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Dynamical chains for molecular tops. II. Applications in molecular spectroscopy

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Résumé. — On montre comment la formulation algébrique de la dynamique rotationnelle, établie en I, peut être utilisée en spectroscopie moléculaire. On considère plus particulièrement les opérateurs scalaires dans G, où G est isomorphe au groupe ponctuel moléculaire, et qui sont associés aux Hamiltoniens effectifs purement rotationnels. Une représentation, en fonction de coordonnées, de l'algèbre dynamique est donnée, ce qui permet de comparer notre approche avec des études antérieures.

Abstract. — It is shown how the algebraic formulation of rotational dynamics, given in part I, may be used in molecular spectroscopy. Special emphasis is placed on scalar operators in G, where G is isomorphic to the molecular point group, and which are associated with pure rotational effective Hamiltonians. A coordinate representation of the dynamical algebra is given which allows us to compare our approach with previous studies.

1. Introduction.

In a previous paper [1] (hereafter referred to as I) we proposed an algebraic treatment of molecular rotational dynamics from the SU(4) compact dynamic algebra. This algebra and the appropriate irreducible representation (IR) Γ_D were found from the known SO(4) degeneracy algebra and standard branching rules. Next we built all the operators having non-zero matrix elements within Γ_D, which may thus describe any rotational operator involved in a molecular Hamiltonian. These operators, which are all realized in terms of boson operators are denoted :

$$\mathbf{R}^{(\Omega 0 \Omega)\, r(j_1, j_2)} \tag{1}$$

where $(\Omega 0 \Omega)$ and (j_1, j_2) are the SU(4) and SO(4) labels respectively ; r is a multiplicity index. Ω is also the degree with regard to the SU(4) generators.

We will show here how these results obtained through purely algebraic methods can be used in molecular spectroscopy. At first, if the model is adequate, the usual zero-order spectrum must be reproduced when only the first invariants of each element in the dynamical

chain are retained [2, 3]. This is shown to be the case for each type of molecular tops. Also the special case of scalar operators in G, where G is isomorphic to the molecular point group, and which are associated with pure rotational effective Hamiltonians is considered. But as we use a compact dynamical algebra, and thus represent systems will a finite number of bound states, we cannot entirely reproduce the ideal rigid tops : these are known to have a representation space of infinite dimension and their energy increases indefinitely with increasing excitation. A coordinate representation of the SU(4) algebra will serve to illustrate the difference between the ideal system and the molecular model we built and to correlate our approach with previous studies.

More generally, it is obvious that the ideal systems (harmonic oscillators, rigid tops) introduced as zero order approximation, which give an infinite number of states whose energy tends to infinity are no longer valid beyond the dissociation limit. The problem is to find a model which allows us to go in a reasonable way, as close as possible to the dissociation limit. For instance, for the vibrational problem, the local mode theory [4] replaces the harmonic oscillators by Morse oscillators, for which a rigorous treatment through a compact dynamical algebra [3, 5, 6] is possible. In this respect we believe our approach to be more « physical » and that the introduction of a model whose highest energy is finite is more appropriate for studies of molecules near the dissociation limit.

Throughout equations of (I) will be denoted (I, x).

2. Spherical tops.

2.1 ZERO ORDER ROTATIONAL HAMILTONIAN. — In this class, we find molecules with two or more symmetry axes of order greater than two. In a given vibrational state, the zero order rotational Hamiltonian is that of a rigid spherical top and may be written in our formalism with the concept of dynamical symmetry [2]. Within this approximation the dynamical algebra is that used so far :

$$\mathrm{SU}(4) \supset \mathrm{SU}(2) \oplus \mathrm{SU}(2) \approx \mathrm{SO}(4) .$$

The SU(4) invariants being constant within a given IR, the Hamiltonian may be written as :

$$\mathbf{H}_0 = A\mathbf{I} + B\mathbf{C}_2(\mathrm{SO}(4)) \tag{2}$$

where $\mathbf{C}_2(\mathrm{SO}(4))$ is the second order Casimir operator (Eq. (I.31)), or in terms of elementary factors (Eq. (I.32)) :

$$\mathbf{H}_0 = A'\,\mathbf{I} + B'\,(2\dot{0}\,;00)(\dot{0}2\,;00)\,. \tag{3}$$

In equations (2, 3) $\mathbf{I}$ is the identity operator and A, B, A', B' are constants. The corresponding eigenvalues within the symmetry adapted bases of (I) are respectively given by :

$$E_0 = A + BJ(J+1) = A' + B'\left[\frac{N}{2}\left(\frac{N}{2}+1\right) - J(J+1)\right]. \tag{4}$$

Identification with the usual formulas give :

$$A = 0 \quad B = B_e$$

where $B_e = \hbar^2/2\,hcI_e$ is the rotational constant [7] ; likewise

$$B' = -B_e \quad A' = B_e \frac{N}{2}\left(\frac{N}{2}+1\right) = B_e J_{\max}(J_{\max}+1)\,. \tag{5}$$

Although the two forms are equivalent, the second has the advantage to put into evidence the correlation which exists between the magnitude of the rotational B_e value and the number of top levels which are observed in actual systems.

