRODUCTION

With the advent of laser spectroscopy techniques and their increased power of resolution, highly excited overtone-combination vibrational spectra of molecules can now be observed. There is therefore a renewed interest in developing theoretical descriptions of the physical processes involved. A detailed analysis of the observed spectral properties, however, is

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quite complicated and different degrees of approximation are used to study the problem, ranging from the simple Dunham energy expansion approach to attempting the solution of the Schrödinger equation by *ab initio* calculations. In 1981 a novel approach based an algebraic methods was proposed: the vibron model [1], which was originally introduced to describe the roto-vibrational structure of diatomic molecules and subsequently extended to include linear polyatomic molecules and non-linear triatomic molecules [2]. An alternative, symmetry-adapted algebraic model for triatomic molecules has been proposed by Bijker *et al.* [3]. An important advantage common to these algebraic approaches is that the powerful methods of group theory provide relatively simple solutions.

It is well known that a reasonable potential to describe the vibrations of diatomic molecules is the Morse potential [4]. This potential is closely associated to the O(4) dynamical symmetry of the vibron model [5], which explains the latter's success in describing molecular vibrational spectra. Although this is a three dimensional result, analogous relations hold in one and two dimensions.

In a one-dimensional system the realization of SU(2) on the sphere can be associated to a Morse potential [6]. The U(2) algebraic model may thus be considered as the one-dimensional limit of the vibron model and can be generalized to molecules with several bonds. In 1984 O.S. van Roosmalen *et al.* analyzed the case of two bonds [7] by considering the stretching vibrational modes of specific molecules like H_2O, SO_2 and O_3. The extension of the U(2) model to arbitrary polyatomic molecules was carried out by Iachello and Oss [8], who studied the vibrational spectra of benzene and several octahedral molecules. Recently the model has been also applied to infinite systems, namely to linear and square crystal lattices [9]. Because of the one-dimensionality of the model, however, the applications to molecular systems were restricted to the description of stretching vibrations.

In this article we extend the U(2) model to describe both the stretching and bending modes of molecules by considering the particular case of triatomic molecules. Iachello and Oss have proposed an extension to incorporate bending modes, but using a different technique [10]. The generalization to molecules with more atoms will be presented in forthcoming publications [11]. The paper is organized as follows: In the next section we present the model of n-coupled Morse oscillators, while in Sect. 3 we consider its extension to incorporate the bending modes. An analysis of the local and normal mode bases is also included in this section. Section 4 contains our main results, corresponding to the vibrational spectra of the molecules $H_2{}^{16}O$, $H_2{}^{32}S$, ${}^{32}S^{16}O_2$, and ${}^{16}O_3$, while the calculation of dipole transition intensities in $H_2{}^{16}O$ is presented in Sect. 5. Finally, in Sect. 6 we summarize our results and make some concluding remarks.

2. ALGEBRAIC MODEL

The model is based on the isomorphism of the U(2) Lie algebra and the one-dimensional Morse oscillator

$$\mathcal{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + D(e^{-2x/d} - 2e^{-x/d}), \tag{2.1}$$

whose eigenstates may be put into a one to one correspondence with the U(2) ⊃ O(2) states [12]. We briefly discuss here how this comes about. Consider the radial equation

$$\frac{1}{2}\left(-\frac{1}{r}\frac{d}{dr}r\frac{d}{dr}+\frac{m^2}{r^2}+r^2\right)\phi(r)=(N+1)\varphi(r), \tag{2.2}$$

which corresponds to a two-dimensional oscillator (in units where $\hbar=\mu=e=1$) and thus to a U(2) symmetry algebra [6]. By carrying out the transformation [6]

$$r^2=(N+1)\exp(-\rho), \tag{2.3}$$

Equation (2.2) transforms into

$$\left[-\frac{d^2}{d\rho^2}+\left(\frac{N+1}{2}\right)^2\left(e^{-2\rho}-2e^{-\rho}\right)\right]\phi(\rho)=-m^2\phi(\rho), \tag{2.4}$$

so defininig $x=\rho\cdot d$ and multiplying by $\hbar^2/2\mu d^2$ we arrive at (2.1), provided that $N+1=\sqrt{8\mu d^2 D/\hbar^2}$ and $E=-\frac{\hbar^2}{2\mu d^2}m^2$. Since $N=0,1,2,\dots$ and $m=\pm N/2,\pm(N-2)/2,\dots$, we see that the Morse spectrum is reproduced twice and that we need to restrict the m-values to non-negative values. We also note the connection between N and the potential depth. In terms of the usual SU(2) algebra, it is then clear from (2.4) that the Morse Hamiltonian has the algebraic realization

$$\hat{\mathcal{H}}=-\frac{\hbar^2}{2\mu d^2}\hat{J}_z^2, \tag{2.5}$$

while N is related to the SU(2) label j through $j=N/2$ [2,10]. We can also write (2.5) in the form

$$\hat{\mathcal{H}}=A\hat{C}_{2\mathrm{O}(2)}, \tag{2.6}$$

where we have defined $\hat{C}_{2\mathrm{O}(2)}\equiv 4\hat{J}_z^2-\hat{N}^2$. The parameter A is thus related to the Morse parameters, while the term $-\hat{N}^2$ is introduced in order to place the ground state at null energy.

We now consider a molecular system where η chemical bonds are involved [8]. In the algebraic model a $\mathrm{U}^i(2)$ algebra is associated to the i-th bond. Therefore the product $\mathrm{U}^1(2)\times\cdots\times\mathrm{U}^\eta(2)$ establishes the dynamical group of the system, which means that every operator may be expanded in terms of generators of the $\mathrm{U}^i(2)$ groups. In particular, the Hamiltonian is given in terms of the invariant (Casimir) operators of the groups involved in the different reductions of the dynamical algebra into its subalgebras. A possible decomposition involves the reduction

$$\mathrm{U}^1(2)\times\mathrm{U}^2(2)\times\cdots\times\mathrm{U}^\eta(2)\supset\mathrm{O}^1(2)\times\cdots\times\mathrm{O}^\eta(2)\supset\mathrm{O}(2), \tag{2.7}$$

where the coupling to the final O(2) group is carried out through the different intermediate couplings $\mathrm{O}^{ij}(2)$. A second chain arises from all the possible couplings of the $\mathrm{U}^{i}(2)$ groups to obtain a total U(2) group, which in turn contains the full O(2) group. The Hamiltonian, up to two-body interactions and restricted to terms conserving the total O(2) quantum number, is then given in terms of η contributions $h_i = A_1\hat{\mathcal{C}}_{2\mathrm{O}^i(2)}$, representing the η–one dimensional independent Morse oscillators, plus two types of bond-bond interactions: $\hat{\mathcal{C}}_{2\mathrm{O}^{ij}(2)}$ and $\hat{\mathcal{M}}_{ij}$, which correspond to the Casimir operators of the $\mathrm{O}^{ij}(2)$ groups and the Majorana operators, respectively [8]. The latter are related to the $\mathrm{U}^{ij}(2)$ Casimir operators $\hat{\mathcal{C}}_{2\mathrm{U}^{ij}(2)}$ by the relation

$$\hat{\mathcal{M}}_{ij} = -\tfrac{1}{2}\left[\hat{\mathcal{C}}_{2\mathrm{U}^{ij}(2)} - \hat{\mathcal{C}}_{2\mathrm{U}^{i}(2)} - \hat{\mathcal{C}}_{2\mathrm{U}^{j}(2)} - 2N_iN_j\right], \qquad (2.8)$$

where N_k corresponds to the number of bosons associated to the $\mathrm{U}^k(2)$ group. The Hamiltonian has thus the general form

$$\hat{\mathcal{H}} = h_0 + \sum_{i=1}^{\eta} A_i\hat{\mathcal{C}}_{2\mathrm{O}^i(2)} + \sum_{i>j}^{\eta} B_{ij}\hat{\mathcal{C}}_{2\mathrm{O}^{ij}(2)} + \sum_{i>j}^{\eta} \lambda_{ij}\hat{\mathcal{M}}_{ij}. \qquad (2.9)$$

The simplest basis to diagonalize the Hamiltonian (2.9) is the one associated with the local-mode chain

$$\big|[N_1], \ldots, [N_\eta], \ldots, v_1, \ldots, v_\eta : V\big\rangle, \qquad (2.10)$$

where we have defined v_i and V,

$$v_i = \frac{N_i}{2} - m_i, \quad V = \sum_{i=1}^{\eta} v_i, \qquad (2.11)$$

in terms of the quantum numbers m_i. The operators involved in the first two sums of the Hamiltonian (2.9) are diagonal in the basis (2.10)

$$\big\langle[N_1], \ldots, [N_\eta]; v_1, \ldots, v_\eta; V\big|\hat{\mathcal{C}}_{2\mathrm{O}^i(2)}\big|[N_1], \ldots, [N_\eta]; v_1, \ldots, v_\eta; V\big\rangle$$
$$= 4(v_i^2 - N_iv_i), \qquad (2.12\mathrm{a})$$

$$\big\langle[N_1], \ldots, [N_\eta]; \ldots, v_i, \ldots, v_j, \ldots; V\big|\hat{\mathcal{C}}_{2\mathrm{O}^{ij}(2)}\big|[N_1], \ldots, [N_\eta]; \ldots, v_i, \ldots, v_j, \ldots; V\big\rangle$$
$$= 4[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j)], \qquad (2.12\mathrm{b})$$

while the Majorana operator $\hat{\mathcal{M}}_{ij}$ has both diagonal and non-diagonal matrix elements

$$\big\langle[N_1], \ldots, [N_\eta]; \ldots, v_i', \ldots, v_j', \ldots; V\big|\hat{\mathcal{M}}_{ij}\big|[N_1], \ldots, [N_\eta]; \ldots, v_i, \ldots, v_j, \ldots; V\big\rangle$$
$$= (N_iv_j + N_jv_i - 2v_iv_j)\delta_{v_i,v_i'}\,\delta_{v_j',v_j} - \sqrt{v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)}\,\delta_{v_i',v_i+1}\,\delta_{v_j',v_j-1}$$
$$- \sqrt{v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)}\,\delta_{v_i',v_i-1}\,\delta_{v_j',v_j+1}. \qquad (2.12\mathrm{c})$$

Thus the local basis owes its name to the fact that in it the individual Morse oscillators are well defined, with v_i the number of quanta in the i–th oscillator [12]. These simple results for the matrix elements allow the diagonalization of $\hat{\mathcal{H}}$ in a straightforward way. The Hamiltonian (2.9), however, is arbitrary and does not in general satisfy the possible symmetry requirements of the molecule, which are considered in the next section.

