A Symmetry Adapted Approach to Molecular Spectroscopy: The Anharmonic Oscillator Symmetry Model

A. Frank\textsuperscript{1,2)}, R. Lemus\textsuperscript{1)}, R. Bijker\textsuperscript{1)}, F. Pérez-Bernal\textsuperscript{3)} and J.M. Arias\textsuperscript{3)}

\textsuperscript{1)} Instituto de Ciencias Nucleares, U.N.A.M.,
A.P. 70-543, 04510 México D.F., México
\textsuperscript{2)} Instituto de Física, Laboratorio de Cuernavaca,
A.P. 139-B, Cuernavaca, Morelos, México
\textsuperscript{3)} Departamento de Física Atómica, Molecular y Nuclear,
Facultad de Física, Universidad de Sevilla,
Apdo. 1065, 41080 Sevilla, España

Abstract

We apply the Anharmonic Oscillator Symmetry Model to the description of vibrational excitations in $D_{3h}$ and $T_d$ molecules. A systematic procedure can be used to establish the relation between the algebraic and configuration space formulations, by means of which new interactions are found in the algebraic model, leading to reliable spectroscopic predictions. We illustrate the method for the case of $D_{3h}$-triatomic molecules and the $T_d$ Be-cluster.
The study of molecular vibrational spectra requires theoretical models in order to analyze and interpret the measurements. These models range from simple parametrizations of the energy levels, such as the Dunham expansion, to \textit{ab initio} calculations, where solutions of the Schrödinger equation in different approximations are sought. In general, the latter involve the use of internal coordinates and the evaluation of force field constants associated to derivatives at the potential minima. While this method can be reliably applied to small molecules, it quickly becomes a formidable problem in the case of larger molecules, due to the size of their configuration spaces. New calculational tools to describe complex molecules are thus needed.

In 1981 an algebraic approach was proposed to describe the roto-vibrational structure of diatomic molecules, subsequently extended to linear tri- and four-atomic molecules and certain non-linear triatomic molecules. Although these were encouraging results, the model could not be extended to polyatomic molecules, due to the impossibility of incorporating the underlying discrete symmetries. This difficulty could be surmounted by treating the vibrational degrees of freedom separately from the rotations. In 1984 Van Roosmalen et al proposed a U(2)-based model to describe the stretching vibrational modes in ABA molecules later extended to describe the stretching vibrations of polyatomic molecules such as octahedral and benzene like molecules. Recently the bending modes have also been included in the framework, which was subsequently applied to describe \( C_{2v} \)-triatomic molecules and the lower excitations of tetrahedral molecules, using a scheme which combines Lie-algebraic and point group methods. In a different approach, it has also been suggested to use a \( U(k + 1) \) model for the \( k = 3n - 3 \) rotational and vibrational degrees of freedom of a \( n \)-atomic molecule. This model has the advantage that it incorporates all rotations and vibrations and takes into account the relevant point group symmetry, but for larger molecules the number of possible interactions and the size of the Hamiltonian matrices increase very rapidly, making it impractical to apply.

Although the algebraic formulations have proved useful, several problems remained, most important of which is the absence of a clear connection to traditional methods. On the other hand, a related problem is the lack of a systematic procedure to construct all physically meaningful interactions in the algebraic space. In this paper we show that both these issues can be resolved by means of a general model for the analysis of molecular vibrational spectra, the Anharmonic Oscillator Symmetry Model (AOSM). In this approach it is possible to construct algebraic operators with well defined physical meaning, in particular interactions fundamental for the description of the degenerate modes present in systems exhibiting high degree of symmetry. The procedure to construct them takes full advantage of the discrete symmetry of the molecule and gives rise to all possible terms in a systematic fashion, providing a clear-cut connection between the algebraic scheme and the traditional analyses based on internal coordinates, which correspond to the harmonic limit of the model.