In order to make the comparison between our algebraic approach and the conventional treatment of rotational dynamics easier, we give in section 4 the realization of the SU(4) algebra in the usual coordinate representation involving the Euler angles. But, without this, we may already find a physical significance to the ladder generators $\mathbf{M}^{(101)(1,1)}$ (Eq. (I.23g-k)). The dynamical algebra we use and the IR chosen, span the $N/2$ first levels of a spherical top, where N may be given any even value ; the ladder generators allow to go through the entire spectrum but also verify :

$$\mathbf{M}^{(101)}{}^{(1,\,1)}_{1\;\;1}\left|\,[\mathrm{N0}]\left\{\frac{N}{2}\right\}\right\rangle = 0 \tag{6}$$

since the spectrum is finite. In fact, an ideal top has an infinite set of levels and one may look for a non-compact algebra [8], which contains SO(4) as a subalgebra, to account for this infinite set of levels. Another way is to let N go to very large values ; we then find that within this limit :

$$\frac{1}{N}\,([\mathrm{N0}]\,J'\,J'\,\|\mathbf{M}^{(101)(1,1)}\|\,[\mathrm{N0}]\,JJ) \sim \frac{1}{2\sqrt{3}}\,(J'\,J'\,\|\mathbf{D}^{(1,1)}\|JJ) \tag{7}$$

where the double tensors **D** [9, 10] are proportional to the direction cosines which relate MFF to SFF, and may also be seen as « ladder » operators for the top. It is also verified that the operators $(1/\mathrm{N})\,\mathbf{M}^{(101)(1,1)}$ (N large) and $\mathbf{D}^{(1,1)}$ satisfy the same commutation relations with angular momentum operators (Eq. (I.25d-e)) ; within this same limit, we find that (Eq. (I.25f)) :

$$\left[\frac{1}{N}\mathbf{M}^{(101)}{}^{(1,\,1)}_{m\;\;m'},\frac{1}{N}\mathbf{M}^{(101)}{}^{(1,\,1)}_{q\;\;q'}\right] \underset{N\to\infty}{\to} 0 \tag{8}$$

as is usual for direction cosines. Moreover, it appears that a consistent scheme is obtained if one chooses all phase factors $e^{i\theta_{N,J}}$, introduced in I, equal to unity.

2.2 INTRODUCTION OF PARITY. — As is usual the dynamical algebra considered so far does not include the discrete operation of parity **P** associated with space inversion [2]. Within our interpretation the space fixed frame and molecular frame are not independent ; the Euler angles are defined for two frames with identical orientation. So we have in fact only one such operation to consider and when this is done the algebra usually splits into two parts corresponding to the positive and negative eigenvalues of this order two operation ; we have the so-called extension by parity of the dynamical algebra [2, 11, 12].

For our problem, the angular momentum operators **L** and $\boldsymbol{\ell}$ verify :

$$[P, \mathbf{L}] = [P, \boldsymbol{\ell}] = 0$$

i.e., they are even with regard to **P**. But with the ladder generators $\mathbf{M}^{(101)(1,1)}$ are now associated two inequivalent tensors, which we denote temporarily by $\mathbf{M}_+$ and $\mathbf{M}_-$, which are respectively even and odd with regard to **P**. Likewise two inequivalent sets are associated with the kets $|\psi\rangle$ previously defined :

$$\begin{aligned} |\psi\rangle_\pm &= |\Pi_\pm\rangle\,|\psi\rangle \\ \mathbf{P}_\pm\,|\psi\rangle_\pm &= \pm\,|\psi\rangle_\pm\,. \end{aligned} \tag{9}$$

From the point of view of groups, the introduction of parity lead us, using the local isomorphism of SU(2) × SU(2) with SO(3) × SO(3), to the Hamiltonian (geometrical) invariance group O(3) × O(3). Likewise using the isomorphism SU(4) ≃ SO(6), we get the group O(6) ; the IR of O(6) appropriate to the description of the top levels is then the self-associate [13, 14] representation $[N/2\,N/2\,N/2]$ which reduces in O(3) × O(3) :

$$\left[\frac{N}{2}\frac{N}{2}\frac{N}{2}\right]_{\mathrm{O}(6)} = \sum_{\substack{J=0\\ \alpha=+,-}}^{\frac{N}{2}} (J_\alpha, J_\alpha) \quad (N \text{ even})\,. \tag{10}$$

Alternatively, we have

$$\left[\frac{N}{2}\frac{N}{2}\frac{N}{2}\right]_{\mathrm{O}(6)} = \left[\frac{N}{2}\frac{N}{2}\frac{N}{2}\right]_{\mathrm{SO}(6)} + \left[\frac{N}{2}\frac{N}{2}-\frac{N}{2}\right]_{\mathrm{SO}(6)} = [\mathrm{N}\dot{0}]_{\mathrm{SU}(4)} + \widetilde{[\mathrm{N}\dot{0}]}_{\mathrm{SU}(4)} \tag{11}$$

which shows that we have the appropriate symmetries and degeneracy for the levels and allows us to readily extend all the previous results to the chain :

$$\mathrm{O}(6) \supset {}^{L}\mathrm{O}(3) \times {}^{M}\mathrm{O}(3) \tag{12}$$

where O(6) is a dynamical group for the spherical top. Usually, parity labels for spherical tops are denoted by u and g [15, 16, 17] ; also to simplify the notation, we shall keep the SU(4) labels for the kets, that is we set :

$$\left|\left[\frac{N}{2}\frac{N}{2}\frac{N}{2}\right] J_\alpha\, M, J_\alpha\, K\right\rangle \equiv |\,[\mathrm{N}0]\, J_\alpha\, M, J_\alpha\, K\rangle\, \alpha = u, g\,. \tag{13}$$

Likewise for tensors acting within these states one may use the notation :

$$\mathbf{R}_\varepsilon^{(\Omega 0 \Omega)\, r(j_{1\alpha}, j_{2\alpha})}\,. \tag{14}$$

With these conventions, all the necessary matrix elements are obtained from those given in (I) by adding parity indices following standard rules :

$$\begin{aligned} \Delta(u, u, g) &= \Delta(g, g, g) = 1\,; \\ \Delta(u, u, u) &= \Delta(u, g, g) = 0\,. \end{aligned} \tag{15}$$

Even operators may appear in the expansion of effective rovibrational, hyperfine and Zeeman Hamiltonians as well as in those of effective transition operators (polarizability tensor, ...) ; odd operators arise only if Stark Hamiltonians are considered and in effective transition operators (dipole moment, hyperpolarizability, tensor, etc.) (see § 2.3).

