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Subm. to Chem.Phys.Lett.

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Spectrum generating algebra for vibrations and rotations of oblate top X_3 molecules

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November 1, 1993

Abstract

A new spectrum generating algebra for rotations and vibrations of polyatomic molecules is introduced. It allows one to treat properly both degenerate and nondegenerate vibrations of a given molecule. An application to nonlinear X_3 molecules shows that this model provides a unified description of rotational and vibrational excitations of an oblate top molecule, in which the point group symmetry is incorporated exactly.

1 Introduction

The progress currently witnessed in experimental techniques for the spectroscopy of large molecules motivates the development of new theoretical tools to interpret and guide such measurements. In view of the proliferation of parameters needed in Dunham expansions and the difficulties encountered in solving a Schrödinger equation with interatomic potentials for polyatomic molecules, it has been suggested to use algebraic methods for analyzing the rotation-vibration spectra [1, 2]. The key ingredient in these methods is the choice of a suitable spectrum generating algebra and its realization in terms of bosons. The underlying group structure greatly facilitates the evaluation of matrix elements and provides complete bases and in some cases analytic solutions. In the simplest case of diatomic molecules the rotational and vibrational degrees of freedom are described in terms of the three components of a dipole ($\pi^\dagger$) boson and a scalar ($\sigma^\dagger$) boson referred to as vibrons [1]. The dipole boson is associated with the radius vector connecting the two atoms. The main reason for the introduction of the scalar boson is to conveniently handle anharmonicities by compactifying the model space, *i.e.* it is assumed that the total

number of bosons, $N = n_\sigma + n_\pi$ is conserved. This confers on the model a group structure of $U(4)$ which serves as a spectrum generating algebra, *i.e.* the hamiltonian of the vibron model is expressed in terms of the generators of the algebra. In limiting cases, in which the hamiltonian is expressed in terms of invariants of a chain of subgroups of $U(4)$, it can be solved analytically. For rigid diatomic molecules the relevant dynamic symmetry is provided by the chain $U(4) \supset SO(4) \supset SO(3)$. The corresponding energy spectrum is similar to that of a Morse potential [1].

Two approaches have been suggested to extend the vibron model to polyatomic molecules. In the first approach [2] rotations and vibrations are treated simultaneously. A molecule with n atoms is described in terms of $n-1$ coupled $U(4)$ groups, one for each relative coordinate. Each $U(4)$ algebra is realized in terms of a set of vibrons (σ_i, π_i), *i.e.* one σ boson for every π boson. In the resulting vibron model the number of bosons, $N_i = n_{\sigma_i} + n_{\pi_i}$, is conserved for each $i = 1, \ldots, n-1$ separately. This version of the model has been applied to linear molecules with $n = 2, 3, 4$ atoms [1, 2, 3] as well as to bent XY_2 molecules [4] and quasi-linear four-atomic molecules [5], all of which only have nondegenerate vibrations. This model, however, encounters difficulties in describing bent molecules with degenerate vibrations, such as for example in nonlinear X_3 molecules.

A second approach [6, 7] for polyatomic molecules relies on a simpler version of the vibron model in which vibrations are treated in terms of coupled one-dimensional anharmonic oscillators. A separate set of coupled $U(2)$ groups is introduced for each type of vibration. The $U(2)$ algebra corresponds to a Morse potential (Pöschl-Teller potential) in the case of stretching (bending) vibrations. The use of symmetry adapted operators ensures the correct transformation properties of the eigenstates under the relevant point group. This simpler version of the vibron model provides a tractable calculation scheme and has been applied to stretching vibrations of triatomic molecules [6], octahedral molecules and CH bends in benzene [7]. This approach, however, ignores rotations and treats stretching and bending vibrations separately while in the case of degenerate vibrations these two types of vibrations belong to the same irreducible representation of the relevant point group.