As a test for this approach we apply the AOSM to the Be\textsubscript{4} cluster and to three \( D_{3h} \)-triatomic molecular
systems, namely \( \text{H}_3^+ \), \( \text{Be}_3 \) and \( \text{Na}_3^+ \). Since small molecules can in general be well described by means of \textit{ab initio} calculations \[15, 16\], we emphasize the basic purpose of this work. We have established an exact correspondence between configuration space and algebraic interactions by studying the harmonic limit of the \( \text{U}(2) \) algebra. This general procedure not only allows to derive the interactions in the AOSM from interactions in configuration space, but can also be applied to cases for which no configuration space interactions are available. The \( \mathcal{D}_{3h} \)-triatomic molecules constitute the simplest systems where degenerate modes appear and where the new interactions in the model become significant. In the case of \( \text{Be}_4 \), a direct comparison with \textit{ab initio} calculations will be presented. The application of these techniques to more complex systems, such as the methane molecules, is presently under investigation \[17\].

The model is based on the isomorphism of the \( \text{U}(2) \) Lie algebra and the one dimensional Morse oscillator

\[
\mathcal{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D(e^{-2x} - 2e^{-x}) ,
\]

whose eigenstates \( \mathcal{E} \) can be associated with \( \text{U}(2) \supset \text{SO}(2) \) states \[18\]. In order to see how this isomorphism comes about, consider the radial equation

\[
\frac{1}{2} \left( -\frac{1}{r} \frac{d}{dr} r \frac{d}{dr} + \frac{m^2}{r^2} + r^2 \right) \phi(r) = (N + 1) \phi(r) ,
\]

which corresponds to a two-dimensional harmonic oscillator (in units where \( \hbar = \mu = e = 1 \)) associated to a \( \text{U}(2) \) symmetry algebra \[19\]. By carrying out the transformation

\[
r^2 = (N + 1)e^{-\rho} ,
\]

equation (2) transforms into

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

which can be identified with (1) after defining \( x = \rho d \) and multiplying by \( \hbar^2/2\mu d^2 \), provided that

\[
D = \frac{\hbar^2}{8\mu d^2} (N + 1)^2 , \quad \mathcal{E} = -\frac{\hbar^2}{2\mu d^2} m^2 .
\]

In the framework of the \( \text{U}(2) \) algebra, the operator \( \hat{N} \) corresponds to the total number of bosons and is fixed by the potential shape according to (4), while \( m \), the eigenvalue of the \( \text{SO}(2) \) generator \( J_z \), takes the values \( m = \pm N/2, \pm (N-2)/2, \ldots \). The Morse spectrum is reproduced twice and consequently for these applications the \( m \)-values must be restricted to be positive. In terms of the \( \text{U}(2) \) algebra, it is clear from (3-5) that the Morse Hamiltonian has the algebraic realization

\[
\hat{H} = -\frac{\hbar^2}{2\mu d^2} \hat{J}_z^2 = -A \hat{J}_z^2 .
\]
In addition, the $U(2)$ algebra includes the raising and lowering operators $\hat{J}_+$, $\hat{J}_-$, which connect different energy states in (3), while the angular momentum operator is given by $\hat{J}^2 = \frac{1}{4} \hat{N} (\hat{N} + 2)$, as can be readily shown.

The Morse Hamiltonian (6) can be rewritten in the more convenient form

$$\hat{H} = A \hat{H}^M = \frac{A}{2} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) - \hat{N}, \quad (7)$$

where we have used the relation $\hat{J}^2 = \hat{J}^2 - \frac{1}{4} (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) + \hat{J}_0 \hat{J}_0$ and added the constant term $A \hat{N}^2$ in order to place the ground state at zero energy. The parameters $N$ and $A$ appearing in (7) are related with the usual harmonic and anharmonic constants $\omega_e$ and $x_e \omega_e$ used in spectroscopy [7]. To obtain this relation it is convenient to introduce the quantum number

$$v = \frac{N}{2} - m, \quad (8)$$

which corresponds to the number of quanta in the oscillator [13]. This is seen by substituting (8) into (7). In terms of $v$, the corresponding energy expression takes the form

$$E_M = -\frac{A}{2} (N + 1/2) + A(N + 1)(v + 1/2) - A(v + 1/2)^2, \quad (9)$$

from which we immediately obtain

$$\omega_e = A(N + 1), \quad x_e \omega_e = A. \quad (10)$$

Thus, in a diatomic molecule the parameters $A$ and $N$ can be determined by the spectroscopic constants $\omega_e$ and $x_e \omega_e$.