2.3 INTEGRITY BASIS FOR SUBGROUP SCALARS. SYMMETRY ADAPTED KETS. — Obviously, in most practical applications one must go beyond the zero order approximation of section 2.1

and account must be taken of centrifugal distortion, vibration-rotation, spin-rotation... interactions. The generalization of the present approach will be described elsewhere ; for the time being, it is sufficient to note that it implies that the O(3) × O(3) symmetry is broken and that non-Casimir rotational operators are to be dealt with.

The invariance group G for a semi-rigid polyatomic molecule in a non degenerate electronic state is usually isomorphic to the molecular point group. For the chain :

$$^{L}\mathrm{O}(3) \times {}^{M}\mathrm{O}(3) \supset {}^{L}\mathrm{O}(3) \times G$$

there is one missing label, so we may find at most two functionally independent subgroup scalars in the $^{M}\mathrm{O}(3)$ enveloping algebra to solve the missing label problem. These have been computed for any group G in [18]. For most common spherical tops where G is a cubic group, the integrity basis is given in our notation by :

$$\mathbf{R}^{(404)\,(0,\,4)}_{A_1} \quad \text{and} \quad \mathbf{R}^{(606)\,(0,\,6)}_{A_1}\,. \tag{16}$$

The normal cubic basis [17] is nothing but that particular basis which diagonalizes the rotational operator $\mathbf{R}^{(404)\,(0,\,4)}_{A_1}$.

Covariant cubic states are obtained, in our formalism, from those determined in (I) by the same transformation :

$$|\,[\mathrm{N}0]\,J_\alpha\,M, J_\alpha\,p\rangle = \sum_K {}^{(J_\alpha)}G^K_p\,|\,[\mathrm{N}0]\,J_\alpha\,M, J_\alpha\,K\rangle \tag{17}$$

where p is a cubic index $p = (n, C, \sigma)$.

Likewise any symmetry adapted tensor is given by :

$$\mathbf{R}^{(\Omega 0 \Omega)\,r\,(j_{1\alpha},\,j_{2\alpha})}_{\varepsilon\;\;m_1\;\;p} = \sum_{m_2} {}^{(j_{2\alpha})}G^{m_2}_p\,\mathbf{R}^{(\Omega 0 \Omega)\,(j_{1\alpha},\,j_{2\alpha})}_{\varepsilon\;\;m_1\;\;m_2} \tag{18}$$

and its matrix elements computed with the equations gathered in the appendix of (I).

Rotational operators used so far in rovibrational Hamiltonian [19, 20] are built with the coupling scheme introduced by Moret-Bailly [19] :

$$\begin{aligned} \mathbf{R}^{\Omega(0,K)} &= [\mathbf{R}^{\Omega - K(0,0)} \times \mathbf{R}^{K(0,K)}]^{(0,K)} \\ &= [\mathbf{R}^{2(0,0)}]^{\frac{\Omega - K}{2}}\,\mathbf{R}^{K(0,K)}\,. \end{aligned} \tag{19}$$

The connection with our formalism can be seen with the following relations (§ 3.5, Eq. (I.46)) :

$$\begin{aligned} \mathbf{R}^{2(0,0)} &= -\frac{1}{\sqrt{3}}\mathbf{J}^2 \\ \mathbf{R}^{K(0,K)} &= [\ell^{(0,1)} \times \ell^{(0,1)}]^{(0,2)} \times \cdots \times [\ell^{(0,1)}]^{(0,K)} \quad K \text{ factors} \end{aligned} \tag{20}$$

That is $\mathbf{R}^{2(0,0)}$ is proportional to the $^{M}\mathrm{O}(3)$ Casimir operator and $\mathbf{R}^{K(0,K)}$ is the « streched » tensor product of the $^{M}\mathrm{O}(3)$ fundamental tensor $\ell^{(0,1)}$:

$$(101\,;\,01)^K \equiv \mathbf{R}^{K(\,0,\,K)}_{\;\;0\;\;K}\,. \tag{21}$$

The operators (19) are thus all functionally independent rotational tensors in the enveloping algebra of $^{M}\mathrm{O}(3)$ [2], which are $^{L}\mathrm{O}(3)$ scalars.

Our method, besides that it clearly establishes the connection between the physical approach used so far [19, 20] and the theory of elementary multiplets and integrity basis, extend these results to all rotational tensors (i.e. which are not ${}^{L}\mathrm{O}(3)$ scalars) which are involved in more general molecular Hamiltonians [16, 21, 22] and in transition operators [23, 24].

3. Symmetric and asymmetric tops.

We shall only briefly outline how these tops can be treated within our formalism, since the same procedure as that used for spherical tops can be applied, although this has not been greatly used so far.

3.1 SYMMETRIC TOPS. — These tops are encountered in molecules which possess one symmetry axis of order greater or equal to three. Hence from the point of view of dynamical algebra, we have the chain :

$$\mathrm{SU}(4) \supset \mathrm{SU}(2) \oplus \mathrm{SU}(2) \supset \mathrm{SU}(2) \oplus \mathrm{SO}(2) \tag{22}$$

where the SO(2) generator is given by equation (I.23d). All the results are readily obtained from previous computations since all the tensors and kets are already symmetrized in SO(2) $\oplus$ SO(2).