In this letter we propose an alternative scheme for the description of n-atomic molecules, in which the point group symmetry of any given molecule can be taken into account *exactly* and which contains *all* vibrational (stretching and bending) and rotational degrees of freedom in one algebraic framework. One and the same hamiltonian is used to describe all rotations and vibrations as well as their coupling and its eigenstates have the correct species of the relevant point group. We introduce one dipole boson for each relative coordinate and a single scalar boson. This leads to a spectrum generating algebra of $U(k+1)$, where $k = 3(n-1)$ is the total number of rotational and vibrational degrees of freedom. By construction only the total number of bosons, $N = n_\sigma + n_\pi$ with $n_\pi = \sum_i n_{\pi_i}$ is conserved. For a diatomic molecule ($k = 3$) we recover the $U(4)$ vibron model. As a first step in implementing this new scheme we focus the discussion on the description of a bent X_3 molecule which is the simplest polyatomic molecule with a degenerate vibration.

For triatomic molecules the six degrees of freedom of the two relative coordinates lead to a spectrum generating algebra of $U(7)$. The building blocks of the $U(7)$ model are the six components of two dipole bosons with $L^p = 1^-$, denoted in second

quantization by $\pi_1^\dagger$ and $\pi_2^\dagger$, and a scalar boson with $L^P = 0^+$, denoted by $\sigma^\dagger$. All many-body states are classified according to the totally symmetric representation $[N]$ of $U(7)$, where $N = n_\sigma + n_{\pi_1} + n_{\pi_2}$ is the total number of bosons. The most general one- and two-body rotationally and parity invariant $U(7)$ hamiltonian that conserves the total number of bosons, N, can be expressed in second quantized form as

$$H = \sum_i \epsilon_i \, a_i^\dagger \cdot \tilde{a}_i + \sum_L \sum_{ijkl} v_{ijkl}^{(L)} \, (a_i^\dagger a_j^\dagger)^{(L)} \cdot (\tilde{a}_l \tilde{a}_k)^{(L)} \, , \tag{1}$$

with $a_0^\dagger = \sigma^\dagger$, $a_1^\dagger = \pi_1^\dagger$ and $a_2^\dagger = \pi_2^\dagger$. There are special choices of the interaction strengths in eq. (1) for which the hamiltonian has a dynamical symmetry and the eigenvalues can be obtained in closed analytic form. In general this is not the case and the eigenvalue problem has to be solved by an exact diagonalization in a convenient basis, *e.g.* the harmonic oscillator basis $|N, (n_1 l_1), (n_2 l_2), lm >$.

2 Point group symmetry

The embedding of discrete point group symmetries in an algebraic model relies on a geometric interpretation of the vibrons. There are several possible interpretations, *e.g.* in terms of bond lengths or mass-weighted coordinates. For nonlinear rigid molecules it is convenient to make use of the isomorphism between the molecular symmetry group and the relevant point group [8]. The elements of the former consist of permutations of identical atoms with or without inversion (parity). The parity of the bosons is well defined and the transformation properties under permutations can be can be realized in terms of finite rotations among the bosons. For bent X_3 molecules we use the isomorphism between the S_3 permutation group and the point group D_3 and associate the two types of dipole bosons, π_1 and π_2, with the relative Jacobi coordinates and their conjugate momenta

$$\vec{\rho} = \frac{1}{\sqrt{2}}(\vec{r}_1 - \vec{r}_2) \, , \qquad \vec{\lambda} = \frac{1}{\sqrt{6}}(\vec{r}_1 + \vec{r}_2 - 2\vec{r}_3) \, , \tag{2}$$

which have well-known transformation properties under permutations. Among the elements of S_3 we use the interchange $P(12)$ and the cyclic permutation $P(123)$. All other permutations can be expressed in terms of these two elementary ones. The transformation properties under S_3 of all operators of interest follow from those of the building blocks,

$$\begin{aligned} P(12) \begin{pmatrix} \sigma^\dagger \\ \pi_1^\dagger \\ \pi_2^\dagger \end{pmatrix} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \sigma^\dagger \\ \pi_1^\dagger \\ \pi_2^\dagger \end{pmatrix} , \\ P(123) \begin{pmatrix} \sigma^\dagger \\ \pi_1^\dagger \\ \pi_2^\dagger \end{pmatrix} &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix} \begin{pmatrix} \sigma^\dagger \\ \pi_1^\dagger \\ \pi_2^\dagger \end{pmatrix} . \end{aligned} \tag{3}$$

