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Spectrum-generating algebra for X_3 molecules

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A spectrum-generating algebra for a unified description of rotations and vibrations in polyatomic molecules is introduced. An application to nonlinear X_3 molecules shows that this model (i) incorporates exactly the relevant point group, (ii) provides a complete classification of oblate top states, and (iii) treats properly both degenerate and nondegenerate vibrations.

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I. INTRODUCTION

The progress currently witnessed in experimental techniques for the spectroscopy of large molecules motivates the development of 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, the use of algebraic methods has been suggested in which the Hamiltonian is expressed in terms of elements of a Lie algebra. The key ingredient is the choice of a suitable spectrum generating algebra.

At present there exist two versions of this method. In the first version [1,2], rotations and vibrations are treated simultaneously and hence rotation-vibration couplings are built in from the outset [3]. In this approach, a molecule with n atoms is described in terms of $n-1$ coupled U(4) groups, one for each independent relative coordinate. Each $\mathrm{u}_i(4)$ algebra is realized in terms of a set of four vibron operators (σ_i, π_i): the three components of a dipole (or π) boson with $L^P=1^-$ and a scalar (or σ) boson with $L^P=0^+$, i.e., one σ boson for every π boson. The scalar boson does not represent an independent degree of freedom, but is merely introduced to conveniently handle anharmonicities by compacting the model space, i.e., the number of bosons $N_i=n_{\sigma_i}+n_{\pi_i}$ is conserved for each $i=1,\ldots,n-1$ separately. This version has been applied successfully to polyatomic molecules with $n=2,3,4$ atoms, but it encounters difficulties in describing bent molecules with degenerate vibrations such as, for example, in nonlinear X_3 molecules [2,4].

In the second version [5,6] rotations are ignored, while 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 (stretching and bending). The use of symmetry-adapted operators ensures the correct transformation properties of the eigenstates under the relevant point group [6]. Since there is no explicit coupling between rotations and vibrations, this scheme becomes particularly useful for molecules in which the rotation-vibration coupling is negligible. In this approach each type of vibration is treated separately with different interactions, although for degenerate vibrations such as, for example, in symmetric top X_3 molecules, stretching and bending vibrations can belong to the same irreducible representation of the relevant point group.

In this paper, we propose an alternative scheme for the description of n-atomic molecules in which the relevant point-group symmetry is taken into account *exactly* and *all* vibrations (stretching and bending) and rotations are contained in a single algebraic framework. We introduce a dipole boson for each independent relative coordinate and a single scalar boson. This leads to a spectrum-generating algebra of $\mathrm{u}(k+1)$, 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 $n_\pi=\Sigma_i n_{\pi_i}$ is conserved. For diatomic molecules $(n=2)$ we recover the u(4) vibron model [1]. For triatomic molecules $(n=3)$ we obtain a u(7) model whose building blocks are a scalar boson and two dipole bosons (σ,π_1,π_2). We present this scheme by studying symmetric (oblate) top X_3 molecules, which form the simplest nontrivial example of a bent polyatomic molecule with a degenerate vibration. We compare our results with those obtained in a $\mathrm{u}(4)\otimes\mathrm{u}(4)$ model [2].

II. POINT-GROUP SYMMETRY

The embedding of discrete point-group symmetries in an algebraic model relies on a geometric interpretation of the vibrons. For nonlinear rigid molecules it is convenient to make use of the established isomorphism between the molecular symmetry group and the relevant point group [7]. The elements of the former consist of permutations of identical nuclei with or without inversion (parity). The parity of the bosons is well defined and the transformation properties under permutations can be realized in terms of finite rotations among the bosons. For bent X_3 molecules with point-group symmetry D_{3h}, we use the isomorphism between the S_3 per-

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mutation group and the point group D_3 ($\subset D_{3h}$). The parity and S_3 labels are equivalent to the classification under D_{3h}. We associate the two types of dipole bosons π_1 and π_2 with the relative Jacobi coordinates

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

and their conjugate momenta, which have well defined transformation properties under permutations ($\vec{x}_i$ denotes the coordinate of the ith atom). The elements of the group S_3 can be expressed in terms of the transposition $P(12)$ and the cyclic permutation $P(123)$, whose matrix representation in the $(\sigma^\dagger,\pi^\dagger_{1,m},\pi^\dagger_{2,m})$ basis is [8]

$$P(12) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad P(123) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1/2 & \sqrt{3}/2 \\ 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix}. \tag{2}$$

The σ boson is a scalar under the permutation group, whereas the two π bosons transform (for each projection $m=0,\pm 1$) as the two components (M_ρ,M_λ) of the two-dimensional irreducible representation (M) of S_3. In general, the symmetric (S), antisymmetric (A), and mixed symmetry (M) classes of S_3 can equivalently be labeled by the irreducible representations of the isomorphic point group D_3 as A_1, A_2, and E, respectively.