The zero order rotational Hamiltonian may then be written :

$$\mathbf{H}_0 = A\mathbf{I} + B\mathfrak{C}_2(\mathrm{SO}(4)) + C\mathfrak{C}_2(\mathrm{SO}(2)) \tag{23a}$$

or

$$\mathbf{H}_0 = A'\,\mathbf{I} + B'(2\dot{0}\,;00)\,(\dot{0}2\,;00) + C'\,\mathbf{R}^{(202)\left(\begin{smallmatrix}0, & 2\\ 0 & 0\end{smallmatrix}\right)} \tag{23b}$$

where $\mathfrak{C}_2(\mathrm{SO}(2))$ is the SO(2) Casimir operator related to $\mathbf{R}^{(202)\left(\begin{smallmatrix}0, & 2\\ 0 & 0\end{smallmatrix}\right)}$ by :

$$\mathbf{R}^{(202)\left(\begin{smallmatrix}0, & 2\\ 0 & 0\end{smallmatrix}\right)} = \frac{1}{\sqrt{6}}\,(3\,\mathbf{J}_z^2 - \mathbf{J}^2) = \frac{1}{\sqrt{6}}\,[3\,\mathfrak{C}_2(\mathrm{SO}(2)) - \mathbf{J}^2]\,. \tag{24}$$

The eigenvalues within the symmetry adapted bases of (I) are :

$$\begin{aligned} E_0 &= A + BJ(J+1) + CK^2 \\ &= A' + B'\left[\frac{N}{2}\left(\frac{N}{2}+1\right) - J(J+1)\right] + \frac{C'}{\sqrt{6}}\,[3\,K^2 - J(J+1)] \end{aligned} \tag{25}$$

which can readily be identified with the usual rotational energies [7] :

$$E_0 = B_e\,J(J+1) + \begin{cases} (A_e - B_e)\,K^2 \text{ for a prolate top} \\ -\,(B_e - C_e)\,K^2 \text{ for an oblate top}\,. \end{cases} \tag{26}$$

In actual molecules from the point of view of groups, we have the chain :

$$\mathrm{O}(6) \supset {}^{L}\mathrm{O}(3) \times {}^{M}\mathrm{O}(3) \supset {}^{L}\mathrm{O}(3) \times D_{\infty h} \supset {}^{L}\mathrm{O}(3) \times G \tag{27}$$

where G is isomorphic to the molecular point group. The missing label problem for the reduction ${}^{M}\mathrm{O}(3) \downarrow G$ could be solved, as for spherical tops, by the diagonalization of an

appropriate subgroup scalar. The integrity basis for subgroups scalars for any subgroup G is given in [18] ; for instance for $G = C_3$, we have with our notation :

$$\begin{aligned} \mathfrak{O}_1 &= \ell^{(101)}{}_{0\,0}^{(0,\,1)} = -\,\ell_z = \mathbf{J}_z \\ \mathfrak{O}_2 &= (101\,;01)^3 + (101\,;01)^{3+} = \frac{1}{2\sqrt{2}}\,(\ell_+^3 + \ell_-^3) \end{aligned} \tag{28}$$

from which a generating function for subgroup scalars may be written down [2]. When the transformation to a basis symmetry adapted to G is known, i.e. when the appropriate subgroup scalar has been diagonalized, symmetry adapted coupling symbols can be computed and the matrix elements of any tensor (Eq. (14)) in the enveloping algebra are obtained with the equations given in the appendix of (I).

3.2 ASYMMETRIC TOPS. — In this case, symmetry axes are of order two at most and the SU(2) symmetry is broken to the discrete subgroup D_2, hence the chain :

$$\mathrm{SU}(4) \supset \mathrm{SU}(2) \oplus \mathrm{SU}(2) \supset \mathrm{SU}(2) \oplus D_2\,. \tag{29}$$

Within the same order of approximation, the Hamiltonian for the rigid asymmetric top is written :

$$\mathbf{H}_0 = A\mathbf{I} + B\mathfrak{C}_2(\mathrm{SO}(4)) + C\mathfrak{C}_2(\mathrm{SO}(2)) + D[\mathbf{R}^{(202)}{}_{0\,2}^{(0,\,2)} + \mathbf{R}^{(202)}{}_{0\,-2}^{(0,\,2)}] \tag{30a}$$

or

$$\mathbf{H}_0 = A'\,\mathbf{I} + B'\,(2\dot{0}\,;00)(\dot{0}2\,;00) + C'\,\mathbf{R}^{(202)}{}_{0\,0}^{(0,\,2)} + D'[(101\,;01)^2 + (101\,;01)^{2+}] \tag{30b}$$

with

$$(101\,;01)^2 + (101\,;01)^{2+} = \frac{1}{2}\,(\ell_-^2 + \ell_+^2)\,. \tag{31}$$

For a given asymmetric top, the correlation between the constants appearing in equation (30a-b) with the usual rotational A_e, B_e, C_e constants [7] is easily obtained with equations (I.31) and (24, 31) ; depending on the choice of the inertia axis which is identified with the z axis of MFF one goes from a I^r (prolate top) to a III^r (oblate top) convention.

For a molecular top, we find the group chain :

$$\mathrm{O}(6) \supset {}^L\mathrm{O}(3) \times {}^M\mathrm{O}(3) \supset {}^L\mathrm{O}(3) \times D_{\infty h} \supset {}^L\mathrm{O}(3) \times G \tag{32}$$

where G is usually one of the groups D_{2h}, D_2, C_{2v}, C_{2h}, S_2 or C_2.