The σ-boson is a scalar under the permutation group and the two π-bosons are transformed amongst each other. There are three different symmetry classes for

the permutation of three objects: a symmetric one, S, an antisymmetric one, A, and a two-dimensional one of mixed symmetry type, denoted by M_1 and M_2. The latter have the same transformation properties as the creation operators, $\pi_1^\dagger$ and $\pi_2^\dagger$. Alternatively, the three symmetry classes can be labeled by the irreducible representations of the point group D_3 (which is isomorphic to S_3) as A_1, A_2 and E, respectively.

To obtain the most general one- and two-body $U(7)$ hamiltonian adequate to a bent X_3 molecule with $D_{3h} \supset D_3 \supset C_2$ point group symmetry we construct a rotationally and parity invariant hamiltonian which is a scalar under the permutation group. For that purpose we use the multiplication rules for S_3 and get

$$\begin{aligned} H \;=\; & \epsilon_\sigma \, \sigma^\dagger \sigma - \epsilon_\pi (\pi_1^\dagger \cdot \tilde{\pi}_1 + \pi_2^\dagger \cdot \tilde{\pi}_2) + u_0 \, \sigma^\dagger \sigma^\dagger \sigma \sigma - u_1 \, \sigma^\dagger (\pi_1^\dagger \cdot \tilde{\pi}_1 + \pi_2^\dagger \cdot \tilde{\pi}_2) \sigma \\ & + v_1 \left[(\pi_1^\dagger \cdot \pi_1^\dagger + \pi_2^\dagger \cdot \pi_2^\dagger) \sigma \sigma + \sigma^\dagger \sigma^\dagger (\tilde{\pi}_1 \cdot \tilde{\pi}_1 + \tilde{\pi}_2 \cdot \tilde{\pi}_2) \right] \\ & + \sum_{\lambda=0,2} c_2 \left[(\pi_1^\dagger \pi_1^\dagger - \pi_2^\dagger \pi_2^\dagger)^{(\lambda)} \cdot (\tilde{\pi}_1 \tilde{\pi}_1 - \tilde{\pi}_2 \tilde{\pi}_2)^{(\lambda)} + 4 \, (\pi_1^\dagger \pi_2^\dagger)^{(\lambda)} \cdot (\tilde{\pi}_2 \tilde{\pi}_1)^{(\lambda)} \right] \\ & + c_1 \, (\pi_1^\dagger \pi_2^\dagger)^{(1)} \cdot (\tilde{\pi}_2 \tilde{\pi}_1)^{(1)} + \sum_{\lambda=0,2} w_2 \, (\pi_1^\dagger \pi_1^\dagger + \pi_2^\dagger \pi_2^\dagger)^{(\lambda)} \cdot (\tilde{\pi}_1 \tilde{\pi}_1 + \tilde{\pi}_2 \tilde{\pi}_2)^{(\lambda)} \, , \end{aligned} \tag{4}$$

with $\tilde{\pi}_{i,m} = (-1)^{1-m} \pi_{i,-m}$. Its eigenstates are all labeled by the total number of bosons, N, and by construction have good angular momentum, parity and permutation (point group) symmetry.

3 Geometry

The hamiltonian in eq. (4) is expressed in terms of algebraic operators. In order to obtain a more intuitive geometric interpretation of these operators, we analyze the model in terms of geometric variables and study its elementary excitations. Geometric properties of the $U(7)$ model can be studied with mean-field techniques. For a system of bosons the variational wave function takes the form of a condensate of N bosons [9],

$$| \, N; c) \;=\; \frac{1}{\sqrt{N!}} \left(b_c^\dagger \right)^N | \, 0) \, , \tag{5}$$