We now consider the $U_i(2) \supset SU_i(2) \supset SO_i(2)$ algebra, generated by the set $\{\hat{G}_i\} \equiv \{\hat{N}_i, \hat{J}_{+,i}, \hat{J}_{-,i}, \hat{J}_{0,i}\}$, satisfying the commutation relations

$$[\hat{J}_{0,i}, \hat{J}_{\pm,i}] = \pm \hat{J}_{\pm,i}, \quad [\hat{J}_{+,i}, \hat{J}_{-,i}] = 2\hat{J}_{0,i}, \quad [\hat{N}_i, \hat{J}_{\mu,i}] = 0, \quad (11)$$

with $\mu = \pm, 0$. As mentioned before, for the symmetric irreducible representation $[N_i, 0]$ of $U_i(2)$ one can show that the Casimir operator is given by $\hat{J}^2 = \hat{N}_i (\hat{N}_i + 2)/4$, from which follows the identification $j_i = N_i/2$. The $SO_i(2)$ label is denoted by $m_i$.

In the algebraic approach each relevant interatomic interaction is associated with a $U_i(2)$ algebra [11]. As a specific example, we consider the Be$_4$ cluster, which has a tetrahedral shape. $D_{3h}$ molecules can be similarly treated. In the Be$_4$ case there are six $U_i(2)$ algebras involved ($i = 1, \ldots, 6$). The operators in the model are expressed in terms of the generators of these algebras, and the symmetry requirements of the tetrahedral group $T_d$ can be readily imposed [13, 20]. The local operators $\{\hat{G}_i\}$ acting on bond $i$
can be projected to any of the fundamental irreps $\Gamma = A_1, E$ and $F_2$. Using the $\hat{J}_{\mu,i}$ generators (11) we obtain the $T_d$ tensors

$$\hat{T}_{\mu,\gamma} = \sum_{i=1}^{6} \alpha_{\gamma,i} \hat{J}_{\mu,i},$$

where $\mu = \pm, 0$ and $\gamma$ denotes the component of $\Gamma$. The explicit expressions are given by

$$\hat{T}^{A_1}_{\mu,1} = \frac{1}{\sqrt{6}} \sum_{i=1}^{6} \hat{J}_{\mu,i},$$

$$\hat{T}^{E}_{\mu,1} = \frac{1}{2\sqrt{3}} \left( \hat{J}_{\mu,1} + \hat{J}_{\mu,2} - 2\hat{J}_{\mu,3} + \hat{J}_{\mu,4} - 2\hat{J}_{\mu,5} + \hat{J}_{\mu,6} \right),$$

$$\hat{T}^{E}_{\mu,2} = \frac{1}{2} \left( \hat{J}_{\mu,1} - \hat{J}_{\mu,2} - \hat{J}_{\mu,4} + \hat{J}_{\mu,6} \right),$$

$$\hat{T}^{F_2}_{\mu,1} = \frac{1}{\sqrt{2}} \left( \hat{J}_{\mu,1} - \hat{J}_{\mu,6} \right),$$

$$\hat{T}^{F_2}_{\mu,2} = \frac{1}{\sqrt{2}} \left( \hat{J}_{\mu,2} - \hat{J}_{\mu,4} \right),$$

$$\hat{T}^{F_2}_{\mu,3} = \frac{1}{\sqrt{2}} \left( \hat{J}_{\mu,3} - \hat{J}_{\mu,5} \right).$$

The Hamiltonian operator can be constructed by repeated couplings of these tensors to a total symmetry $A_1$, since it must commute with all operations in $T_d$. This is accomplished by means of the $T_d$-Clebsch-Gordan coefficients [13, 20]