To solve the missing label problem for the reduction ${}^M\mathrm{O}(3) \supset G$ one may proceed, as previously, with the determination of the integrity basis for subgroup scalars and the diagonalization of the scalar operator appropriate to the top under study.

For instance, for $G = D_2$, the integrity basis is given by :

$$\begin{aligned} \mathfrak{O}_1 &= \mathbf{R}^{(202)}{}_{0\,0}^{(0,\,2)} = \ell_z^2 \\ \mathfrak{O}_2 &= (101\,;01)^2 + (101\,;01)^{2+} \\ &= \frac{1}{2}\,(\ell_+^2 + \ell_-^2)\,. \end{aligned} \tag{33}$$

All subgroup scalars may be extracted from a term (Eq. (I.17)) :

$$(2\dot{0}\,;00)^b\ (\dot{0}2\,;00)^b\ (101\,;01)^f\,. \tag{34}$$

Time reversal invariance imposes $\Omega = 2\,b + f$ even ; taking into account hermicity conditions we obtain a general totally symmetric D_2 operator :

$$\mathbf{H}(J) = \sum_{\substack{b,f,m\\ m\,\text{even}}} c_{b,f,m}(2\dot{0}\,;00)^b\ (\dot{0}2\,;00)^b[\mathbf{R}^{(f0f)}\,{}^{(0,\,f)}_{0\ \ m} + \mathbf{R}^{(f0f)}\,{}^{(0,\,f)}_{0\ -m}]\,. \tag{35}$$

Using previous results (Eqs. (I.23), (I.31)), the preceding generating function may be converted to the standard notation [25] :

$$\mathbf{H}(J) = \sum_{\ell,p,q} A_{1pq}\,\mathbf{J}^{2\ell}\,\{\ell_z^{2p}[\ell_+^{2q} + \ell_-^{2q}]\} = \sum_{\ell pq} \mathbf{H}_{\ell pq}(J) \tag{36}$$

where we set $\{\mathbf{R}_1\,\mathbf{R}_2\} = \mathbf{R}_1\,\mathbf{R}_2 + \mathbf{R}_2\,\mathbf{R}_1$.

Usually Wang basis functions [7] which are symmetry adapted to D_2 are introduced ; in our notation, these are given by :

$$\begin{aligned} |\,[\mathrm{N}0]\,JM\,;J0\rangle_+ &= |\,[\mathrm{N}0]\,JM, J0\rangle \\ |\,[\mathrm{N}0]\,JM\,;JK\rangle_\pm &= \frac{1}{\sqrt{2}}\,\{|\,[\mathrm{N}0]\,JM, JK\rangle \pm |\,[\mathrm{N}0]\,JM, J-K\rangle\} \quad K>0 \end{aligned} \tag{37}$$

and the subgroup scalar which is diagonalized is the Hamiltonian operator H_{010} (Eqs. (36, 33)) although another operator has been proposed [18].

Also the present approach could be generalized to introduce non polynomial expansion of Hamiltonian operators.

4. Correlation with previous treatments of rotational dynamics.

One of the advantages of the algebraic formulation is that it allows a group theoretical treatment and we are free of any explicit coordinate representation. Once the appropriate dynamical algebra is found and realized in terms of boson operators, all the results are obtained with standard techniques. More precisely, a model is built from what is actually observed ; the physical significance of this algebraic model may be specified or not. Incidentally one may note that several « physical interpretations » may be inferred from a given set of observations.

In order to correlate our approach with conventional treatments of rotational dynamics, we give a coordinate representation of the SU(4) algebra. This will also serve to illustrate the difference between the ideal rigid top usually considered and the molecular model we build.

4.1 COORDINATE REPRESENTATION OF THE SU(4) ALGEBRA. — The appropriate realization of the SU(4) algebra is easily obtained if one starts from the parametrization of the four dimensional sphere in terms of Euler's angles given by Judd [9] :

$$\begin{aligned} x_1 &= r\sin\beta/2\sin\,(\alpha-\gamma)/2 \\ x_2 &= -\,r\sin\beta/2\cos\,(\alpha-\gamma)/2 \\ x_3 &= -\,r\cos\beta/2\sin\,(\alpha+\gamma)/2 \\ x_4 &= r\cos\beta/2\cos\,(\alpha+\gamma)/2\,. \end{aligned} \tag{38}$$

The boson operators $\mathbf{a}_i^+$, $\mathbf{a}_i$ are thus realized as differential operators in a four dimensional harmonic oscillator space [26, 27]. That is, the set of operator equations :

$$\begin{aligned}
\mathbf{N}\,|\,[\mathrm{N0}]\,JM, JK\rangle &= N\,|\,[\mathrm{N0}]\,JM, JK\rangle \\
\mathbf{J}^2\,|\,[\mathrm{N0}]\,JM, JK\rangle &= J(J+1)\,|\,[\mathrm{N0}]\,JM, JK\rangle \\
\mathbf{J}_Z\,|\,[\mathrm{N0}]\,JM, JK\rangle &= M\,|\,[\mathrm{N0}]\,JM, JK\rangle \\
\mathbf{J}_z\,|\,[\mathrm{N0}]\,JM, JK\rangle &= K\,|\,[\mathrm{N0}]\,JM, JK\rangle\ .
\end{aligned} \tag{39}$$

in the Hilbert space spanned by the eigenkets $\{\,|\,[\mathrm{N0}]\,JM, JK\rangle\}$ is replaced by the set of partial differential equations :

$$\begin{aligned}
\mathbf{N}\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle &= N\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle \\
\mathbf{J}^2\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle &= J(J+1)\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle \\
\mathbf{J}_Z\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle &= M\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle \\
\mathbf{J}_z\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle &= K\,\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle\ .
\end{aligned} \tag{40}$$