The transformation properties under S_3 of all operators of interest follow from those of the building blocks. In particular, the most general one- and two-body u(7) Hamiltonian that is a scalar under S_3 as well as rotationally and parity invariant is found to be

$$\begin{aligned} H={}& \epsilon_\sigma\, \sigma^\dagger\sigma - \epsilon_\pi\, (\pi_1^\dagger\cdot\tilde{\pi}_1+\pi_2^\dagger\cdot\tilde{\pi}_2) + u_0\, \sigma^\dagger\sigma^\dagger\sigma\sigma - u_1\, \sigma^\dagger(\pi_1^\dagger\cdot\tilde{\pi}_1+\pi_2^\dagger\cdot\tilde{\pi}_2)\sigma \\ &+ v_0\, [(\pi_1^\dagger\cdot\pi_1^\dagger+\pi_2^\dagger\cdot\pi_2^\dagger)\sigma\sigma+\sigma^\dagger\sigma^\dagger(\tilde{\pi}_1\cdot\tilde{\pi}_1+\tilde{\pi}_2\cdot\tilde{\pi}_2)] \\ &+ \sum_{\lambda=0,2} c_\lambda\, [(\pi_1^\dagger\pi_1^\dagger-\pi_2^\dagger\pi_2^\dagger)^{(\lambda)}\cdot(\tilde{\pi}_1\tilde{\pi}_1-\tilde{\pi}_2\tilde{\pi}_2)^{(\lambda)}+4\,(\pi_1^\dagger\pi_2^\dagger)^{(\lambda)}\cdot(\tilde{\pi}_2\tilde{\pi}_1)^{(\lambda)}] \\ &+ c_1\, (\pi_1^\dagger\pi_2^\dagger)^{(1)}\cdot(\tilde{\pi}_2\tilde{\pi}_1)^{(1)} + \sum_{\lambda=0,2} w_\lambda\, (\pi_1^\dagger\pi_1^\dagger+\pi_2^\dagger\pi_2^\dagger)^{(\lambda)}\cdot(\tilde{\pi}_1\tilde{\pi}_1+\tilde{\pi}_2\tilde{\pi}_2)^{(\lambda)}, \end{aligned} \tag{3}$$

where $\cdot$ denotes the usual scalar product with $\tilde{\pi}_{i,m}=(-1)^{1-m}\pi_{i,-m}$ and $i=1,2$. The corresponding eigenstates are labeled by the total number of bosons N and, by construction, have good angular momentum, parity, and permutation (point-group) symmetry.

III. GEOMETRY

The Hamiltonian of Eq. (3) is expressed in terms of abstract algebraic interactions. A more intuitive geometric visualization can be obtained by using mean-field techniques to study the geometric properties of the u(7) model. For a system of bosons the variational wave function takes the form of a coherent state [9], which is a condensate of N bosons

$$|N;c\rangle = \frac{1}{\sqrt{N!}}(b_c^\dagger)^N|0\rangle, \tag{4}$$

with

$$b_c^\dagger=(1+R^2)^{-1/2}[\sigma^\dagger+r_1\ \pi^\dagger_{1,z}+r_2\ (\pi^\dagger_{2,z}\cos\theta+\pi^\dagger_{2,x}\sin\theta)], \tag{5}$$

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 ($r_1,r_2\geq 0$ 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 $\vec{r}_1$, and $\vec{r}_2$ is rotated by an angle θ about the out-of-plane y axis, $\vec{r}_1\cdot\vec{r}_2=r_1r_2\cos\theta$. The expectation value of the Hamiltonian of Eq. (3) in the condensate defines a classical energy surface $E(r_1,r_2,\theta)$. 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 is characterized by $r_1=r_2$ and $\theta=\pi/2$. These two conditions are precisely those satisfied by the Jacobi coordinates of Eq. (1) for an equilateral triangular shape and suggest the association of the algebraic shape parameters in Eq. (5) with these coordinates, i.e., $r_1\leftrightarrow\rho$ and $r_2\leftrightarrow\lambda$.