All calculations can be carried out in a symmetry-adapted basis, which is projected from the local basis

$$U_1(2) \otimes \cdots \otimes U_6(2) \supset SO_1(2) \otimes \cdots \otimes SO_6(2) \supset SO(2)$$

$$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow$$

$$| N_1 \rangle, \ldots, | N_6 \rangle; \quad v_1, \ldots, v_6; \quad V \rangle$$

in which each anharmonic oscillator is well defined. By symmetry considerations, $N_i = N$ for the six oscillators, $v_i = N_i/2 - m_i$ denotes the phonon number in bond $i$ and $V = \sum_i v_i$ is the total number of phonons [13, 19]. The one-phonon states $V = 1$ are denoted by $| i \rangle$ with $v_i = 1$ and $v_{j\neq i} = 0$. Using the same projection technique as for the generators (13), we find the six fundamental modes

$$1 \phi_{\gamma} = \sum_{i=1}^{6} \alpha_{\gamma,i} | i \rangle.$$ 

The expansion coefficients are the same as in (13). The higher phonon states $V \phi_{\gamma}$ can also be constructed using the Clebsch-Gordan coefficients of $T_d$ [13, 20]. Since all operators are expressed in terms of powers of the $U_i(2)$ generators, their matrix elements can be easily evaluated in closed form. The symmetry-adapted operators (13) and states (15) are the building blocks of the model. Note that for more complex molecules, the method allows the exact elimination of spurious states [17].
We now proceed to explicitly construct the Be₄ Hamiltonian. For interactions that are at most quadratic in the generators the procedure yields

\[ \hat{H}_0 = a_1 \hat{H}_{A_1} + a_2 \hat{H}_E + a_3 \hat{H}_{F_2} + b_2 \hat{V}_E + b_3 \hat{V}_{F_2}, \]  

(16)

with

\[ \hat{H}_\Gamma = \frac{1}{2N} \left( \hat{T}_- \cdot \hat{T}_+ + \hat{T}_+ \cdot \hat{T}_- \right), \]
\[ \hat{V}_\Gamma = \frac{1}{N} \hat{T}_0 \cdot \hat{T}_0 . \]

(17)

Note that we have not included \( \hat{V}_{A_1} \) in (16), since the combination

\[ \sum_\Gamma (\hat{H}_\Gamma + \hat{V}_\Gamma) = \frac{3}{2}(N + 2), \]

(18)

is a constant. The five interaction terms in Eq. (16) correspond to linear combinations of the ones obtained in lowest order in \([11, 13]\). However, it is necessary to include interactions which are related to the vibrational angular momenta associated with the degenerate modes \( E \) and \( F_2 \). These kind of terms is absent in the former versions of the model \([11, 13]\). We now proceed to show how they can be obtained in the AOSM. In configuration space the vibrational angular momentum operator for the \( E \) mode is given by \([22]\)

\[ \hat{l}_A = -i \left( q_E \frac{\partial}{\partial q_E} - q_E \frac{\partial}{\partial q_E} \right), \]

(19)

where \( q_E \) and \( q_E \) are the normal coordinates associated to the \( E \) mode. This relation can be transformed to the algebraic space by means of the harmonic oscillator operators

\[ \hat{b}_E = \frac{1}{\sqrt{2}} \left( q_E - \frac{\partial}{\partial q_E} \right), \quad \hat{b}_E = \frac{1}{\sqrt{2}} \left( q_E + \frac{\partial}{\partial q_E} \right), \]

(20)

to obtain

\[ \hat{l}_A = -i \left( \hat{b}_E \hat{b}_E - \hat{b}_E \hat{b}_E \right). \]

(21)

Here \( \hat{b}_E = \sum_i \alpha_{\gamma,i} b_i \), with a similar form for \( \hat{b}_E \), while the \( \alpha_{\gamma,i} \) can be read from (13). In order to find the algebraic expression for \( \hat{l}_A \) we first introduce a scale transformation in (11)

\[ \bar{b}_i = \hat{b}_i / \sqrt{N_i}, \quad \bar{b}_i = \hat{b}_i / \sqrt{N_i}. \]

(22)

The relevant commutator can be expressed as

\[ [\bar{b}_i, \bar{b}_j] = \frac{1}{N_i} [\hat{J}_{+,i}, \hat{J}_{-,j} = \frac{1}{N_i} 2\hat{J}_{0,i} = 1 - \frac{2\hat{\nu}_i}{N_i}, \]

(23)

where

\[ \hat{\nu}_i = \frac{\hat{N}_i}{2} - \hat{J}_{0,i}. \]