The algebraic model can also provide transition intensities. In the traditional approach, the use of the Born-Oppenheimer approximation has as a consequence that the effective transition operator is not given directly by the dipole operator. Instead, the dipole function is expanded in terms of single bond coordinates

$$d(r) = \sum_{n=0}^{\infty} a_n (r - r_e)^n .$$

It is also possible to perform a Taylor expansion in powers of the Morse variable

$$y = 1 - e^{-\alpha(r - r_e)},$$

rather than in powers of $(r - r_e)$. It has been shown that the most convenient form, which has the appropriate limit behavior, is [13]

$$d(r) = d_0 r e^{-\gamma r}. \tag{2.13}$$

In the algebraic approach the dipole function is expanded in terms of elements of the dynamical algebra. It has been suggested that in the SU(2) model the matrix elements of the transition operator $\hat{t}_i$, associated to the i–th bond, can be parametrized in the form [8]

$$\left\langle [N_1], \ldots, [N_\eta]; \ldots, v_i', \ldots; V \middle| \hat{t}_i \middle| [N_1], \ldots, [N_\eta]; \ldots, v_i, \ldots; V \right\rangle = e^{-\beta |v_i' - v_i|}. \tag{2.14}$$

The operators $\hat{t}_i$ are thus associated to the i–th bond in the local picture. The molecular dipole transition operator is then given in terms of an expansion of the local operators $\hat{t}_i$. For any molecular system the dipole operator $\hat{T}$ has three components, given in terms of local operators. Up to linear terms, for example,

$$\hat{T}_\xi = \sum_{i=1}^{\eta} \alpha_i^\xi \, \hat{t}_i, \qquad (\xi = x, y, z), \tag{2.15}$$

where the relative values of the coefficients α_i^ξ are determined according to the molecular symmetry.

The transition intensities $I_{i \to f}$, from an initial state i to a final state f, are then computed in the usual form

$$I_{i \to f} \simeq \sum_{\xi} \left| \langle f | \hat{T}_\xi | i \rangle \right|^2, \tag{2.16}$$

where the states $|i\rangle$ and $|f\rangle$ may be expressed in terms of the local basis

$$|i\rangle = \sum_{\{v_i\}} a^i_{v_1,v_2,\ldots v_\eta} \big|[N_1],\ldots,[N_\eta];v_1,\ldots,v_\eta;V^i\big\rangle, \tag{2.17a}$$

$$|f\rangle = \sum_{\{v_i\}} a^f_{v_1,v_2,\ldots v_\eta} \big|[N_1],\ldots,[N_\eta];v_1,\ldots,v_\eta;V^f\big\rangle, \tag{2.17b}$$

with the coefficients $a^i_{v_1,\ldots,v_\eta}$ and $a^f_{v_1,\ldots,v_\eta}$ provided by the diagonalization of the Hamiltonian.

Expressions (2.9) and (2.15) are still quite general and we shall see that symmetry considerations impose certain conditions on the parameters. In the next section we present the particular form of the Hamiltonian and the infrared operators $\hat{T}_\xi$ for the molecules we consider in this paper.

3. NON-LINEAR TRIATOMIC MOLECULES

In the standard approach the potentials between nuclei are expressed in terms of a set of internal coordinates. For bent triatomic molecules the usual set corresponds to the bond distances r_1, r_2 and the angle θ between them, as shown in Fig. 1. The potential is then expanded in the form

$$V(r_1,r_2,\theta) = V_0 + \sum_{\alpha\beta\gamma} a_{\alpha\beta\gamma}\, r_1^\alpha\, r_2^\beta\, \theta^\gamma. \tag{3.1}$$

It is equally possible, however, to expand the potential in terms of r_3 (the distance between the A atoms in Fig. 1) instead of the angle θ

$$V(r_1 r_2 r_3) = V_0 + \sum_{\alpha\beta\gamma} b_{\alpha\beta\gamma}\, r_1^\alpha\, r_2^\beta\, r_3^\gamma, \tag{3.2}$$

and the Schrödinger equation can be written in terms of either (3.1) or (3.2).

In the algebraic approach the bond coordinates r_1 and r_2 are replaced by U(2) Lie algebraic structures. This procedure essentially corresponds to the potential (3.1) with θ constant, which leads to a description of stretching modes only. In this paper we propose to generalize the algebraic description following the scheme (3.2). We can then replace the three coordinates r_1, r_2 and r_3 by U(2) algebraic structures, which leads to a description of both the stretching and bending modes in terms of Morse potentials. We shall show that this approach is valid and consistent, and compute both energy and intensity fits, which turn out to have the same level of accuracy as other methods. The alternative description in Fig. 1 has the additional advantage of providing a natural way to incorporate the bending degree of freedom to molecules like O_3, for which a successful algebraic description has not been presented.

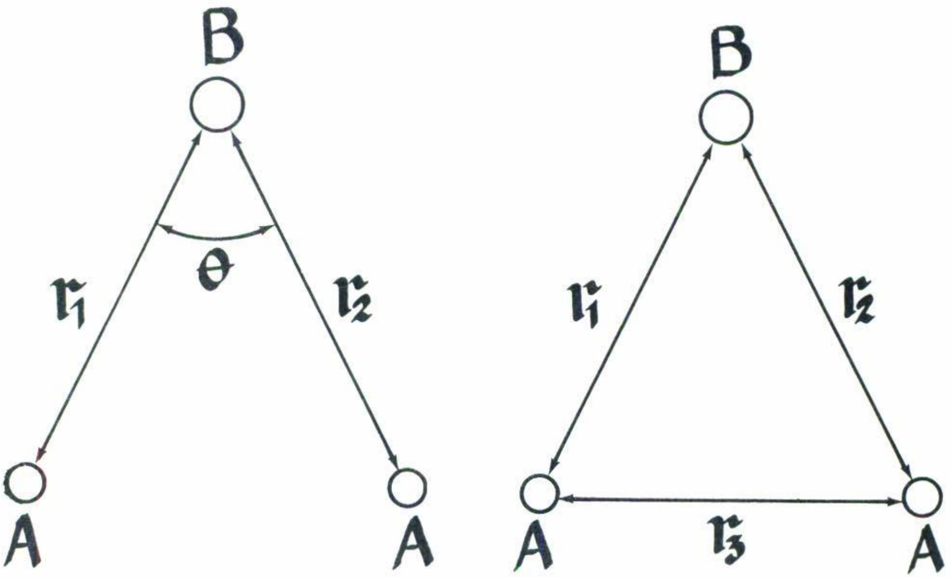

FIGURE 1. a) Traditional and b) alternative internal coordinates used to describe the vibrational degrees of freedom in bent triatomic molecules.

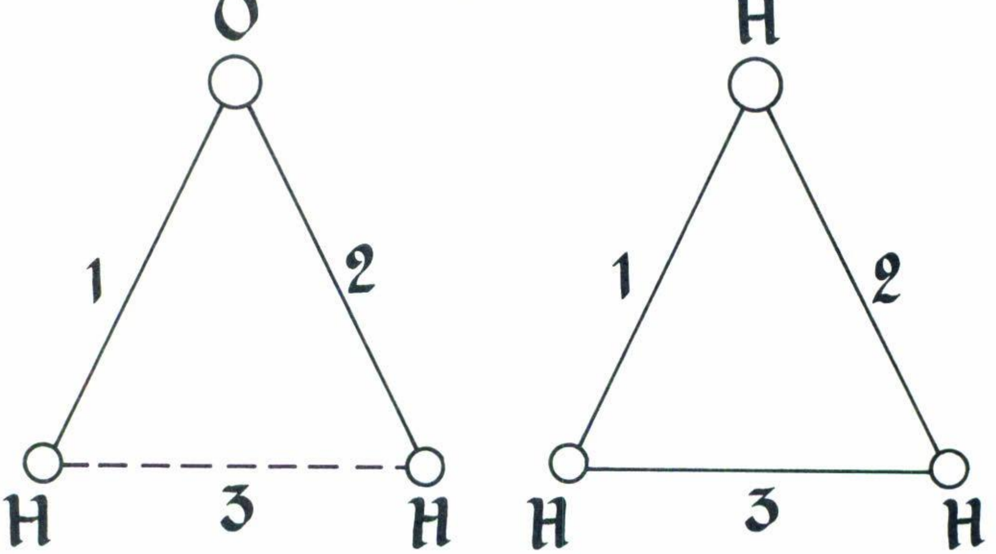

FIGURE 2. Geometrical structure of a) water-like molecules H_2O, H_2S, SO_2, $O_3(\mathcal{C}_{2v})$ and b) $\mathcal{D}_{3h}$ molecules showing the assignment of the U(2) algebraic structures.