with

$$b_c^\dagger \;=\; (1 + R^2)^{-1/2} \left[\sigma^\dagger + r_1 \, \pi_{1,z}^\dagger + r_2 \left(\cos\theta \, \pi_{2,z}^\dagger + \sin\theta \, \pi_{2,x}^\dagger \right) \right] , \tag{6}$$

where $R^2 = r_1^2 + r_2^2$. The condensate is parametrized in terms of two (real) coordinates, r_1 and r_2, and an angle, θ. The range of the parameters is $r_1 \geq 0$, $r_2 \geq 0$ and $0 \leq \theta \leq \pi$. The two vectors $\vec{r}_1$ and $\vec{r}_2$ span the xz-plane. We have chosen the z-axis along the direction of $\vec{r}_1$ $(= r_1 \hat{z})$ and $\vec{r}_2$ is rotated by an angle θ about the y-axis, $\vec{r}_1 \cdot \vec{r}_2 = r_1 r_2 \cos\theta$. The expectation value of the S_3-invariant $U(7)$ hamiltonian of eq. (4) in the condensate defines a classical energy surface,

$$E(r_1, r_2, \theta) \;=\; E_0 + \frac{N(N-1)}{(1+R^2)^2} \left[a \, R^2 + b \, R^4 + c \, r_1^2 r_2^2 \sin^2\theta \right] . \tag{7}$$

The coefficients a, b and c are linear combinations of the interaction strengths in eq. (4). The equilibrium shape is determined by minimizing the energy surface with respect to r_1, r_2 and θ. The nonlinear rigid and stable equilibrium shape of the hamiltonian(4) is characterized by $r_1 = r_2$ and $\theta = \pi/2$. These two conditions are precisely those satisfied by the Jacobi coordinates of eq. (2) for an equilateral triangular shape. This suggests to associate the algebraic shape parameters in eq. (6) with these coordinates, *i.e.* $r_1 \leftrightarrow \rho$ and $r_2 \leftrightarrow \lambda$.

4 Excitations

It is instructive to consider separately the vibrational and rotational excitations described by the hamiltonian in eq. (4). With the techniques introduced in [10] for the interacting boson model, an arbitrary $U(7)$ hamiltonian can be decomposed uniquely into intrinsic (vibrational) and collective (rotational) parts,

$$H = H_{\rm int} + H_{\rm coll} \cdot \tag{8}$$

4.1 Vibrations

The intrinsic part by definition annihilates the ground state condensate and has the same energy surface as the original hamiltonian. For the rigid nonlinear equilibrium shape, characterized by $r_1 = r_2$ and $\theta = \pi/2$, we find

$$\begin{aligned} H_{\rm int} &= \xi_1 \left(R^2 \sigma^\dagger\sigma^\dagger - \pi_1^\dagger\cdot\pi_1^\dagger - \pi_2^\dagger\cdot\pi_2^\dagger\right)\left(R^2\sigma\sigma - \tilde\pi_1\cdot\tilde\pi_1 - \tilde\pi_2\cdot\tilde\pi_2\right) \\ &+\xi_2\left[\left(\pi_1^\dagger\cdot\pi_1^\dagger - \pi_2^\dagger\cdot\pi_2^\dagger\right)\left(\tilde\pi_1\cdot\tilde\pi_1 - \tilde\pi_2\cdot\tilde\pi_2\right) + 4\left(\pi_1^\dagger\cdot\pi_2^\dagger\right)\left(\tilde\pi_2\cdot\tilde\pi_1\right)\right] , \end{aligned} \tag{9}$$

with $R^2 = r_1^2 + r_2^2$. Characteristics of the vibrational spectrum can be obtained by analyzing the intrinsic hamiltonian in more detail. To this end we introduce a set of orthonormal deformed vibrons, consisting of the ground state condensate boson $b_c^\dagger$ of eq. (6) with $r_1 = r_2$ and $\theta = \pi/2$,

$$b_c^\dagger = (1+R^2)^{-1/2}\left[\sigma^\dagger + R\left(\pi_{1,z}^\dagger + \pi_{2,z}^\dagger\right)/\sqrt{2}\right] , \tag{10}$$