(24)
The other two commutators in (11) are not modified by (22). In the harmonic limit, which is defined by \(N_i \to \infty\), Eq. (23) reduces to the standard boson commutator \([\bar{b}_i, \bar{b}^\dagger_i] = 1\). This limit corresponds to a contraction of \(SU(2)\) to the Weyl algebra and can be used to obtain a geometric interpretation of AOSM operators in terms of those in configuration space. In the opposite sense, Eq. (22) provides a procedure to construct the anharmonic representation of harmonic operators through the correspondence \(\hat{b}_i^\dagger \to \bar{b}_i^\dagger = \hat{J}_{-i}/\sqrt{N_i}\) and \(\hat{b}_i \to \bar{b}_i = \hat{J}_{+i}/\sqrt{N_i}\). Applying this method to the vibrational angular momentum (21) we find
\[
\hat{\ell}_{A2} = -\frac{i}{N} \left( \hat{J}_E^{-1,1} \hat{J}_E^{1,2} - \hat{J}_E^{-1,2} \hat{J}_E^{1,1} \right) .
\] (25)
For the vibrational angular momentum \(\hat{\ell}_{F1}\) associated with the \(F_2\) mode we find a similar expression. The AOSM form of the corresponding Hamiltonian interactions is
\[
\hat{H}_1 = c_2 \hat{\ell}_{A2} \hat{\ell}_{A2} + c_3 \sum_\gamma \hat{\ell}_{F1} \hat{\ell}_{F1} + d_3 \left( \hat{H}_{F2} + \hat{V}_{F2} \right)^2 + e_3 \hat{O}_{33} ,
\] (26)
With this method we can obtain an algebraic realization of arbitrary configuration space interactions. As a simple example, a one-dimensional harmonic oscillator Hamiltonian \(\hat{H}_0 = 1/2(\hat{b}_i^\dagger \hat{b}_i + \hat{b}_i \hat{b}_i^\dagger)\), transforms into
\[
\frac{1}{2N} (\hat{J}_{-i} \hat{J}_{+i} + \hat{J}_{+i} \hat{J}_{-i}) = \frac{1}{N} (\hat{J}_0^2 - \hat{J}_{0,1}^2) = \hat{v}_i + 1/2 - \frac{\hat{v}_i^2}{N} ,
\] (27)
where in the last step we used relation (24). The spectrum of (27) has an anharmonic correction, analogous to the quadratic term in the Morse potential spectrum. We are thus substituting harmonic oscillators by Morse oscillators in the AOSM.

A more interesting application is to use our model to fit the spectroscopic data of several polyatomic molecules. In the case of Be$_4$ the energy spectrum was analyzed by \textit{ab initio} methods in [13], where force-field constants corresponding to an expansion of the potential up to fourth order in the normal coordinates and momenta were evaluated. We have generated the \textit{ab initio} spectrum up to three phonons using the analysis in [22]. For the algebraic Hamiltonian we take
\[
\hat{H} = \hat{H}_0 + c_3 \sum_\gamma \hat{\ell}_{F1} \hat{\ell}_{F1} + d_3 (\hat{H}_{F2} + \hat{V}_{F2})^2 + e_3 \hat{O}_{33} ,
\] (28)
where \(\hat{H}_0\) was defined in (16). The term \(\hat{O}_{33}\) is the algebraic form of the corresponding \(F_2\)-mode interaction in [22] which is responsible for the splitting of the vibrational levels with the same \(l\) in the \(F_2\) overtones. For \(D_{3h}\) molecules we can follow an analogous procedure, namely, we can construct the \(D_{3h}\) symmetry-adapted operators and states corresponding to (13) and (15) and carry out the building up procedure to construct the Hamiltonian and higher phonon states, using in this case the appropriate projection operators and Clebsch-Gordan coefficients [13, 20]. Here we omit the details for lack of space and only present the fit to the energy spectrum [23, 24].

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Note that the $\text{Be}_4$ Hamiltonian (28) preserves the total phonon-number $V$. This is a good approximation for this case according to the analysis of [22, 25], but it is known that Fermi resonances can occur for certain molecules when the fundamental mode frequencies are such that $(V, V')$ states with $V \neq V'$ are close in energy. These interactions can be introduced in the Hamiltonian but the size of the energy matrices grows very rapidly, so the best way to deal with this problem is through perturbation theory.