We now proceed to establish the Hamiltonian for the triatomic molecules H_2O, H_2S, SO_2, and O_3. In Fig. 2 we display the representative geometrical structure for these molecules, which corresponds to a $\mathcal{C}_{2v}$ symmetry. In the same figure we show for completeness a configuration with $\mathcal{D}_{3h}$ symmetry, which would correspond to molecules such as H_3^+ which, however, are not considered in this article.

We now consider molecules with C_{2v} symmetry by noting that the subgroup $C_2 \subset C_{2v}$ is enough to label the vibrational modes, since the three atoms define a plane. According to the general procedure presented in Ref. [14], we first establish the isomorphism between the C_2 and S_2 groups:

$$\begin{aligned} E &\rightarrow (e), \\ C_2 &\rightarrow (12)(3). \end{aligned} \tag{3.3}$$

The S_2 invariant Hamiltonian is then obtained in a straightforward way. Taking into account up to two-body interactions we find

$$\begin{aligned} \hat{\mathcal{H}}^1_{C_{2v}} = h_0 &+ A_1(\hat{C}_{2O^1(2)} + \hat{C}_{2O^2(2)}) + A_3\hat{C}_{2O^3(2)} \\ &+ B_{12}C_{2O^{12}(2)} + B_{13}(\hat{C}_{2O^{13}(2)} + \hat{C}_{2O^{23}(2)}) \\ &+ \lambda_{12}\hat{\mathcal{M}}_{12} + \lambda_{13}(\hat{\mathcal{M}}_{13} + \hat{\mathcal{M}}_{23}), \end{aligned} \tag{3.4}$$

which is symmetric against the permutation of labels 1 and 2, as it should be. While the Hamiltonian (3.4) describes the general features of the spectrum, it is usually unable to provide results of spectroscopic quality, which require adding the next order (quartic) terms to $\mathcal{H}^1_{C_{2v}}$. The Hamiltonian providing the desired accuracy is then given by

$$\begin{aligned} \hat{\mathcal{H}}_{C_{2v}} = \hat{\mathcal{H}}^1_{C_{2v}} &+ A_1^{[2]}\left[\hat{C}^2_{2O^1(2)} + \hat{C}^2_{2O^2(2)}\right] + B_{12}^{[2]}\hat{C}^2_{2O^{12}(2)} \\ &+ A_3^{[2]}\hat{C}^2_{2O^3(2)} + B_{13}^{[2]}\left[\hat{C}^2_{2O^{13}(2)} + C^2_{2O^{23}(2)}\right]. \end{aligned} \tag{3.5}$$

For C_{2v} molecules, 9 parameters (λ_{13} is not needed as we show in Sect. 4) plus the number of bosons N_1 and N_3, are thus needed to produce high quality fits.

The Hamiltonians (3.5) can be diagonalized in the local basis (2.10). For C_{2v} molecules $N_1 = N_2$ and the basis takes the form

$$\left|[N_1][N_3]; v_1 v_2 v_3; V\right\rangle. \tag{3.6}$$

The diagonalization of the Hamiltonian couples the local oscillators. This interbond coupling is induced by the non-diagonal Majorana operators, giving rise to a transition towards normal modes. The true behavior of a molecule is in general in-between the local and normal schemes and can be reproduced by choosing the appropriate parameters in (3.4) and (3.5). The local limit is obtained by taking the λ parameters equal to zero, while in the normal limit all the A and B parameters should be null. Intermediate situations can be gauged by the local-normal transition parameters ξ introduced by Child and Halonen [13], which for C_{2v} molecules is defined as [15]

$$\xi = \frac{2}{\pi}\tan^{-1}\left(\frac{11\cdot\lambda_{12}}{A_1 + B_{12}}\right). \tag{3.7}$$

Since the Majorana parameters λ can take positive and negative values, the range of the parameter ξ is $-1 \leq \xi \leq 1$. Thus $|\xi| = 1$ for a purely normal mode behavior and $\xi = 0$ in the local mode limit [13]. The factor 11 in (3.10) is introduced as a normalization.

In molecules near the local limit, *e.g.* H_2S, the quantum numbers (3.6) provide a natural labeling of states. When the normal mode behavior is dominant, however, normal labeling is more appropriate. We next present the connection between these bases [12], for which it is convenient to use angular momentum labels $|j\mu\rangle$. In terms of these indices the local mode basis (3.6) takes the form

$$\begin{array}{ccccccccccccc} \mathrm{U}^1(2) & \times & \mathrm{U}^2(2) & \times & \mathrm{U}^3(2) & \supset & \mathrm{O}^1(2) & \times & \mathrm{O}^2(2) & \times & \mathrm{O}^3(2) & \supset & \mathrm{O}(2) \\ \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow & & \downarrow \\ |j_1 & , & j_2 & , & j_3 & , & \mu_1 & , & \mu_2 & , & \mu_3 & , & \mu\rangle \end{array} \tag{3.8}$$

where

$$j_1 = j_2 = \frac{N_1}{2}, \qquad j_3 = \frac{N_3}{2}, \qquad \mu_i = m_i$$

and

$$\mu = \mu_1 + \mu_2 + \mu_3.$$

The Majorana operator $\hat{\mathcal{M}}_{12}$ in (3.4) is diagonal in the basis

$$\begin{array}{ccccccc} \mathrm{U}^1(2) & \times & \mathrm{U}^2(2) & \supset & \mathrm{U}^{12}(2) & \supset & \mathrm{O}(2) \\ \downarrow & & \downarrow & & \downarrow & & \downarrow \\ |j_1 & , & j_2 & , & j_{12} & , & \mu_{12}\rangle \ , \end{array} \tag{3.9}$$

which means that this wave function is a normal basis with respect to the bonds 1 and 2, and is related to the local basis $|j_1\mu_1\rangle|j_2\mu_2\rangle$ by the coupling coefficients [16]

$$|j_1 j_2 j_{12}; j\mu\rangle = \sum_{\mu_1\mu_2} C(j_1 j_2 j_{12}; \mu_1\mu_2)\, |j_1\mu_1\rangle\, |j_2\mu_2\rangle. \tag{3.10}$$

We now proceed to establish the relation between the normal labels v_A, v_B (symmetric and antisymmetric normal modes) and the angular momentum labels in (3.9). Applying the $\hat{C}_2$ rotation [permutation (12)] to (3.10) we obtain

$$\hat{C}_2 |j_1 j_2; j_{12}\mu_{12}\rangle = (-)^{j_1+j_2-j_{12}}\, |j_1 j_2; j_{12}\mu_{12}\rangle, \tag{3.11}$$

which suggests the following normal labeling for the antisymmetric mode

$$v_B = j_1 + j_2 - j_{12} = N_1 - j_{12}. \tag{3.12}$$

Since $j_{12} = N_1, N_1 - 1, \ldots, 0$, we have that $v_B = 0, 1, \ldots, N_1$, and the wave function changes sign according to the parity of v_B, as expected. The symmetric quantum number

v_A should be defined in such a way that the parity of (3.10) is determined by v_3 for any value of v_A. We thus propose

$$v_A = j_{12} - \mu_{12}, \tag{3.13}$$

where $v_A = 0, 1, 2, \ldots, j_{12}$ since $\mu_{12} = j_{12}, j_{12} - 1, \ldots, 0$. This result involves the stretching modes only. A normal mode analysis shows that for one phonon, $\mathcal{C}_{2v}$ molecules display two symmetric and one antisymmetric normal mode. The antisymmetric mode is associated to stretching vibrations in accordance with (3.12). In turn, the symmetric modes have the property that one of them is almost a pure stretching mode while the other is a pure bending mode. This fact allows us to propose the relation

$$v_A^{(3)} = j_3 - \mu_3, \tag{3.14}$$

with $v_A^{(3)} = 0, 1, 2, \ldots, j_3$. We have introduced the superindex 3 to indicate that the label comes directly from the $\mathrm{SU}^3(2)$ algebra, which in this case is associated to a pure bending mode. We thus consider the (nearly) normal basis for $\mathcal{C}_{2v}$ molecules

$$|j_1 j_2; j_{12}\mu_{12}\rangle\, |j_3\mu_3\rangle \equiv |[N_1], [N_3]; v_A v_B v_A^{(3)}\rangle. \tag{3.15}$$

Although the set (3.15) is not exactly normal, it does constitute a very good approximation to the normal mode labeling, as we shall prove later on.

Finally, we discuss the transition operators. Equation (2.15) gives the general form of these operators. For $\mathcal{C}_{2v}$ molecules the components of the dipole operator (z, y) transform as the C_2 representations A and B, respectively. There is no contribution from the $x-$ component since we have selected the x axis orthogonal to the plane of the molecule. By projecting the $\hat{t}_i$ onto A and B, we find up to linear terms

$$\hat{T}_z^A = \alpha_1(\hat{t}_1 + \hat{t}_2) + \alpha_2\hat{t}_3, \tag{3.16a}$$

$$\hat{T}_y^B = \alpha_4(\hat{t}_1 - \hat{t}_2), \tag{3.16b}$$

where by symmetry considerations the same parameter β, Eq. (2.14), has been associated to $\hat{t}_1$ and $\hat{t}_2$. We have found, however, that the approximation (3.16) is not enough to reproduce the experimental intensities and it is necessary to add the next order terms $\hat{t}_3(\hat{t}_1 - \hat{t}_2)$ and $t_3(\hat{t}_1 + \hat{t}_3)$:

$$\hat{T}_z^A = \alpha_1(\hat{t}_1 + \hat{t}_2) + \alpha_2\hat{t}_3 + \alpha_3\hat{t}_3(\hat{t}_1 + \hat{t}_2), \tag{3.17a}$$

$$\hat{T}_y^B = \alpha_4(\hat{t}_1 - \hat{t}_2) + \alpha_5\hat{t}_3(\hat{t}_1 - \hat{t}_2). \tag{3.17b}$$

If β_1 is the parameter associated to $\hat{t}_1$ and $\hat{t}_2$, and β_3 is the parameter corresponding to $\hat{t}_3$, we have 7 free parameters in all. In the next section we present a fit to the dipole transitions for the $H_2{}^{16}O$ molecule using the form (3.17).