Straightforward computations lead to :

$$\begin{aligned}
\mathbf{a}_1^+ &= \mathrm{e}^{i(\alpha+\gamma)/2}\left\{\frac{r}{2}\cos\frac{\beta}{2} - \frac{i}{2\,r\cos\beta/2}\left(\frac{\partial}{\partial\alpha}+\frac{\partial}{\partial\gamma}\right) + \frac{1}{r}\sin\frac{\beta}{2}\frac{\partial}{\partial\beta} - \frac{1}{2}\cos\frac{\beta}{2}\frac{\partial}{\partial r}\right\} \\
\mathbf{a}_2^+ &= \mathrm{e}^{i(\alpha-\gamma)/2}\left\{-\frac{r}{2}\sin\frac{\beta}{2} - \frac{i}{2\,r\sin\beta/2}\left(-\frac{\partial}{\partial\alpha}+\frac{\partial}{\partial\gamma}\right) + \frac{1}{r}\cos\frac{\beta}{2}\frac{\partial}{\partial\beta} + \frac{1}{2}\sin\frac{\beta}{2}\frac{\partial}{\partial r}\right\} \\
\mathbf{a}_3^+ &= \mathrm{e}^{-i(\alpha-\gamma)/2}\left\{-\frac{r}{2}\sin\frac{\beta}{2} - \frac{i}{2\,r\sin\beta/2}\left(\frac{\partial}{\partial\alpha}-\frac{\partial}{\partial\gamma}\right) + \frac{1}{r}\cos\frac{\beta}{2}\frac{\partial}{\partial\beta} + \frac{1}{2}\sin\frac{\beta}{2}\frac{\partial}{\partial r}\right\} \\
\mathbf{a}_4^+ &= \mathrm{e}^{-i(\alpha+\gamma)/2}\left\{\frac{r}{2}\cos\frac{\beta}{2} + \frac{i}{2\,r\cos\beta/2}\left(\frac{\partial}{\partial\alpha}+\frac{\partial}{\partial\gamma}\right) + \frac{1}{r}\sin\frac{\beta}{2}\frac{\partial}{\partial\beta} - \frac{1}{2}\cos\frac{\beta}{2}\frac{\partial}{\partial r}\right\}\ .
\end{aligned} \tag{41}$$

The corresponding expressions for the annihilation operators can be obtained with the substitutions :

$$i \to -i \qquad \frac{\partial}{\partial q} \to -\frac{\partial}{\partial q} \qquad q : \alpha, \beta, \gamma, r\ . \tag{42}$$

From these, the expressions for the SU(4) generators (Eq. (I.23)), and of any operator (Eq. (I.13), Tab. I.2), can be determined. In particular, we have for the operators in equation (40) :

$$\begin{aligned}
\mathbf{N} &= -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{3}{2\,r}\frac{\partial}{\partial r} + \frac{2\,\mathbf{J}^2}{r^2} + \frac{r^2}{2} - 2 \\
\mathbf{J}^2 &= -\left\{\frac{1}{\sin^2\beta}\left[\frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\gamma^2} - 2\cos\beta\,\frac{\partial^2}{\partial\alpha\,\partial\gamma}\right] + \frac{\partial^2}{\partial\beta^2} + \operatorname{cotg}\beta\,\frac{\partial}{\partial\beta}\right\} \\
\mathbf{J}_Z &= \frac{1}{i}\frac{\partial}{\partial\alpha}\ ; \quad \mathbf{J}_z = i\,\frac{\partial}{\partial\gamma}\ .
\end{aligned} \tag{43}$$

These equations show first that, as expected, the well-known expressions [9, 28] for the SO(4) generators are recovered ; secondly equations (40) are separable and have solutions of the form :

$$\langle r, \alpha, \beta, \gamma\,|\,[\mathrm{N0}]\,JM, JK\rangle = A_{\mathrm{N},J}\,F_{\mathrm{N},J}(r)\,\psi_{M\,K}^{(J,\,J)}(\alpha, \beta, \gamma) \tag{44}$$

where $A_{N,J}$ is a normalization factor and where the angular functions are the usual symmetric top eigenfunctions [9, 10, 28] :

$$\psi_{M\ K}^{(J,\ J)} = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} \mathfrak{D}_{M\ K}^{(J)\ *}(\alpha, \beta, \gamma) . \tag{45}$$

The radial functions $F_{N,J}(r)$ are then the solutions of (Eqs. (40), (43)) :

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{3}{2r}\frac{\partial}{\partial r} + \frac{r^2}{2} + \frac{2J(J+1)}{r^2} - 2\right] F_{N,J}(r) = N F_{N,J}(r) \tag{46}$$

which are given by :

$$F_{N,J}(r) = r^{2J} e^{-r^2/2} L_{N/2-J}^{2J+1}(r^2) \tag{47}$$

where L is a Laguerre polynomial [27, 29].

4.2 CORRELATION WITH PREVIOUS TREATMENTS OF TOPS. — The preceding results imply that any operator involving only powers of the SO(4) generators (Eqs. (I.23a-f)) can be expressed in terms of the usual rotational operators referred to SFF or MFF. To find the physical meaning of the other operators we built, one must remember that the algebraic model introduced is that of a system with a finite (but arbitrary) number of bound states ; for a given N, the maximum J value is $N/2$. The equivalence of these operators with known quantities will thus be obtained in the limit N large corresponding to the ideal top. To check this, the easiest way is through the computation of matrix elements. We shall only consider two examples, the first being the important case of the ladder generators (Eqs. (I.23g-k)).