We now present the results of our least-square fits to the energy spectra of $\text{Be}_4$, $\text{Be}_3$, $\text{Na}_3^+$ and $\text{H}_3^+$. In Table I we show the fit to $\text{Be}_4$ using the Hamiltonian (28). The r.m.s. deviation obtained is $2.3 \text{ cm}^{-1}$, which can be considered of spectroscopic quality. We point out that in [22, 25] several higher order interactions are present which we have neglected. Since our model can be put into a one to one correspondence with the configuration space calculations, it is in fact possible to improve the accuracy of the fit considerably, but we have used a simpler Hamiltonian than the one of [22, 25]. When no \textit{ab initio} calculations are available (or feasible) the AOSM approach can be used empirically, achieving increasingly good fits by the inclusion of higher order interactions [17]. In Table II we present AOSM fits to the spectra of $\text{Be}_3$, $\text{Na}_3^+$ and $\text{H}_3^+$ up to three phonons. While remarkably accurate descriptions of the first two molecules can be achieved using a four-parameter Hamiltonian, we were forced to include four additional higher order terms in the $\text{H}_3^+$ Hamiltonian in order to properly describe this molecule. This is in accordance with the work of Carter and Meyer [16], who were forced to include twice as many terms in the potential energy surface for $\text{H}_3^+$ than for the $\text{Na}_3^+$ molecule. The $\text{H}_3^+$ ion is a very “soft” molecule which, due to the light mass of its atomic constituents carries out large amplitude oscillations from its equilibrium positions [16].

A finer test for the model is to use the wave functions to evaluate infrared and Raman transitions. The algebraic realization of the transition operators can be obtained from their expression in configuration space using the large $N$ connection, or purely algebraically by their tensorial properties under the relevant point group [24]. We remark that the model can also be extended to include the rotational degrees of freedom, by coupling the vibrational wave functions to rotational states properly symmetrized to carry the point group representations [22].

The AOSM is based on symmetry methods which systematically incorporate group theoretical techniques, providing a clear methodological procedure that can be applied to more complex molecules. We define symmetry adapted operators that have a specific action over the function space. This is a general procedure which gives rise to a clear physical interpretation of the interactions and has the additional advantage of considerably improving the convergence during the least square energy fits. Based on the harmonic limit of the SU(2) algebra we have found a systematic approach to derive an algebraic realization of interactions given in configuration space. The model surmounts one of the main objections raised against the use of algebraic models, where it was not possible to obtain a direct correspondence with the configuration-space approaches. For the general case when there is no information about the form
of these interactions in configuration space, we have devised an algebraic procedure to derive them using their tensorial structure under the point group. The combination of the different methodologies leads to the AOSM, which can be applied in the same fashion to more complex molecules.

We believe that the AOSM represents a systematic, simple but accurate alternative to the traditional methods, particularly for polyatomic molecules, where the integro-differential approaches are too complex to be applied or require very large numerical calculations. Since the model provides manageable wave functions, it is possible to evaluate the matrix elements of arbitrary physical operators, which have a simple representation in the algebraic space. The study of electromagnetic intensities, as well as the application of the model to more complex molecules is currently under investigation [17, 21].

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References

[1] J. Michael Hollas, Modern Spectroscopy, John Wiley 1992; Kazuo Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds. Wiley - Interscience publication, 1978.

[2] Gerard Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, van Nostrand, New York, 1950.

[3] E.B. Wilson, Jr., J.C. Decious and P. Cross, Molecular Vibrations, Dover, New York, 1980.

[4] W.T. Raynes, P. Lazzeretti, R. Zanesi, A.J. Sadly and P.W. Fowler, Mol. Phys. 60 (1987) 509; G.D. Carney and R.N. Porter, J. Chem. Phys. 65 (1976) 3547.

[5] D.L. Gray and A.G. Robiette, Mol. Phys. 37 (1979) 1901.

[6] J.F. Ogilvie, J. Mol. Spect., 69 (1978) 169; W. Meyer and P. Botschwina, J. Chem. Phys., 84 (1986) 891.

[7] F. Iachello, Chem. Phys. Lett. 78 (1981) 581; F. Iachello and R.D. Levine, J. Chem. Phys. 77 (1982) 3046.

[8] F. Iachello, S. Oss and R. Lemus, J. Mol. Spect. 146 (1991) 56; Ibidem 149 (1991) 132.