4. RESULTS

We have applied the SU(2) model to study the vibrational structure of the $\mathcal{C}_{2v}$ molecules H_2O, H_2S, SO_2 and O_3 which do not present a chemical bond between equivalent atoms [17].

Using the Hamiltonian (3.5) we have carried out three least-square fits of vibrational levels for the molecules H_2O, H_2S and SO_2. In addition to the N_1 and N_3 boson numbers there are 10 free parameters: six quadratic and four quartic in the generators. A first fit was performed taking into account quadratic terms only, during which problems of convergence were found if the six parameters were included. The problem was solved by eliminating the λ_{13} parameter, which represents the coupling between the SU(2)'s associated to the chemical bonds and the SU(2) associated to the interaction between equivalent atoms. The exclusion of this parameter is physically justified, given that the normal modes are almost purely stretching or bending and this interaction mixes them. The number of parameters involved in this fit was then $5+2$, including the two boson numbers. A second fit was carried out including the first two quartic terms in (3.5) which are associated to the parameters $A_1^{[2]}$ and $A_{12}^{[2]}$, totalling $7+2$ parameters. The third and final fit includes all the quartic terms in (3.5) and thus $9+2$ parameters. Table I shows the parameters obtained for the three fits, as well as the corresponding rms deviations.

The boson numbers N_1 and N_3 were varied in order to obtain the best fits. For the N_1 boson number the search was started from the value predicted for the corresponding diatomic molecules. This is achieved by writting explicitly the eigenvalue of the Morse Hamiltonian (2.6) and identifying the harmonic ω_e and anharmonic $x_e\omega_e$ constants in terms of the parameters A and N:

$$\omega_e = -4A(N+1),$$

$$x_e\omega_e = -4A.$$

For diatomic molecules the number of bosons is then given by

$$N = \omega_e / x_e\omega_e - 1. \tag{4.1}$$

In Table II we compare the estimated and calculated boson numbers N_1.

In turn, the N_3 boson number is associated with the interaction between equivalent atoms where no chemical bond is present. Since this parameter is related to the depth of the potential, N_3 is expected to be small and in fact this is so as seen in Table I.

In the case of the O_3 molecule, only one fit was performed. The higher order ones are not feasible due to a lack of experimental information for bending excitations. The high reactivity of ozone makes it difficult to measure its infrared spectrum. The difference between the estimated N_1 and the value obtained in the fit is due to the double bonding in diatomic oxygen in contrast to the single-double bond resonance structure in O_3. The parameters used for this molecule are also included in Table I.

An analysis of the rms deviations in Table I provides a measure of the effect of the different sets of parameters in the fitting procedure. For example, for H_2O the deviations are 10.44, 4.26 and 3.79, respectively, showing a considerable improvement from fit 1 to

TABLE I. Parameters used in the calculation of energy levels for H_2O, H_2S, SO_2, and O_3. All parameters in cm^{-1}, except N_1, N_3 which are dimensionless.

Parameters ($\mathcal{C}_{2v}$ symmetry)	H_2O			H_2S			SO_2			O_3
	1	2	3	1	2	3	1	2	3	1
N_1	44	44	44	47	47	47	152	152	152	54
N_3	28	28	28	37	37	37	28	28	28	34
A_1	−19.376	−18.574	−17.793	−12.011	−11.925	−11.482	−1.360	−1.284	−0.983	−5.118
A_3	− 6.211	− 6.590	− 5.340	− 1.549	− 1.3900	− 0.274	−0.133	−0.394	−0.636	5.241
B_{12}	− 0.181	− 2.256	− 3.317	− 0.289	− 0.354	− 0.553	−0.933	−1.097	−1.072	4.596
B_{13}	− 5.352	− 4.953	− 5.771	− 5.105	− 5.243	− 6.125	−0.830	−0.779	−0.739	−6.538
λ_{12}	1.015	1.014	1.012	0.141	0.143	0.142	0.677	0.677	0.682	0.711
$A_1^{[2]}$		−2.96(−4)	−5.489(−4)		−0.128(−4)	−0.881(−4)		−0.018(−4)	−0.051(−4)	
$A_3^{[2]}$		9.66(−4)	−4.992(−4)		−0.927(−4)	−6.025(−4)		1.64 (−4)	−3.54 (−4)	
$B_{12}^{[2]}$			2.532(−4)			−0.532(−4)			0.059(−4)	
$B_{13}^{[2]}$			2.560(−4)			1.456(−4)			0.126(−4)	
Number of levels	52	52	52	20	20	20	41	41	41	30
rms (cm^{-1})	10.44	4.26	3.79	1.19	1.1	1.05	3.92	3.82	3.71	13.42

TABLE II. Estimated boson numbers according to spectroscopic constants [17] and boson numbers N obtained in the fits.

Molecule	ω_e	$\omega_e x_e$	$\omega_e/x_e\omega_e - 1$	N_1
$^{16}O^1H$	3737.76	84.881	43.03	44
$^1H^{32}S$	2711.6	59.9	44.26	47
$^{16}O^{32}S$	1149.22	5.63	203.12	152
^1H–^1H	4395.9	117.9	37.28	30
^{16}O–^{16}O	1580.361	12.073	131.6	54

fit 2, while the inclusion of all quartic terms does not have a significant effect in the last fit. For the H_2S, SO_2, and O_3 molecules the deviations for the first fit are 1.19, 3.92 and 13.42, respectively. The inclusion of the quartic interactions associated to the parameters $B_{12}^{[2]}$ and $B_{13}^{[2]}$ does not give rise to a significant gain in accuracy. However, we note that the introduction of additional quartic terms in (3.5), such as

$$[\hat{C}_{2O^1(2)} + \hat{C}_{2O^2(2)}][\hat{C}_{2O^3(2)}], \tag{4.2}$$

could improve the calculation. Operators of the type of (4.2) are diagonal in the local basis and their inclusion is straightforward.

In Tables III, IV and V we present the comparison between experimental and calculated energies for H_2O, H_2S and SO_2, respectively. In these tables we display the predicted energies up to seven quanta. The assignment of states was done according to the maximum component in the wave function. In molecules with local behavior, like H_2S, a strong mixing of the normal basis (3.15) is present, the local labeling being more appropriate in this case. On the contrary, the SO_2 molecule presents normal behavior and thus strong mixing of states appears in the local basis. The H_2O molecule is in-between so the mixing occurs with respect to both bases. The mixing increases in all cases for higher multiplets, while for lower energies there is no strong mixing and the labeling coincides with previous assignments [17].

Comparison of our results with the experimental values for O_3 are presented in Table VI. This molecule has been studied previously by using algebraic methods [2,7,22]. The corresponding deviation was 23.7 cm^{-1} [7] while our result is 13.42 cm^{-1}. Since this molecule has atoms with the same mass, normal behavior is expected. One of the advantages of the algebraic model is that the local↔normal mode transition can be analyzed in a simple way, *e.g.*, through the ξ coefficient defined by Eq. (3.7), where the parameters should correspond to the first fit. In Table VII we show the value of ξ corresponding to this calculation, which turns out to be -0.96, close to the normal limit $|\xi| = 1$, in agreement with the results of Refs. [13]. The same analysis can be applied to H_2O, H_2S and SO_2. From this set of molecules, SO_2 has similar atomic masses, while H_2O and H_2S involve very different ones, particularly for the latter. We then expect to obtain an almost local behavior far H_2S, while SO_2 should be close to normal and H_2O in an intermediate situation. The values obtained are -0.33, 0.08 and -0.82 for H_2O, H_2S and SO_2 respectively, again in accordance with Refs. [13,15].