and the following six bosons

$$\begin{aligned} b_u^\dagger &= (1+R^2)^{-1/2}\left[-R\sigma^\dagger + \left(\pi_{1,z}^\dagger + \pi_{2,z}^\dagger\right)/\sqrt{2}\right] , \\ b_v^\dagger &= \left(-\pi_{1,z}^\dagger + \pi_{2,z}^\dagger\right)/\sqrt{2} , \\ b_w^\dagger &= \left(\pi_{1,x}^\dagger + \pi_{2,z}^\dagger\right)/\sqrt{2} , \\ b_x^\dagger &= \left(\pi_{1,y}^\dagger + \pi_{2,y}^\dagger\right)/\sqrt{2} , \\ b_y^\dagger &= \left(-\pi_{1,x}^\dagger + \pi_{2,z}^\dagger\right)/\sqrt{2} , \\ b_z^\dagger &= \left(-\pi_{1,y}^\dagger + \pi_{2,y}^\dagger\right)/\sqrt{2} . \end{aligned} \tag{11}$$

The bosons $b_i^\dagger$ represent excitations of the condensate involving radial ($i = u, v$), angular ($i = w$) and rotational modes ($i = x, y, z$).

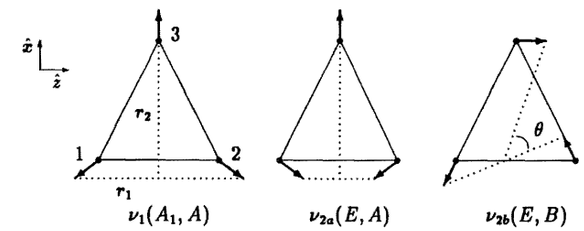

Figure 1: Schematic representation of the normal vibrations of a nonlinear X_3 molecule. The Jacobi coordinates are indicated by the dotted lines. The transformation character under the $D_3 \supset C_2$ point group is shown in parenthesis.

The normal modes can be found by rewriting the intrinsic hamiltonian in terms of the deformed vibrons of eqs. (10) and (11), replacing the condensate bosons, b_c and $b_c^\dagger$, by their classical mean-field value $\sqrt{N}$ and examining the Bogoliubov image of $H_{\rm int}$ [11, 12]. As a result we find to leading order in $1/N$

$$\frac{1}{N}H_{\rm int} = \epsilon_1\, b_u^\dagger b_u + \epsilon_2\,(b_v^\dagger b_v + b_w^\dagger b_w) + \mathcal{O}(1/\sqrt{N}) , \tag{12}$$

with eigenfrequencies

$$\begin{aligned} \epsilon_1 &= 4\xi_1\, R^2 , \\ \epsilon_2 &= 4\xi_2\, R^2(1+R^2)^{-1} . \end{aligned} \tag{13}$$

This identifies the deformed bosons that correspond to the three fundamental vibrations: a symmetric stretching (u), an antisymmetric stretching (v) and a bending vibration (w). The first two are radial excitations, whereas the third is an angular mode which corresponds to oscillations in the angle θ between the two Jacobi coordinates (ν_1, ν_{2a} and ν_{2b}, respectively in figure 1). The angular mode is degenerate with the antisymmetric radial mode. This is in agreement with the point group classification of the fundamental vibrations for a symmetric X_3 configuration [13]. This shows that $H_{\rm int}$ describes the vibrational excitations of an oblate symmetric top. The rotational bosons (x, y, z) are not present in eq. (9), since they correspond to massless Goldstone bosons associated with the rotational symmetry which is spontaneously broken in the condensate.

Eq. (12) shows that in the large N limit the vibrational spectrum is harmonic,

$$E_{\rm vib} = N[\epsilon_1\, n_u + \epsilon_2\,(n_v + n_w)] . \tag{14}$$

For finite values of N the correction terms of order $\mathcal{O}(1/\sqrt{N})$ give rise to anharmonicities. These can be studied numerically by diagonalizing $H_{\rm int}$ in a convenient basis.