[9] F. Iachello and S. Oss, J. Mol. Spect. 142 (1990) 85.

[10] O.S. van Roosmalen, I. Benjamin and R.D. Levine, J. Chem. Phys. 81 (1984) 5986.
[11] F. Iachello and S. Oss, Phys. Rev. Lett. 66 (1991) 2976; Chem. Phys. Lett. 187 (1991) 500; F. Iachello and S. Oss. Chem. Phys. Lett. 205 (1993) 285; J. Chem. Phys. 99 (1993) 7337.

[12] J.M. Arias, A. Frank, R. Lemus and F. Pérez-Bernal, Rev. Mex. Fís. (1995).

[13] R. Lemus and A. Frank, J. Chem. Phys. 101 (1994) 8321; A. Frank and R. Lemus, Phys. Rev. Lett. 68 (1992) 413.

[14] R. Bijker, A.E.L. Dieperink and A. Leviatan, to be published in Phys. Rev. A.

[15] A.P. Rendell, T.J. Lee and P.R. Taylor, J. Chem. Phys. 92 (1990) 7050.

[16] S. Carter and W. Meyer, J. Chem. Phys. 93 (1990) 8902.

[17] A. Frank, F. Pérez-Bernal, R. Bijker, J.M. Arias and R. Lemus, to be published.

[18] Y. Alhassid, F. Gürsey and F. Iachello, Ann. of Phys. 148 (1983) 346.

[19] A. Frank and P. Van Isacker, Algebraic Methods in Molecular and Nuclear Structure Physics, Wiley, New York, 1994.

[20] S.L. Altmann and P. Herzig, Point Group Theory Tables, Clarendon Press, Oxford, 1994.

[21] M. Hamermesh, Group Theory and its Applications to Physical Problems, Addison-Wesley, 1962.

[22] K.T. Hecht, J. Mol. Spect. 5 (1960) 355.

[23] J.K.G. Watson, J. Mol. Spect. 103 (1984) 350; Ibid, Can. J. Phys. 72 (1994) 238; J. Tennyson and J.R. Henderson, J. Chem. Phys. 91 (1989) 3815.

[24] A. Frank, R. Lemus, J. Pérez-Bernal, R. Bijker and J.M. Arias, to be published.

[25] A.P. Rendell, T.J. Lee and P.R. Taylor, J. Chem. Phys. 92 (1990) 7050.
Table I: Fit to ab initio \cite{11} calculations for Be$_4$. The values of the parameters are $N = 40$, $a_1 = 646.95$, $a_2 = 463.51$, $a_3 = 675.54$, $b_2 = 129.46$, $b_3 = 317.01$, $c_3 = -14.285$, $d_3 = 10.688$, and $e_3 = -1.948$. The parameters and energies are given in cm$^{-1}$. $(\nu_1, \nu_2^m, \nu_3^l)$ denotes the number of phonons in the $A_1$, $E$ and $F_2$, respectively, and $m$ and $l$ the value of the vibrational angular momenta \cite{16}.