TABLE III. Comparison between calculated and experimental energies for H_2O, and predicted energies up to 7 quanta. All energies in cm^{-1}.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	Exp.	Theor. − Expt.
(0 0+ 1)	(0 1 0)	1594.52	1595.00	−0.48
(0 0+ 2)	(0 2 0)	3152.23	3151.40	0.83
(0 1+ 0)	(1 0 0)	3661.99	3657.00	4.99
(0 1− 0)	(0 0 1)	3751.05	3755.90	−4.85
(0 0+ 3)	(0 3 0)	4675.53	4667.00	8.53
(0 1+ 1)	(1 1 0)	5238.01	5234.90	3.11
(0 1− 1)	(0 1 1)	5327.06	5331.20	−4.14
(0 0+ 4)	(0 4 0)	6166.61	6168.70	−2.09
(0 1+ 2)	(1 2 0)	6776.50	6775.00	1.50
(0 1− 2)	(0 2 1)	6865.55	6871.50	−5.95
(0 2+ 0)	(2 0 0)	7207.14	7201.50	5.64
(0 2− 0)	(1 0 1)	7246.73	7249.80	−3.07
(1 1+ 0)	(0 0 2)	7442.51	7445.00	−2.49
(0 1+ 3)	(1 3 0)	8279.86	8274.00	5.86
(0 1− 3)	(0 3 1)	8368.91	8374.00	−5.09
(0 2+ 1)	(2 1 0)	8764.43	8761.50	2.93
(0 2− 1)	(1 1 1)	8804.02	8807.00	−2.98
(1 1+ 1)	(0 1 2)	8999.80	9000.10	−0.30
(0 2+ 2)	(2 2 0)	10283.49	10284.40	−1.91
(0 2− 2)	(1 2 1)	10323.08	10328.70	−5.62
(1 1+ 2)	(0 2 2)	10518.86	10524.30	−5.44
(0 3+ 0)	(3 0 0)	10601.68	10599.60	2.09
(0 3− 0)	(2 0 1)	10611.06	10613.40	−2.34
(1 2+ 0)	(1 0 2)	10868.91	10868.80	0.11
(1 2− 0)	(0 0 3)	11033.60	11032.40	1.20
(0 3+ 1)	(3 1 0)	12140.02	12139.20	0.82
(0 3− 1)	(2 1 1)	12149.40	12151.20	−1.80
(1 2+ 1)	(1 1 2)	12407.25	12407.60	−0.35
(1 2− 1)	(0 1 3)	12571.93	12565.00	6.93
(0 3+ 2)	(3 2 0)	13639.45	13642.00	−2.55
(0 4+ 0)	(2 0 2)	13828.36	13828.30	0.06
(1 2+ 2)	(1 2 2)	13906.68	13910.80	−4.12
(1 2− 2)	(0 2 3)	14071.36	14066.10	5.26
(1 3+ 0)	(4 0 0)	14222.71	14221.10	1.61
(1 3− 0)	(1 0 3)	14315.79	14318.80	−3.01
(2 2+ 0)	(0 0 4)	14545.94	14536.80	9.14
(0 4+ 1)	(2 1 2)	15347.52	15344.40	3.12
(0 4− 1)	(3 1 1)	15348.76	15347.90	0.86
(1 3+ 1)	(4 1 0)	15741.87	15742.70	−0.83
(1 3− 1)	(1 1 3)	15834.95	15832.70	2.25
(0 4+ 1)	(2 1 2)	15347.52	15344.40	3.12
(0 4+ 2)	(2 2 2)	16827.12	16821.60	5.52
(0 4− 2)	(3 2 1)	16828.36	16825.20	3.16
(0 5+ 0)	(3 0 2)	16896.51	16898.40	−1.89
(0 5− 0)	(2 0 3)	16896.63	16898.80	−2.17
(1 3+ 2)	(4 2 0)	17221.46	17227.70	−6.24
(1 3− 2)	(1 2 3)	17314.55	17312.50	2.05
(1 4+ 0)	(5 0 0)	17460.12	17458.20	1.92
(1 4− 0)	(4 0 1)	17492.20	17495.50	−3.30
(2 3+ 0)	(1 0 4)	17744.70	17748.00	−3.30
(2 3− 0)	(0 0 5)	17967.53	17970.90	

rms deviation (cm) 3.79

TABLE III. Cont. Predicted energies.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	$(n\ m\ \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.
(0 0 + 5)	(0 5 0)	7627.50	(1 3 − 3)	(1 3 3)	18756.98
(0 0 + 6)	(0 6 0)	9060.00	(1 4 + 1)	(5 1 0)	18959.89
(0 1 + 4)	(1 4 0)	9750.29	(2 2 + 3)	(0 3 4)	18987.13
(0 1 − 4)	(0 4 1)	9839.35	(1 4 − 1)	(4 1 1)	18991.97
(0 0 + 7)	(0 7 0)	10465.76	(2 3 + 1)	(1 1 4)	19244.47
(0 1 + 5)	(1 5 0)	11189.82	(2 3 − 1)	(0 1 5)	19467.30
(0 1 − 5)	(0 5 1)	11278.87	(0 6 + 0)	(4 0 2)	19813.42
(0 2 + 3)	(2 3 0)	11766.73	(0 6 − 0)	(3 0 3)	19813.43
(0 2 − 3)	(1 3 1)	11806.32	(0 5 + 2)	(3 2 2)	19855.84
(1 1 + 3)	(0 3 2)	12002.10	(0 5 − 2)	(2 2 3)	19855.95
(0 1 + 6)	(1 6 0)	12600.25	(1 4 + 2)	(5 2 0)	20419.45
(0 1 − 6)	(0 6 1)	12689.31	(1 4 − 2)	(4 2 1)	20451.53
(0 2 + 4)	(2 4 0)	13216.35	(1 5 + 0)	(6 0 0)	20535.20
(0 2 − 4)	(1 4 1)	13255.94	(1 5 − 0)	(5 0 1)	20541.00
(1 1 + 4)	(0 4 2)	13451.72	(2 3 + 2)	(1 2 4)	20704.02
(0 2 + 5)	(2 5 0)	14634.36	(2 4 + 0)	(6 0 0)	20895.71
(0 2 − 5)	(1 5 1)	14673.95	(2 3 − 2)	(0 2 5)	20926.86
(1 1 + 5)	(0 5 2)	14869.73	(2 4 − 0)	(1 0 5)	21043.08
(0 3 + 3)	(3 3 0)	15102.38	(0 6 + 1)	(4 1 2)	21293.58
(0 3 − 3)	(2 3 1)	15111.76	(0 6 − 1)	(3 1 3)	21293.58
(1 2 + 3)	(1 3 2)	15369.61	(3 3 + 0)	(0 0 6)	21305.92
(1 2 − 3)	(0 3 3)	15534.29	(1 5 + 1)	(6 1 0)	22015.36
(2 2 + 1)	(0 1 4)	16065.10	(1 5 − 1)	(5 1 1)	22021.15
(0 3 + 4)	(3 4 0)	16531.00	(2 4 + 1)	(6 1 0)	22375.86
(0 3 − 4)	(2 4 1)	16540.38	(2 4 − 1)	(1 1 5)	22523.24
(1 2 + 4)	(1 4 2)	16798.23	(0 7 + 0)	(3 0 4)	22583.27
(1 2 − 4)	(0 4 3)	16962.92	(0 7 − 0)	(4 0 3)	22583.27
(2 2 + 2)	(0 2 4)	17544.70	(3 3 + 1)	(0 1 6)	22786.07
(0 4 + 3)	(2 3 2)	18269.55	(1 6 + 0)	(5 0 2)	23446.12
(0 4 − 3)	(3 3 1)	18270.78	(1 6 − 0)	(6 0 1)	23446.77
(0 5 + 1)	(3 1 2)	18396.28	(2 5 + 0)	(7 0 0)	22966.00
(0 5 − 1)	(2 1 3)	18396.39	(2 5 − 0)	(4 0 3)	24031.33
(1 3 + 3)	(4 3 0)	18663.89	(3 4 + 0)	(1 0 6)	24291.41
			(3 4 − 0)	(0 0 7)	24557.37

In Sect. 3 the normal basis for C_{2v} molecules was constructed. The eigenfunctions can thus be expressed in terms of them, leading to useful information for the classification of states. As explained before, the states (3.15) are a close approximation to the normal basis but are not exact. In addition, the molecules we have studied involve behaviors from local ($\xi = -0.08$) to normal ($\xi = -0.96$). Therefore, the eigenfunctions in the normal basis are certainly not pure and are often strongly mixed, specially for highly excited states.

Since the rms deviations corresponding to the best fits are rather small, *e.g.*, 3.70, 1.02, 3.71 and 13.42 for H_2O, H_2S, SO_2 and O_3, respectively, the theoretical energies can be used to predict overtones and combinations not yet measured. In Tables III–VI we present the calculated energies up to $v_1 + v_2 + v_3 = 7$.

TABLE IV. Comparison between calculated and experimental energies for H_2S, and predicted energies up to 7 quanta. All energies in cm^{-1}.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	Exp.	Theor. − Expt.
(0 0 + 1)	(0 1 0)	1183.61	1182.60	1.01
(0 0 + 2)	(0 2 0)	2353.07	2354.00	−0.93
(0 1 + 0)	(1 0 0)	2615.26	2614.40	0.86
(0 1 − 0)	(0 0 1)	2628.61	2628.50	0.11
(0 1 + 1)	(1 1 0)	3778.12	3779.20	−1.08
(0 1 − 1)	(0 1 1)	3791.47	3789.30	2.17
(0 1 − 2)	(0 2 1)	4939.74	4939.20	0.54
(0 2 + 0)	(2 0 0)	5145.42	5145.10	0.32
(0 2 − 0)	(1 0 1)	5145.22	5147.40	−0.18
(0 2 + 1)	(2 1 0)	6287.36	6288.20	−0.84
(0 2 − 1)	(1 1 1)	6289.16	6289.20	−0.04
(1 1 + 1)	(0 1 2)	6385.86	6388.70	−2.84
(0 3 + 0)	(1 0 2)	7575.87	7576.30	−0.43
(0 3 − 0)	(2 0 1)	7575.97	7576.31	−0.34
(1 2 + 0)	(3 0 0)	7753.38	7751.90	1.48
(1 2 − 0)	(0 0 3)	7779.41	7779.20	0.21
(0 3 − 1)	(2 1 1)	8696.82	8697.30	−0.48
(0 4 − 0)	(3 0 1)	9910.19	9911.10	−0.91
(1 3 − 0)	(1 0 3)	10194.07	10194.50	−0.43
(0 4 − 1)	(3 1 1)	11009.78	11008.80	0.98