A similar analysis of the S_3-invariant intrinsic (one- and two-body) hamiltonian of the $U(4) \otimes U(4)$ model yields that in this case, the two radial modes associated

with the Jacobi coordinates are uncoupled and have the same frequency. These features do not agree with the point group classification of the normal vibrations of a symmetric X_3 shape, in which one of the radial modes (the antisymmetric stretching) is degenerate with the bending vibration. The difference with the $U(7)$ model can be traced back to the occurrence of terms in the hamiltonian of eq. (9) in which only the total number of dipole bosons is conserved. These terms cannot appear in a $U(4) \otimes U(4)$ description which requires that each type of bosons is conserved separately. This problem can be overcome by introducing higher-order terms (four-body) in the $U(4) \otimes U(4)$ hamiltonian by suitable insertions of monopole bosons [12]. A $U(2) \otimes U(2)$ description will yield only the the symmetric (A_1, A) and the antisymmetric (E, A) stretching. The second member of the degenerate vibration (the (E, B) bending) requires a separate treatment.

4.2 Rotations

On top of each vibrational excitation there is a whole series of rotational states. In a geometric description the rotational excitations are labeled by the angular momentum, L, its projection on the threefold symmetry axis, $K = 0, 1, \ldots$, parity, and the transformation character under the permutation group. In the algebraic model the rotational excitations (and rotation-vibration coupling) are described by the collective part of the hamiltonian. By construction $H_{\rm coll}$ consists of interaction terms which do not affect the shape of the energy surface [10]. Its energy surface is independent of r_1, r_2 and θ. The collective hamiltonian, $H_{\rm coll} = H - H_{\rm int}$, can be written as

$$\begin{aligned} H_{\rm coll} &= \epsilon \hat{N} + \kappa_0 \hat{N}(\hat{N}-1) + \kappa_1 (\hat{A}_1 \cdot \hat{A}_1 + \hat{A}_2 \cdot \hat{A}_2 - 6\hat{n}_\sigma - \hat{n}_\pi) \\ &\quad + \kappa_2 (\hat{B}_1 \cdot \hat{B}_1 + \hat{B}_2 \cdot \hat{B}_2 - 2\hat{n}_\pi) + \kappa_3 (\hat{L} \cdot \hat{L} - 2\hat{n}_\pi) + \kappa_4 (\hat{K}_y^2 - \hat{n}_\pi) \end{aligned} \quad (15)$$

with

$$\begin{aligned} &\hat{A}_1 = i(\pi_1^\dagger \sigma + \sigma^\dagger \tilde{\pi}_1)^{(1)}, && \hat{A}_2 = i(\pi_2^\dagger \sigma + \sigma^\dagger \tilde{\pi}_2)^{(1)}, \\ &\hat{B}_1 = (\pi_1^\dagger \tilde{\pi}_2 + \pi_2^\dagger \tilde{\pi}_1)^{(1)}, && \hat{B}_2 = (\pi_1^\dagger \tilde{\pi}_1 - \pi_2^\dagger \tilde{\pi}_2)^{(1)}, \\ &\hat{L} = \sqrt{2}(\pi_1^\dagger \tilde{\pi}_1 + \pi_2^\dagger \tilde{\pi}_2)^{(1)}, && \hat{K}_y = -i\sqrt{3}(\pi_1^\dagger \tilde{\pi}_2 - \pi_2^\dagger \tilde{\pi}_1)^{(0)}, \\ &\hat{n}_\sigma = \sigma^\dagger \sigma, && \hat{n}_\pi = \sqrt{3}(\pi_1^\dagger \tilde{\pi}_1 + \pi_2^\dagger \tilde{\pi}_2)^{(0)}. \end{aligned} \quad (16)$$