| V | $(\nu_1, \nu_2^m, \nu_3^l)$ | $\Gamma$ | Ab initio | Present | V | $(\nu_1, \nu_2^m, \nu_3^l)$ | $\Gamma$ | Ab initio | Present |
|---|-----------------|-------|-----------|---------|---|-----------------|-------|-----------|---------|
| 1 | $(1, 0^0, 0^0)$ | $A_1$ | 638.6 | 638.3 | 3 | $(1, 0^0, 2^0)$ | $A_1$ | 2106.8 | 2110.1 |
|   | $(0, 1^1, 0^0)$ | $E$ | 453.6 | 454.8 |   | $(1, 0^0, 2^2)$ | $E$ | 2000.1 | 2005.2 |
|   | $(0, 0^0, 1^1)$ | $F_2$ | 681.9 | 681.1 |   | $F_2$ | 2056.8 | 2058.6 |
| 2 | $(2, 0^0, 0^0)$ | $A_1$ | 1271.0 | 1271.2 |   | $(0, 3^1, 0^0)$ | $E$ | 1341.3 | 1347.1 |
|   | $(1, 1^1, 0^0)$ | $E$ | 1087.1 | 1085.1 |   | $(0, 3^3, 0^0)$ | $A_1$ | 1355.5 | 1352.3 |
|   | $(1, 0^0, 1^1)$ | $F_2$ | 1312.6 | 1312.8 | | $A_2$ | 1355.5 | 1353.0 |
|   | $(0, 2^0, 0^0)$ | $A_1$ | 898.3 | 903.0 |   | $(0, 2^0, 1^1)$ | $F_2$ | 1565.5 | 1565.4 |
|   | $(0, 2^2, 0^0)$ | $E$ | 905.4 | 905.7 |   | $F_2$ | 1584.4 | 1583.3 |
|   | $(0, 1^1, 1^1)$ | $F_2$ | 1126.7 | 1126.1 |   | $(0, 2^3, 1^1)$ | $F_1$ | 1578.5 | 1576.2 |
|   | | $F_1$ | 1135.5 | 1134.8 |   | $(0, 1^1, 2^0)$ | $E$ | 1821.4 | 1821.9 |
|   | $(0, 0^0, 2^0)$ | $A_1$ | 1484.0 | 1485.8 | | $E$ | 1929.5 | 1928.6 |
|   | $(0, 0^0, 2^2)$ | $E$ | 1377.3 | 1378.1 |   | $(0, 1^1, 2^2)$ | $A_1$ | 1813.3 | 1814.8 |
|   | | $F_2$ | 1434.1 | 1433.6 | | $A_2$ | 1830.8 | 1830.7 |
| 3 | $(3, 0^0, 0^0)$ | $A_1$ | 1897.0 | 1898.8 | | $F_1$ | 1874.5 | 1873.9 |
|   | $(2, 1^1, 0^0)$ | $E$ | 1714.3 | 1710.0 | | $F_2$ | 1883.2 | 1881.9 |
|   | $(2, 0^0, 1^1)$ | $F_2$ | 1937.0 | 1939.1 | | $(0, 0^0, 3^1, 3^1)$ | $F_2$ | 2136.5 | 2137.5 |
|   | $(1, 2^0, 0^0)$ | $A_1$ | 1526.6 | 1525.5 | | $F_2$ | 2327.3 | 2328.1 |
|   | $(1, 2^2, 0^0)$ | $E$ | 1533.7 | 1527.8 | | $(0, 0^0, 3^2)$ | $F_1$ | 2199.8 | 2200.2 |
|   | $(1, 1^1, 1^1)$ | $F_2$ | 1752.2 | 1750.1 | | $A_1$ | 2256.5 | 2257.5 |
|   | $F_1$ | 1761.0 | 1758.1 |
Table II: Least square energy fit for H$_3^+$, Be$_3$ and Na$_3^+$ using the Hamiltonian (7.1). We show the energy differences $\Delta E = E_{th} - E_{exp}$. The values of the energies $E_{exp}$ are given in Table V.

| $(v_A v_E^I)$ | Symmetry | $H_3^+$ | Be$_3$ | Na$_3^+$ |
|---------------|----------|---------|--------|----------|
| $(01^1)$      | $e$      | -1.55   | 0.51   | 0.93     |
| $(10^0)$      | $a_1$    | 0.42    | 0.02   | 1.95     |
| $(02^0)$      | $a_1$    | 7.48    | -0.74  | 0.37     |
| $(02^2)$      | $e$      | -5.69   | 0.17   | 0.84     |
| $(11^1)$      | $e$      | -0.61   | 0.82   | 1.68     |
| $(20^0)$      | $a_1$    | -0.11   | -0.04  | 1.26     |
| $(03^1)$      | $e$      | -4.46   | -2.05  | -1.19    |
| $(03^3)$      | $a_1$    | 3.18    | -1.23  | -0.34    |
| $(03^3)$      | $a_2$    | 2.44    | 0.61   | -0.33    |
| $(12^0)$      | $a_1$    | 0.66    | 1.90   | -0.01    |
| $(12^2)$      | $e$      | -5.0    | -1.36  | 0.34     |
| $(21^1)$      | $e$      | 4.07    | 0.79   | -0.19    |
| $(30^0)$      | $a_1$    | -1.23   | -1.66  | -2.06    |

|       | rms      | 3.6     | 0.98   | 1.10     |
| Number of Parameters | 8 4 4 |