rms deviation (cm) 1.05

TABLE IV. Cont. Predicted energies.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	$(n\ m\ \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.
(0 0 + 3)	(0 3 0)	3512.31	(0 5 + 0)	(3 0 2)	12149.89
(0 1 + 2)	(1 2 0)	4926.40	(5 0 − 0)	(2 0 3)	12149.89
(0 0 + 4)	(0 4 0)	4665.04	(1 2 + 4)	(3 4 0)	12159.75
(1 1 + 0)	(0 0 2)	5243.92	(1 2 − 4)	(0 4 3)	12185.79
(0 0 + 5)	(0 5 0)	5814.73	(1 3 + 2)	(4 2 0)	12372.37
(0 1 + 3)	(1 3 0)	6064.02	(1 3 − 2)	(1 2 3)	12377.44
(0 1 − 3)	(0 3 1)	6077.37	(2 2 + 2)	(0 2 4)	12476.14
(0 0 + 6)	(0 6 0)	6964.61	(1 4 + 0)	(1 0 4)	12524.76
(0 1 + 4)	(1 4 0)	7194.70	(1 4 − 0)	(4 0 1)	12525.11
(0 1 − 4)	(0 4 1)	7208.05	(2 3 + 0)	(5 0 0)	12696.69
(0 2 + 2)	(2 2 0)	7414.29	(2 3 − 0)	(0 0 5)	12734.68
(0 2 − 2)	(1 2 1)	7416.09	(0 4 + 3)	(2 3 2)	13165.42
(1 1 + 2)	(0 2 2)	7512.79	(0 4 − 3)	(3 3 1)	13165.43
(0 0 + 7)	(0 7 0)	8117.69	(0 5 + 1)	(3 1 2)	13228.06
(0 1 + 5)	(1 5 0)	8321.90	(5 0 − 1)	(2 1 3)	13228.06
(0 1 − 5)	(0 5 1)	8335.25	(1 3 + 3)	(4 3 0)	13444.25
(0 2 + 3)	(2 3 0)	8530.15	(1 3 − 3)	(1 3 3)	13449.31

TABLE IV. Cont. Predicted energies.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	$(n\ m\ \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.
(0 2 − 3)	(1 3 1)	8531.95	(2 2 + 3)	(0 3 4)	13548.01
(1 1 + 3)	(0 3 2)	8628.65	(1 4 + 1)	(1 1 4)	13602.93
(0 3 + 1)	(1 1 2)	8696.73	(1 4 − 1)	(4 1 1)	13603.28
(1 2 + 1)	(3 1 0)	8874.23	(2 3 + 1)	(5 1 0)	13774.86
(1 2 − 1)	(0 1 3)	8900.26	(2 3 − 1)	(0 1 5)	13812.85
(0 1 + 6)	(1 6 0)	9448.86	(0 5 + 2)	(3 2 2)	14290.01
(0 1 − 6)	(0 6 1)	9462.21	(5 0 − 2)	(2 2 3)	14290.01
(0 2 + 4)	(2 4 0)	9638.63	(0 6 + 0)	(2 0 4)	14295.69
(0 2 − 4)	(1 4 1)	9640.44	(6 0 − 0)	(3 0 3)	14295.69
(1 1 + 6)	(0 4 2)	9737.13	(1 4 + 2)	(1 2 4)	14664.88
(0 3 + 2)	(1 2 2)	9802.15	(1 4 − 2)	(4 2 1)	14665.23
(0 3 − 2)	(2 2 1)	9802.25	(1 5 + 0)	(2 0 4)	14763.42
(0 4 + 0)	(2 0 2)	9910.18	(1 5 − 0)	(5 0 1)	14663.43
(1 2 + 2)	(3 2 0)	9979.66	(2 3 + 2)	(5 2 0)	14836.81
(1 2 − 2)	(0 2 3)	10005.69	(2 3 − 2)	(0 2 5)	14874.80
(1 3 + 0)	(4 0 0)	10189.01	(2 4 + 0)	(6 0 0)	15037.16
(2 2 + 0)	(0 0 4)	10292.77	(2 4 − 0)	(3 0 3)	15046.55
(0 2 + 5)	(2 5 0)	10743.22	(3 3 + 0)	(0 0 6)	15148.11
(0 2 − 5)	(1 5 1)	10745.02	(0 6 + 1)	(2 1 4)	15352.27
(1 1 + 5)	(0 5 2)	10841.72	(6 0 − 1)	(3 1 3)	15352.27
(0 3 + 3)	(1 3 2)	10896.10	(1 5 + 1)	(2 1 4)	15820.00
(0 3 − 3)	(2 3 1)	10896.19	(1 5 − 1)	(5 1 1)	15820.02
(0 4 + 1)	(2 1 2)	11009.78	(2 4 + 1)	(6 1 0)	16093.74
(1 2 + 3)	(3 3 0)	11073.60	(2 4 − 1)	(3 1 3)	16103.13
(1 2 − 3)	(0 3 3)	11099.63	(3 3 + 1)	(0 1 6)	16204.70
(1 3 + 1)	(4 1 0)	11288.60	(7 0 + 0)	(3 0 4)	16348.22
(1 3 − 1)	(1 1 3)	11293.67	(0 7 − 0)	(4 0 3)	16348.22
(2 2 + 1)	(0 1 4)	11392.37	(1 6 + 0)	(5 0 2)	16907.97
(0 3 + 4)	(1 4 2)	11982.25	(1 6 − 0)	(6 0 1)	16907.97
(0 3 − 4)	(2 4 1)	11982.34	(2 5 + 0)	(7 0 0)	17279.64
(0 4 + 2)	(2 2 2)	12093.55	(2 5 − 0)	(6 0 1)	17280.46
(0 4 − 2)	(3 2 1)	12093.55	(3 4 + 0)	(7 0 0)	17447.08
			(3 4 − 0)	(0 0 7)	17496.25

5. DIPOLE TRANSITIONS

In Sect. 2 we presented the general form of the dipole operator and indicated the way to compute transition intensities in the framework of the algebraic approach. In this section we calculate the dipole intensities for the H_2O molecule.

Although the linear expansion of the transition operator (2.15) is not sufficient to fit the data, we have found that the dipole operators (3.17a-b), which include quadratic terms,

TABLE V. Comparison between calculated and experimental energies for SO_2, and predicted energies up to 7 quanta. All energies in cm^{-1}

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	Exp.	Theor. − Expt.
(0 0+ 1)	(0 1 0)	518.61	517.87	0.74
(0 0+ 2)	(0 2 0)	1034.46	1035.13	−0.67
(0 1+ 0)	(1 0 0)	1150.95	1151.71	−0.76
(0 1− 0)	(0 0 1)	1358.12	1362.06	−3.94
(0 0+ 3)	(0 3 0)	1549.25	1551.75	−2.50
(0 1+ 1)	(1 1 0)	1667.40	1666.33	1.07
(0 1− 1)	(0 1 1)	1874.57	1875.79	−1.22
(0 0+ 4)	(0 4 0)	2064.55	2066.87	−2.32
(0 1+ 2)	(1 2 0)	2180.97	2179.51	1.46
(0 2+ 0)	(2 0 0)	2293.92	2295.80	−1.88
(0 1− 2)	(0 2 1)	2388.14	2388.92	−0.78
(0 2− 0)	(1 0 1)	2498.78	2499.87	−1.09
(0 0+ 5)	(0 5 0)	2581.77	2582.30	−0.53
(0 1+ 3)	(1 3 0)	2693.36	2693.63	−0.27
(1 1+ 0)	(0 0 2)	2706.91	2713.38	−6.47
(0 2+ 1)	(2 1 0)	2808.21	2807.19	1.02
(0 2− 1)	(1 1 1)	3013.06	3010.32	2.74
(1 1+ 1)	(0 1 2)	3221.19	3222.25	−1.06
(1 2+ 0)	(3 0 0)	3428.94	3431.19	−2.25
(0 3− 0)	(2 0 1)	3631.56	3629.61	1.95
(1 1+ 2)	(0 2 2)	3732.46	3730.90	1.56
(0 3+ 0)	(1 0 2)	3837.40	3837.06	0.34
(1 2+ 1)	(3 1 0)	3941.04	3939.90	1.14
(0 3− 0)	(2 0 1)	3631.56	3629.61	1.95
(1 1+ 2)	(0 2 2)	3732.46	3730.90	1.56
(0 3+ 0)	(1 0 2)	3837.40	3837.06	0.34
(1 2+ 1)	(3 1 0)	3941.04	3939.90	1.14
(0 2− 3)	(1 3 1)	4034.31	4029.39	4.92
(1 2− 0)	(0 0 3)	4046.38	4054.00	−7.62
(1 1+ 3)	(0 3 2)	4242.44	4241.50	0.94
(0 2+ 4)	(2 4 0)	4339.69	4342.70	−3.01
(1 2+ 2)	(3 2 0)	4450.01	4446.90	3.11
(1 2− 1)	(0 1 3)	4558.48	4560.10	−1.62
(0 4− 0)	(3 0 1)	4754.48	4751.23	5.25
(0 3+ 2)	(1 2 2)	4858.47	4848.14	10.33
(1 2+ 3)	(3 3 0)	4957.56	4958.00	−0.44
(1 3− 0)	(1 0 3)	5166.80	5163.62	3.18
(1 4− 0)	(4 0 1)	5873.53	5872.10	1.43
(1 4+ 0)	(1 0 4)	6487.02	6489.20	−2.18
(2 3− 0)	(0 0 5)	6697.43	6689.40	8.03