IV. EXCITATIONS

We consider separately the vibrational and rotational excitations described by the Hamiltonian in Eq. (3). With the techniques introduced in [10] for the nuclear interacting boson model, an arbitrary u(7) Hamiltonian can be decomposed uniquely into intrinsic (vibrational) and collective (rotational and rotation-vibration coupling) parts

$$H=H_{\mathrm{int}}+H_{\mathrm{coll}}. \tag{6}$$

A. Vibrations

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

$$\begin{aligned}H_{\mathrm{int}}=\xi_1\ &(R^2\ \sigma^\dagger\sigma^\dagger-\pi_1^\dagger\cdot\pi_1^\dagger-\pi_2^\dagger\cdot\pi_2^\dagger)\\&\times(R^2\,\sigma\sigma-\tilde{\pi}_1\cdot\tilde{\pi}_1-\tilde{\pi}_2\cdot\tilde{\pi}_2)+\xi_2[(\pi_1^\dagger\cdot\pi_1^\dagger-\pi_2^\dagger\cdot\pi_2^\dagger)\\&\times(\tilde{\pi}_1\cdot\tilde{\pi}_1-\tilde{\pi}_2\cdot\tilde{\pi}_2)+4\ (\pi_1^\dagger\cdot\pi_2^\dagger)\ (\tilde{\pi}_2\cdot\tilde{\pi}_1)].\end{aligned}\tag{7}$$

To get more insight into the vibrational structure, we perform a normal-mode analysis of the above Hamiltonian. This is done by introducing a set of orthonormal deformed vibrons, consisting of the condensate boson of Eq. (5) with $r_1=r_2$ and $\theta=\pi/2$, and six additional bosons that represent excitations of the condensate. The normal modes can be found by rewriting the intrinsic Hamiltonian in terms of the deformed vibrons and replacing the condensate bosons by their classical mean-field value $\sqrt{N}$ [11,12]. As a result, we find, to leading order in N,

$$\frac{1}{N}H_{\mathrm{int}}=\epsilon_1\ b_u^\dagger b_u+\epsilon_2\ (b_v^\dagger b_v+b_w^\dagger b_w)+O(1/\sqrt{N}),\tag{8}$$

with eigenfrequencies $\epsilon_1=4\xi_1R^2$ and $\epsilon_2=4\xi_2R^2(1+R^2)^{-1}$. 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),

$$\begin{aligned}b_u^\dagger&=(1+R^2)^{-1/2}[-R\ \sigma^\dagger+(\pi_{1,z}^\dagger+\pi_{2,x}^\dagger)/\sqrt{2}],\\b_v^\dagger&=(-\pi_{1,z}^\dagger+\pi_{2,x}^\dagger)/\sqrt{2},\\b_w^\dagger&=(\pi_{1,x}^\dagger+\pi_{2,z}^\dagger)/\sqrt{2}.\end{aligned}\tag{9}$$

The first two are radial excitations, whereas the third is an angular mode that corresponds to oscillations in the angle θ between the two Jacobi coordinates [12] (ν_1, ν_{2a}, and ν_{2b}, respectively, in the usual spectroscopic notation). 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] and shows that H_{int} describes the vibrational excitations of an oblate symmetric top. Intrinsic states representing excited vibrations (ν_1,ν_2^l) are obtained, for large N, by replacing the condensate bosons in Eq. (4) by the appropriate number of deformed bosons of Eq. (9). Accordingly, the intrinsic state for such vibration (having $+l$ projection of the vibrational angular momentum on the symmetry y axis) takes the form $(b_{\theta,1}^\dagger)^{(\nu_2+l)/2}(b_{\theta,-1}^\dagger)^{(\nu_2-l)/2}(b_u^\dagger)^{\nu_1}(b_c^\dagger)^{N-\nu_1-\nu_2}|0\rangle$, where $b_{\theta,\pm1}^\dagger=(b_v^\dagger\pm ib_w^\dagger)/\sqrt{2}$.

By construction, H_{int} has an exactly degenerate ground band whose rotational members are obtained by projection from the equilibrium condensate. Its excited states also tend to cluster into bands. Equation (8) shows that in the large N limit the vibrational spectrum is harmonic. For finite values of N the correction terms of order $1/\sqrt{N}$ give rise to anharmonicities. These can be studied numerically by diagonalizing H_{int} in a convenient basis.