Equation (I.A.10) with $\Omega = 1$, $a = c = 1$ (or Eq. (I.44)) gives :

$$([N0]\,J'\,J' \,\|\mathbf{M}^{(101)(1,1)}\|\, [N0]\,JJ) =$$

$$= \begin{cases} \left[\left(\frac{N}{2} - J\right)\left(\frac{N}{2} + J + 2\right)(2J+1)(2J+3)\right]^{1/2} & J' = J+1 \\ -\left(\frac{N}{2}+1\right)(2J+1) & J' = J \\ \left[\left(\frac{N}{2} - J + 1\right)\left(\frac{N}{2} + J + 1\right)(2J-1)(2J+3)\right]^{1/2} & J' = J-1 . \end{cases} \tag{48}$$

So that in the limit N large we find [9, 22] :

$$\frac{1}{N}\mathbf{M}^{(101)(1,1)} \sim \frac{1}{2\sqrt{3}}\mathbf{D}^{(1,1)} \tag{49}$$

where the double tensors $\mathbf{D}^{(1,1)}$ are, with our phase conventions, defined by [10] :

$$\mathbf{D}_{m\ m'}^{(1,\ 1)} = \sqrt{3}\,\mathfrak{D}_{m\ m'}^{(1)\ *}(\alpha, \beta, \gamma) .$$

The correlation with other double-tensors $\mathbf{D}^{(j,j)}$ could be extended as well. The other example we shall consider is that of the J raising and lowering operators introduced by Shaffer *et al.* [30] :

$$\mathbf{\Omega}_{\pm}(J)\,\psi_{M\ K}^{(J,\ J)} = \mathcal{N}_{\pm}(J, M, K)\,\psi_{M\ K}^{(J\pm 1,\ J\pm 1)} . \tag{50}$$

From the rotational operators we defined in (I) we may build two operators $\mathbf{R}_{\pm}(N, J)$ such that :

$$\mathbf{R}_{\pm}(N, J)\,|\,[\mathrm{N0}]\,J \pm 1\, M, J \pm 1\, K\rangle = \mathfrak{L}_{\pm}(N, J, M, K)\,|\,[\mathrm{N0}]\,J \pm 1\, M, J \pm 1\, K\rangle\,. \tag{51}$$

These are given by :

$$\begin{aligned}\mathbf{R}_{\pm} = x_{\pm}\,\mathbf{M}^{(101)}{}^{(1,\,1)}_{0\;\;0} + y_{\pm}\left\{\frac{1}{2}\left(\mathbf{T}^{(202)1}{}^{(1,\,1)}_{0\;\;0} - \mathbf{T}^{(202)2}{}^{(1,\,1)}_{0\;\;0}\right) - \mathbf{M}^{(101)}{}^{(1,\,1)}_{0\;\;0}\right\}\\ + z_{\pm}\left\{\frac{1}{2}\left(\mathbf{T}^{(202)1}{}^{(1,\,1)}_{0\;\;0} + \mathbf{T}^{(202)2}{}^{(1,\,1)}_{0\;\;0}\right) - \frac{N}{2}\,\mathbf{M}^{(101)}{}^{(1,\,1)}_{0\;\;0}\right\}\end{aligned} \tag{52}$$

where

$$\begin{aligned} x_{+} &= J+1\,; \quad y_{+} = 1\,; \quad z_{+} = \frac{N/2+1}{J+1}\\ x_{-} &= J\,; \quad y_{-} = -1\,; \quad z_{-} = \frac{N/2+1}{J+1}\,.\end{aligned} \tag{53}$$

The tensor operators appearing in (52) are defined by equations (I.10), (I.13), (I.16) and in table I.2 ; $\mathbf{R}_{\pm}$ have been written so as put into evidence the correlation with the corresponding operators in the expressions for $\mathbf{\Omega}_{\pm}$ of Shaeffer *et al.* (Eqs. (5a-b) of [30]) ; in the limit N large :

$$\frac{1}{N/2+1}\,\mathbf{M}^{(101)}{}^{(1,\,1)}_{0\;\;0} \sim \cos\beta \tag{54a}$$

$$\frac{1}{N/2+1}\left\{\frac{1}{2}\left(\mathbf{T}^{(202)1}{}^{(1,\,1)}_{0\;\;0} - \mathbf{T}^{(202)2}{}^{(1,\,1)}_{0\;\;0}\right) - \mathbf{M}^{(101)}{}^{(1,\,1)}_{0\;\;0}\right\} \sim \sin\beta\,\frac{\partial}{\partial\beta} \tag{54b}$$

$$\left\{\frac{1}{2}\left(\mathbf{T}^{(202)1}{}^{(1,\,1)}_{0\;\;0} + \mathbf{T}^{(202)2}{}^{(1,\,1)}_{0\;\;0}\right) - \frac{N}{2}\,\mathbf{M}^{(101)}{}^{(1,\,1)}_{0\;\;0}\right\} \tag{54}$$

$$= -\,\mathbf{L}^{(101)}{}^{(1,\,0)}_{0\;\;0}\,\boldsymbol{\ell}^{(101)}{}^{(0,\,1)}_{0\;\;0} = -\,\mathbf{J}_Z\,\mathbf{J}_z \tag{54c}$$

so that : $\dfrac{1}{N/2+1}\,\mathbf{R}_{\pm} \sim \mathbf{\Omega}_{\pm}$.