rms deviation (cm) 3.71

TABLE V. Cont. Predicted energies.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.
(0 1 − 3)	(0 3 1)	2900.52	(1 3 − 4)	(0 4 3)	6082.69
(0 0 + 6)	(0 6 0)	3102.22	(2 3 + 1)	(5 1 0)	6182.85
(0 1 + 4)	(1 4 0)	3206.12	(0 4 − 3)	(3 3 1)	6278.16
(0 2 + 2)	(2 2 0)	3319.48	(0 5 − 0)	(2 0 3)	6279.53
(0 1 − 4)	(0 4 1)	3413.29	(1 3 + 2)	(0 2 4)	6393.12
(0 2 − 2)	(1 2 1)	3524.34	(0 4 + 3)	(2 3 2)	6481.78
(0 0 + 7)	(0 7 0)	3627.05	(0 5 + 1)	(3 1 2)	6582.72
(0 1 + 5)	(1 5 0)	3720.70	(2 3 + 2)	(5 2 0)	6687.19
(0 2 + 3)	(2 3 0)	3829.45	(1 3 − 3)	(1 3 3)	6688.49
(0 1 − 5)	(0 5 1)	3927.87	(2 4 + 0)	(6 0 0)	6786.36
(0 3 − 1)	(2 1 1)	4143.66	(0 5 − 1)	(2 1 3)	6787.23
(0 1 + 6)	(1 6 0)	4238.38	(1 4 − 2)	(4 2 1)	6885.58
(0 3 + 1)	(1 1 2)	4349.50	(1 3 + 3)	(0 3 4)	6898.24
(0 1 − 6)	(0 6 1)	4445.54	(1 5 − 0)	(5 0 1)	6982.76
(0 2 − 4)	(1 4 1)	4544.54	(1 4 + 1)	(1 1 4)	6994.72
(1 3 + 0)	(4 0 0)	4556.00	(0 5 + 2)	(3 2 2)	7087.06
(0 3 − 2)	(2 2 1)	4652.64	(0 6 + 0)	(4 0 2)	7182.18
(1 1 + 4)	(0 4 2)	4752.67	(2 3 − 1)	(0 1 5)	7205.14
(1 3 + 0)	(4 0 0)	4556.00	(0 5 + 2)	(3 2 2)	7087.06
(0 3 − 2)	(2 2 1)	4652.64	(0 6 + 0)	(4 0 2)	7182.18
(1 1 + 4)	(0 4 2)	4752.67	(2 3 − 1)	(0 1 5)	7205.14
(0 2 + 5)	(2 5 0)	4851.60	(0 5 − 2)	(2 2 3)	7291.58
(0 4 + 0)	(2 0 2)	4960.10	(2 4 + 1)	(6 1 0)	7291.85
(0 2 − 5)	(1 5 1)	5056.46	(0 6 − 0)	(3 0 3)	7384.56
(1 3 + 1)	(4 1 0)	5065.91	(1 5 − 1)	(5 1 1)	7488.25
(0 3 − 3)	(2 3 1)	5160.19	(1 4 + 2)	(1 2 4)	7499.06
(0 4 − 1)	(3 1 1)	5266.38	(0 6 + 0)	(2 0 4)	7589.87
(0 3 + 3)	(1 3 2)	5366.02	(2 3 − 2)	(0 2 5)	7709.48
(1 3 + 0)	(0 0 4)	5376.55	(1 5 − 0)	(1 0 5)	7798.04
(0 4 + 1)	(2 1 2)	5470.00	(3 4 + 0)	(7 0 0)	7889.68
(1 3 + 2)	(4 2 0)	5572.58	(0 6 − 1)	(3 1 3)	7890.06
(1 2 − 3)	(0 3 3)	5575.00	(2 4 + 0)	(0 0 6)	8009.04
(0 3 − 4)	(2 4 1)	5667.87	(2 5 − 0)	(6 0 1)	8084.16
(2 3 + 0)	(5 0 0)	5675.14	(0 6 + 1)	(2 1 4)	8095.36
(1 3 − 1)	(1 1 3)	5676.71	(1 6 + 0)	(5 0 2)	8281.59
(0 4 − 2)	(3 2 1)	5773.05	(1 5 − 1)	(1 1 5)	8303.53
(0 3 + 4)	(1 4 2)	5873.71	(0 7 − 0)	(4 0 3)	8481.93
(1 3 + 1)	(0 1 4)	5886.46	(2 4 + 1)	(0 1 6)	8514.53
(0 4 + 2)	(2 2 2)	5976.67	(0 7 + 0)	(3 0 4)	8685.12
(0 5 + 0)	(3 0 2)	6075.02	(1 6 − 0)	(2 0 5)	8891.12
(1 3 + 3)	(4 3 0)	6077.69	(2 5 + 0)	(1 0 6)	9099.89
			(3 4 − 0)	(0 0 7)	9311.39

TABLE VI. Comparison between calculated and experimental energies for O_3, and predicted energies up to 7 quanta. All energies in cm^{-1}.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	Exp.	Theor. − Expt.
(0 0+ 1)	(0 1 0)	720.34	701.00	19.34
(0 1+ 0)	(1 0 0)	1033.13	1042.00	−8.87
(0 1− 0)	(0 0 1)	1109.89	1102.00	7.89
(0 1+ 1)	(1 1 0)	1727.32	1726.00	1.32
(0 1− 1)	(0 1 1)	1804.08	1796.00	8.08
(0 2+ 0)	(2 0 0)	2049.66	2058.00	−8.34
(0 2− 0)	(1 0 1)	2102.08	2110.00	−7.92
(1 1+ 0)	(0 0 2)	2212.40	2201.00	11.40
(0 2+ 1)	(2 1 0)	2717.70	2726.00	−8.30
(0 2− 1)	(1 1 1)	2770.12	2785.00	−14.88
(1 1+ 1)	(0 1 2)	2880.44	2886.00	−5.56
(0 3+ 0)	(3 0 0)	3043.63	3046.00	−2.37
(0 3− 0)	(2 0 1)	3071.56	3084.00	−12.44
(1 2+ 0)	(1 0 2)	3180.24	3185.00	−4.76
(1 2− 0)	(0 0 3)	3302.99	3289.00	13.99
(0 4+ 0)	(4 0 0)	4003.02	4000.00	3.02
(0 4− 0)	(3 0 1)	4012.74	4009.00	3.74
(1 3+ 0)	(2 0 2)	4141.35	4139.00	2.35
(1 3− 0)	(1 0 3)	4241.74	4238.00	3.74
(2 2+ 0)	(0 0 4)	4382.12	4371.00	11.12
(0 5− 0)	(4 0 1)	4919.44	4922.00	−2.56
(1 4− 0)	(2 0 3)	5165.71	5170.00	−4.29
(2 3− 0)	(0 0 5)	5449.15	5443.00	6.15
(0 6+ 0)	(4 0 2)	5786.92	5767.00	19.92
(1 5+ 0)	(6 0 0)	6038.55	5997.00	41.55
(1 5+ 0)	(2 0 4)	6204.06	6204.00	0.06
(3 3+ 0)	(0 0 6)	6504.07	6506.00	−1.93
(1 6− 0)	(6 0 1)	6950.14	6987.00	−36.86
(2 5− 0)	(4 0 3)	7218.25	7227.00	−8.75
(3 4− 0)	(0 0 7)	7546.72	7555.00	−8.28

rms deviation (cm) 13.42

lead to a satisfactory description for the intensities in this molecule. Using the parameter values $\alpha_1 = 15.8$, $\alpha_2 = 450.0$, $\alpha_3 = -35.0$, $\alpha_4 = 55.0$, $\alpha_5 = 235.0$, $\beta_1 = 1.1$ and $\beta_3 = 2.5$ we obtain the result given in Table VIII. Although these parameters were not obtained by a least squares fit procedure, but rather varied to search for the best fit, this is not difficult since the effect of each parameter on the intensities is very specific. A fit to these intensities was carried out previously by Iachello and Oss [15], within the U(4) algebraic method. Although in that case energy fits are quite straightforward, the fit to intensities is very difficult due to the model's sensitivity to parameter values, in contrast to the case of

TABLE VI. Cont. Predicted energies.