The first two terms only depend on the total number operator, $\hat{N} = \hat{n}_\sigma + \hat{n}_\pi$, which is a conserved quantity. These terms only contribute to the binding energy and henceforth will be discarded. The remaining four terms in the collective hamiltonian determine the rotational spectrum. The collective hamiltonian of eq. (15) can be rewritten in terms of the two-body parts of the Casimir operators of a particular group chain, $U(7) \supset SO(7) \supset SO(6) \supset SO(3) \otimes SO(2)$ [14]. The last two terms in eq. (15), $H_{\rm rot} = \kappa_3 \hat{L} \cdot \hat{L} + \kappa_4 \hat{K}_y^2$, commute with any S_3-invariant hamiltonian and thus correspond to *exact* symmetries. Their eigenvalues are similar in form to those of a symmetric top,

$$E_{\rm rot} = \kappa_3 L(L+1) + \kappa_4 K_y^2 . \quad (17)$$

For the rotational excitations of the ground state condensate the value of K_y coincides with that of the projection of the angular momentum on the threefold symmetry axis, denoted by K.

The third and fourth term in eq. (15) do not correspond to exact symmetries of a S_3-invariant hamiltonian operator and do not commute with the intrinsic hamiltonian of eq. (9). Therefore, in addition to shifting and splitting the bands generated by $H_{\rm int}$, they can also mix them and hence contain the rotation-vibration couplings. Their effect on the spectrum can be studied numerically. However, just as was done for the intrinsic hamiltonian, we can gain physical insight of the different rotational terms by studying the large N limit,

$$\begin{aligned} \frac{1}{N} H_{\rm coll} &= -\eta_1 (b_u^\dagger - b_u)^2 - \eta_2 \left[(b_v^\dagger - b_v)^2 + (b_w^\dagger - b_w)^2\right] \\ &\quad + \eta_3 \left[(b_x^\dagger + b_x)^2 + (b_z^\dagger + b_z)^2\right] - \eta_4 (b_y^\dagger - b_y)^2 + \mathcal{O}(1/\sqrt{N}) , \end{aligned} \quad (18)$$

with

$$\begin{aligned} \eta_1 &= \kappa_1 , \\ \eta_2 &= (1+R^2)^{-1}[\kappa_1 + (-\kappa_1 + \tfrac{1}{2}\kappa_2)R^2] , \\ \eta_3 &= (1+R^2)^{-1}[\kappa_1 + (-\kappa_1 + \tfrac{1}{2}\kappa_2 + \tfrac{1}{2}\kappa_3)R^2] , \\ \eta_4 &= (1+R^2)^{-1}[\kappa_1 + (-\kappa_1 + \kappa_3 + \kappa_4)R^2] . \end{aligned} \quad (19)$$

The b_x, b_y and b_z bosons are the Goldstone bosons connected with rotations in configuration space, whereas the b_u, b_v and b_w bosons correspond to generalized rotations in a higher dimensional space. Eqs. (18,19) show that the κ_1-term is associated with rotations in a six-dimensional space (u, v, w, x, y, z) and the κ_2-term with rotations in a five-dimensional subspace (v, w, x, y, z). The κ_3-term, $\hat{L} \cdot \hat{L}$, corresponds to ordinary three-dimensional (x, y, z) rotations and the κ_4-term, $\hat{K}_y^2$, is associated with a rotation about the threefold symmetry y-axis. The equality of the coefficients of the (v, w) and the (x, z) terms in eq. (18) is a reflection of the oblate-top nature of the S_3-invariant mass operator.

The above analysis shows that a S_3-invariant $U(7)$ mass operator corresponds geometrically to rotations and vibrations of an oblate symmetric top. There are six independent terms in the hamiltonian that determine the excitation spectrum: two for the vibrational excitations and four for the rotational excitations. The two vibrational terms cluster the states into bands. Two of the rotational terms correspond to exact symmetries of the mass operator and their eigenvalues are obtained in closed form. Whereas these terms are diagonal and hence only cause band splitting, the remaining two rotational terms may in addition cause band mixing. As an illustration we present in figure 2 a schematic spectrum of an oblate top X_3 molecule in the $U(7)$ model. The levels are in agreement with [13].