In fact we may note that equation (54c) holds strictly for any N value since it involves only SO(4) generators (Eq. (43)) ; also the exact values for the matrix elements of $R_{\pm}$ (Eq. (52)), computed with the expressions given in the appendix of (I), may be written :

$$\mathfrak{L}_{\pm}(N, J, M, K) = \mathcal{N}_{\pm}(J, M, K)\left[\left(\frac{N}{2}+1\right)^2 - (J+\varepsilon_{\pm})^2\right]^{1/2} \tag{55}$$

with $\varepsilon_{+} = 1$, $\varepsilon_{-} = 0$ and where the coefficients $\mathcal{N}_{\pm}$ (Eq. (50)) are the matrix elements of $\mathbf{\Omega}_{\pm}$ in the standard symmetric top basis (Eqs. (13a-b) of Ref. [30]).

The correlation with previous group theoretical treatments [8, 12, 31, 32] of tops can also be made at least partially, since in these papers only the generators and Casimir operators are considered. It is also clear (Eq. (43)) that if one restricts the analysis to the degeneracy algebra, there is, up to normalization factors, a one to one correspondence between the various realizations of generators. For instance, with [8, 31, 32], we have :

$$\begin{array}{lll} & [8] & [31] \qquad [32] \\ \mathbf{L}^{(101)}{}^{(1,\,0)}_{m\;\;0} \leftrightarrow & \bar{\mathbf{Q}}_{9,\,10,\,13}\,; & \mathbf{J}_3, \mathbf{J}_{\pm}\,; \quad \mathbf{J}_3, \mathbf{J}_{\pm} \\ \boldsymbol{\ell}^{(101)}{}^{(0,\,1)}_{0\;\;m'} \leftrightarrow & \bar{\mathbf{Q}}_{11,\,12,\,14}\,; & \mathbf{L}_3, \mathbf{L}_{\pm}\,; \quad \mathbf{K}_3, \mathbf{K}_{\pm}\,. \end{array} \tag{56}$$

Also in [31, 32], the Wigner functions are realized as boson polynomials. Differences appear when one considers the ladder generators which are included to find a dynamical algebra. In [8], where SU(2, 2) is proposed, these are time dependent and of half-integer rank in $SU(2) \oplus SU(2)$; hence the representation space is spanned by all Wigner functions $\mathfrak{D}^{(j)}_{mm'}$ with integer and half-integer j values. Problems arise if one wants to keep only physical states associated with integer j values.

In [12], the representation space chosen is really appropriate to the symmetric top only, since the K degeneracy is lifted in zero order. Between the generators of the contracted algebra of [12] and our generators, in the limit N large, the following correspondence can be established (Eq. (49)) :

$$\mathbf{J}(q) \leftrightarrow \mathbf{L}^{(101)}{}^{(1,\ 0)}_{q\ \ 0}$$

$$\mathbf{A}(q) = a\mathbf{D}^{(1,\ 1)}_{q\ \ 0} \leftrightarrow \frac{1}{N}\mathbf{M}^{(101)}{}^{(1,\ 1)}_{q\ \ 0}$$

$$\mathbf{B}(q) = b[\mathbf{D}^{(1,\ 1)}_{q\ \ 1} + \mathbf{D}^{(1,\ 1)}_{q\ -1}] \leftrightarrow \frac{1}{N}[\mathbf{M}^{(101)}{}^{(1,\ 1)}_{q\ \ 1} + \mathbf{M}^{(101)}{}^{(1,\ 1)}_{q\ -1}]$$

where a and b are constants. Thus the algebra includes only nine out of the fifteen rigid top operators. The six remaining operators, denoted $\mathbf{A}\cdot\mathbf{J}$, $\mathbf{B}\cdot\mathbf{J}$, $\mathbf{C}\cdot\mathbf{J}$ and $\mathbf{C} = \mathbf{A}\wedge\mathbf{B}$ in [12], appear then as members of the $E^2(3)$ enveloping algebra.

5. Conclusion and perspectives.

The procedure we developed to treat the rotational dynamics of molecules will be, together with our previous results [6], a starting point for the global treatment of rovibrational interactions in semi-rigid polyatomic molecules in their non-degenerate electronic ground state. For instance, within the Born-Oppenheimer approximation and assuming that in zero order the vibrational and rotational movements are separated, a basis for the Hilbert space of physical states is given by the direct product of the IR ${}^{V}\Gamma_D$ and ${}^{R}\Gamma_D$ of the corresponding vibrational ${}^{V}D$ and rotational ${}^{R}D$ dynamical algebras. These being oriented with regard to their respective degeneracy algebra the zero order vibrational and rotational Hamiltonians are simply given by the first invariants (mostly Casimir operators). The terms in the effective Hamiltonian adapted to the study of a given set of vibrational levels, as well as in the effective transition moments, are easily written down since all operators are members of the enveloping algebras of ${}^{V}D$ and ${}^{R}D$. It should be noted that several choices for ${}^{V}D$ are possible depending on the molecule under study (even for identical molecular symmetry group) and on the type of internal motions considered. Different choices imply of course different zero order spectrum but also reveal a modification of the orders of magnitude of the various contributions. For instance in the harmonic oscillator approximation, the usual Coriolis term appears naturally, for degenerate modes, as the dominant rovibrational interaction operator, but it is no longer the case [33, 34] if one assumes a Morse like potential, as for instance for streching modes.

One may also expect that a similar approach will be possible, to include other degrees of freedom, for instance spin ones, and thus a unified treatment, in terms of generalized Schwinger boson operators, could be performed. Some important features of the method can be underlined, among which the fact that, with such an approach all computations can be made with group theoretical technics, without explicit coordinate representation. With the introduction of a compact dynamical algebra, appropriate to the study of systems with a finite

number of bound states, all physically significant operators appear as members of its enveloping algebra. Also the use of the generating function method is a necessary and convenient tool to work within an enveloping algebra and allows us to solve consistently the missing label problem within a subduction chain.

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