$(n\ m \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.	$(n\ m\ \pm\ v_2)$	$(v_1\ v_2\ v_3)$	Theor.
(0 0+ 2)	(0 2 0)	1482.61	(1 3+ 2)	(2 2 2)	5414.76
(0 0+ 3)	(0 3 0)	2286.80	(0 5+ 1)	(3 1 2)	5506.92
(0 1+ 2)	(1 2 0)	2463.44	(0 5− 1)	(4 1 1)	5509.04
(0 1− 2)	(0 2 1)	2540.20	(1 3− 2)	(1 2 3)	5515.15
(0 0+ 4)	(0 4 0)	3132.92	(2 2+ 2)	(0 2 4)	5655.53
(0 1+ 3)	(1 3 0)	3241.48	(2 3+ 1)	(5 1 0)	5688.03
(0 1− 3)	(0 3 1)	3318.24	(1 4− 1)	(2 1 3)	5755.30
(0 2+ 2)	(2 2 0)	3427.66	(0 6− 0)	(3 0 3)	5787.25
(0 2− 2)	(1 2 1)	3480.08	(1 4+ 1)	(1 1 4)	5886.36
(1 1+ 2)	(0 2 2)	3590.41	(0 2+ 5)	(2 5 0)	5809.12
(0 3+ 1)	(3 1 0)	3685.52	(0 1+ 6)	(1 6 0)	5827.16
(0 3− 1)	(2 1 1)	3713.45	(0 2− 5)	(1 5 1)	5861.54
(1 2+ 1)	(1 1 2)	3822.13	(0 3+ 4)	(3 4 0)	5862.75
(1 2− 1)	(0 1 3)	3944.89	(0 3− 4)	(2 4 1)	5890.67
(0 0+ 5)	(0 5 0)	4020.96	(0 1− 6)	(0 6 1)	5903.92
(0 1+ 4)	(1 4 0)	4061.45	(0 0+ 7)	(0 7 0)	5922.83
(0 1− 4)	(0 4 1)	4138.21	(1 1+ 5)	(0 5 2)	5971.86
(0 2+ 3)	(2 3 0)	4179.56	(0 4+ 3)	(4 3 0)	5976.02
(0 2− 3)	(1 3 1)	4231.98	(0 4− 3)	(3 3 1)	5985.74
(1 1+ 3)	(0 3 2)	4342.30	(1 2+ 4)	(1 4 2)	5999.35
(0 3+ 2)	(3 2 0)	4369.34	(2 3− 1)	(0 1 5)	6038.74
(0 3− 2)	(2 2 1)	4397.27	(1 5− 0)	(5 0 1)	6071.10
(1 2+ 2)	(1 2 2)	4505.95	(2 4− 0)	(1 0 5)	6339.18
(0 4+ 1)	(4 1 0)	4618.76	(1 3+ 3)	(2 3 2)	6114.35
(0 4− 1)	(3 1 1)	4628.48	(1 2− 4)	(0 4 3)	6122.11
(1 2− 2)	(0 2 3)	4628.70	(0 5+ 2)	(3 2 2)	6138.44
(1 3+ 1)	(2 1 2)	4757.09	(0 5− 2)	(4 2 1)	6140.55
(1 3− 1)	(1 1 3)	4857.48	(1 3− 3)	(1 3 3)	6214.74
(0 5+ 0)	(3 0 2)	4917.33	(2 3+ 2)	(5 2 0)	6319.55
(0 1+ 5)	(1 5 0)	4923.34	(0 6+ 1)	(4 1 2)	6350.36
(0 0+ 6)	(0 6 0)	4950.93	(0 6− 1)	(3 1 3)	6350.69
(0 2+ 4)	(2 4 0)	4973.37	(2 2+ 3)	(0 3 4)	6355.12
(2 2+ 1)	(0 1 4)	4997.86	(1 4− 2)	(2 2 3)	6386.82
(0 1− 5)	(0 5 1)	5000.10	(1 4+ 2)	(1 2 4)	6517.87
(0 2− 4)	(1 4 1)	5025.79	(1 5+ 1)	(6 1 0)	6601.99
(0 3+ 3)	(3 3 0)	5095.08	(0 7+ 0)	(5 0 2)	6614.30
(2 3+ 0)	(5 0 0)	5098.44	(0 7− 0)	(4 0 3)	6614.34
(0 3− 3)	(2 3 1)	5123.01	(1 5− 1)	(5 1 1)	6634.54
(1 1+ 4)	(0 4 3)	5136.12	(2 3− 2)	(0 2 5)	6670.25
(1 2+ 3)	(1 3 2)	5231.69	(1 5+ 1)	(2 1 4)	6767.50
(0 4+ 2)	(4 2 0)	5276.43	(2 4− 1)	(1 1 5)	6902.62
(0 4− 2)	(3 2 1)	5286.15	(1 6+ 0)	(7 0 0)	6940.37
(1 4+ 0)	(1 0 4)	5296.77	(3 3+ 1)	(0 1 6)	7067.51
(1 2− 3)	(0 3 3)	5354.44	(3 4+ 0)	(7 0 0)	7113.44
			(2 5+ 0)	(1 0 6)	7371.35

TABLE VII. Values of the ξ parameter for the molecules analyzed in Table II.

Molecule	ξ
H_2O	−0.33
H_2S	−0.08
SO_2	−0.82
O_3	−0.96

the U(2) model. In Table VIII we also present the results of Ref. [15], as well as previous calculations using simple dipole functions.

From Table VIII we conclude that traditional calculations fail completely to describe the observed intensities. Even though the accuracy of our results is of the same order of magnitude than the one of Ref. [15], we have used a much simpler procedure with nearly half the number of parameters. These results emphasize the usefulness of the U(2) model when only vibrational degrees of freedom are involved. Our fitting programs are available on request.

6. CONCLUSIONS

We have presented an extension of the U(2) model which incorporates the description of bending modes in triatomic molecules. In addition to the energy fits we have calculated dipole intensities for the H_2O molecule.

The rms deviations obtained for the best fits are of the order of a few cm^{-1} or less (with the exception of O_3). This result, together with the simplicity of the model (no coupling coefficients are involved in computing the matrix elements) makes it particularly attractive for the study of overtones and combinations with high number of quanta. This is in contrast with the traditional approach, based on integrodifferential techniques, where the potential is modeled in terms of the force field constants through complex calculations [27]. Using the parameters obtained in the quadratic fits we also computed the parameter ξ, which gives a measure of the local-normal behavior of the molecules. In addition, our analysis shows that the definition of quantum numbers proposed for the normal states are very close to the exact quantum number for molecules with normal behavior. Our relatively simple dipole intensity calculation in H_2O gives a reasonably good description of the experimental observations, with similar quality to more involved methods. The method can be improved in several ways. The interactions included in the Hamiltonian (3.5) assume the conservation of the total number of quanta V. This restriction means that only some physically meaningful interactions, such as the Darling-Dennison interactions, have been taken into account, while others, like those leading to Fermi resonances, have not been included in the Hamiltonian. Phonon non-conservation, however, can be readily included in the model through the other generators of the SU(2) group. In particular, the raising and lowering operators, $\hat{J}_+$ and $\hat{J}_-$, or their hermitean sum $\hat{J}_x = \frac{1}{2}(\hat{J}_+ + \hat{J}_-)$, mix the multiplets in precisely the required form for Fermi-like interactions.

TABLE VIII. Calculated intensities $(0,0,0) \rightarrow (v_1\ v_2\ v_3)$ in H_2O.

$v_1\ v_2\ v_3$	Obs. [23]	Present work	Iachello Oss	Lawton & Child [24]	Stamard *et al.* [25]	Carney *et al.* [26]
0 1 0	1040.0	973	1040		1040.0	1040
1 0 0	49.5	55.3	51	49.5	43.0	35.6
0 0 1	720.0	670.4	732	74.1	241.9	493.0
0 2 0	7.6	6.5	4.7		0.043	5.4
1 1 0	3.7	1.8	5.7		0.051	1.3
0 1 1	80.4	82.4	82.8		26.7	162.5
2 0 0	4.6	5.1	7.7	0.037	0.004	4.3
1 0 1	64.3	74.2	28	0.054	0.004	22.2
0 0 2	0.58	1.0	2.2	0.01	0.0	0.15
0 3 0	0.04	0.044	0.02		0.0014	0.02
1 2 0	0.31	0.012	0.08		0.06	0.08
0 2 1	5.1	0.55	1.1		0.05	1.7
2 1 0	0.042	0.16	0.03		0.0013	
1 1 1	4.95	9.13	3.9		0.0036	
0 1 2	0.16	0.034	0.001		0.29	
3 0 0		0.62	1.61			
2 0 1		7.96	4.69			
1 0 2	5(−6)	0.059	0.16			
0 0 3		0.27	0.12			
0 4 0	0.002	0.0003	0.0004		0.0039	
1 3 0	0.023	0.00008	0.0008		0.0024	
0 3 1	0.089	0.0037	0.011		0.058	
Number of parameters		7	12			

The matrix elements of $\hat{J}_x$ in the local basis take the form

$$\left\langle [N]v+1 \middle| \hat{J}_x \middle| [N]v \right\rangle = \tfrac{1}{2}\sqrt{(N-v)(v+1)}\,,$$

$$\left\langle [N]v-1 \middle| \hat{J}_x \middle| [N]v \right\rangle = \tfrac{1}{2}\sqrt{v(N-v+1)}\,.$$

The algebraic model can thus naturally incorporate such terms in a simple fashion.

On the other hand, the study of vibrational isotopic effects in molecules is of major importance due to the fact that to a very high degree of approximation these molecules correspond to the same energy potentials. The differences in vibrational frequencies are due mainly to the presence of different masses. From these considerations it is possible to establish additional equations that determine the force field constants. In the algebraic approach, however, there is no explicit distinction between the kinetic and the potential energy terms. All structural information is contained in the Hamiltonian parameters, so we cannot reproduce the traditional studies in a straightforward way. It is possible, nevertheless, to study any isotopic molecule by means of the same algebraic scheme considering the change to lower symmetry, if present. Once we have at our disposal fits to a set of isotopic molecules we can analyze the scaling properties of the Hamiltonian parameters as a function of their masses, which allows the prediction of the vibrational spectrum of other isotopic species [15]. It is also possible to correlate the Hamiltonian parameters with the force field constants by means of closed energy expressions for the fundamentals and first overtones, as explained in Ref. [15] for the case of H_2O.

We remark that although the generalization of the U(2) model has only been presented for the case of triatomic molecules, it is possible to extend our considerations to polyatomic molecules, although a careful analysis of spurious degrees of freedom has to be made [10,11]. The model seems to represent a very promising framework for the description of infrared spectroscopic properties of complex molecules.

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