5 Summary and conclusions

In this letter we have introduced a $U(7)$ spectrum generating algebra for the description of triatomic molecules. Particular emphasis was put on the ability of the

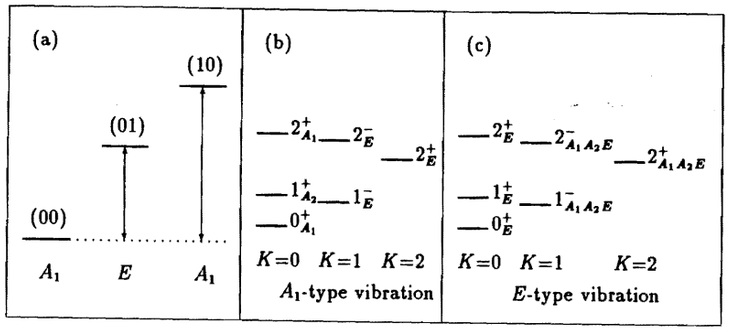

Figure 2: Schematic representation of the (a) vibrational and (b,c) rotational excitations of an oblate top X_3 molecule in the $U(7)$ model. The vibrational levels are labeled by the spectroscopic notation $(v_1, v_2) = (n_u, n_v + n_w)$ and by their transformation character under the D_3 point group. The rotational levels built on vibrations of type A_1 (b) and on vibrations of type E (c) are labeled by K, L^π_t, where t denotes the overall (vibrational plus rotational) permutation symmetry. Each E state is doubly degenerate.

model to adequately treat degenerate vibrations as they occur in bent X_3 molecules, by imposing the discrete point group symmetry on the hamiltonian. In a normal mode analysis we showed explicitly that the characteristic pattern of fundamental vibrations of a symmetric X_3 molecule, *i.e.* a single symmetric stretching mode and a degenerate doublet of an antisymmetric stretching and an angular bending mode, is recovered in the $U(7)$ model. We showed that the $U(7)$ model has all necessary ingredients for a proper description of the vibrations and rotations of oblate top X_3 molecules.

Although we have focussed the discussion to nonlinear X_3 molecule, the model can be applied to any triatomic molecule both linear and bent. For X_3 molecules we found it convenient to associate the dipole vibrons with the relative Jacobi coordinates. This interpretation can also be applied to rigid bent molecules ($\theta = \pi/2$ for XY_2 molecule) and linear molecules (for which $r_2 = |\vec{\lambda}| = 0$). For bent XY_2 molecules the hamiltonian then has to be invariant under S_2 (generated by $P(12)$). The model permits however other interpretations for the vibrons, *e.g.* in terms of bond lengths. In this case the hamiltonian describing a XY_2 molecule is required to be invariant under $\pi_1 \leftrightarrow \pi_2$. This bond-length interpretation may be useful for describing vibrations which are local. In the $U(7)$ model one can construct a hamiltonian for each interpretation and for each geometry, for which the normal mode analysis is in accord with that dictated by the relevant point group [14]. For example, for linear triatomic molecules one recovers the one-dimensional symmetric and antisymmetric stretching modes and the two-dimensional bending mode, in agreement with the $C_{\infty v}$ or $D_{\infty h}$ point groups.

We have compared the $U(7)$ model with two other approaches. The main difference between the models lies in the choice of the model space. In the $U(7)$ model the two types of dipole degrees of freedom are treated on equal footing in the sense that the distribution of quanta among them is determined dynamically by the hamiltonian, whereas in the case of the $U(4) \otimes U(4)$ model (or its simplified $U(2) \otimes U(2)$ version) the number of bosons in each mode is restricted separately. The existence of generators in the $U(7)$ algebra that mix the two types of dipole bosons is the new ingredient that enables an exact treatment of the point group symmetry and a proper description of degenerate vibrations.

Since the procedure is completely general, it can be extended without difficulty to larger molecules, resulting in a spectrum generating algebra of $U(3n-2)$ as a candidate for a unified description of *all* vibrations and rotations of n-atomic molecules in which the underlying point group symmetry of any given molecule can be taken into account exactly. Work along these lines is in progress and will be reported separately.

Acknowledgements

This work is supported in part by the Stichting voor Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the Israeli Science Ministry.

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