A similar analysis [12] of the S_3-invariant intrinsic (one- and two-body) Hamiltonian of the u(4)⊗u(4) model yields that, in this case, the two radial modes associated with the Jacobi coordinates are uncoupled and have the same frequency, in disagreement with the point-group classification of the normal vibrations of a symmetric X_3 shape. The difference with the u(7) model can be traced back to the occurrence of terms in the Hamiltonian of Eq. (7) in which only the total number of dipole bosons is conserved. These terms cannot appear in a u(4)⊗u(4) description, which requires that each type of boson be conserved separately. A u(2)⊗u(2) description will yield only the symmetric $\nu_1(A_1)$ and the antisymmetric $\nu_{2a}(E)$ stretching vibrations. The second member of the degenerate vibration [the $\nu_{2b}(E)$ bending] requires a separate treatment.

B. 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 and its projection K $(=0,1,\dots)$ on the threefold symmetry axis, parity $P=(-1)^K$, and the transformation property t under the point group. In the present algebraic model the rotations (and rotation-vibration couplings) are described by the collective part of the Hamiltonian. By construction, $H_{\mathrm{coll}}=H-H_{\mathrm{int}}$ consists of interaction terms that do not affect the shape of the energy surface [10,11]. Discarding $\hat{N}$-dependent terms that do not contribute to the excitation spectrum, we find

$$\begin{aligned}H_{\mathrm{coll}}=\kappa_1\ &(\hat{A}_1\cdot\hat{A}_1+\hat{A}_2\cdot\hat{A}_2)+\kappa_2\ (\hat{B}_1\cdot\hat{B}_1+\hat{B}_2\cdot\hat{B}_2)\\&+\ \kappa_3\ \hat{L}\cdot\hat{L}+\kappa_4\ \hat{K}_y\cdot\hat{K}_y,\end{aligned}\tag{10}$$

with

$$\begin{aligned}&\hat{A}_1=i\ (\pi_1^\dagger\sigma+\sigma^\dagger\tilde{\pi}_1)^{(1)}, &&\hat{A}_2=i\ (\pi_2^\dagger\sigma+\sigma^\dagger\tilde{\pi}_2)^{(1)},\\&\hat{B}_1=(\pi_1^\dagger\tilde{\pi}_2+\pi_2^\dagger\tilde{\pi}_1)^{(1)}, &&\hat{B}_2=(\pi_1^\dagger\tilde{\pi}_1-\pi_2^\dagger\tilde{\pi}_2)^{(1)},\\&\hat{L}=\sqrt{2}\ (\pi_1^\dagger\tilde{\pi}_1+\pi_2^\dagger\tilde{\pi}_2)^{(1)}, &&\hat{K}_y=-i\sqrt{3}\ (\pi_1^\dagger\tilde{\pi}_2-\pi_2^\dagger\tilde{\pi}_1)^{(0)}.\end{aligned}\tag{11}$$

The angular momentum $\hat{L}$ commutes with any rotational-invariant Hamiltonian. The Hamiltonian of Eq. (3) commutes also with the operator $\hat{K}_y$. Consequently, the resulting eigenstates $|L^P,K_y\rangle$ have good angular momentum L, parity P, and K_y. The states $|L^P,\pm K_y\rangle$ are degenerate since $P(12)\ |L^P,K_y\rangle\ =\ (-1)^{K_y}\ |L^P,-K_y\rangle$ and $P(12)$ commutes with any S_3-invariant Hamiltonian. The operator $\hat{K}_y$ is related to the cyclic permutation $P(123)=\exp(-i2\pi\hat{K}_y/3)$ and the absolute value $|K_y|$ determines the $S_3\approx D_3$ symmetry [14]

$$|K_y|=\begin{cases}0\ (\mathrm{mod}\ 3) & \text{for}\ A_1,A_2\\ 1,2\ (\mathrm{mod}\ 3) & \text{for}\ E.\end{cases}\tag{12}$$

States with well defined permutation symmetry (t) can be formed by taking the two linear combinations $|L_t^P,|K_y|\rangle\propto[1\pm P(12)]|L^P,K_y\rangle$, which can be used to distinguish between $t=A_1$ and A_2 for $|K_y|=0$ (mod 3) and between the components E_ρ and E_λ for $|K_y|=1,2$ (mod 3).

By examining the projection of intrinsic states on the symmetry axis, it is possible to show that for a (ν_1,ν_2^l) vibration, the algebraic quantum number $|K_y|$ and the geometric K are related by

$$|K_y| = |K \pm 2l|. \tag{13}$$

The + (−) sign corresponds to the $+l$ $(-l)$ projections of the vibrational angular momentum along the symmetry axis. The $|K_y|$ quantum number is analogous to the G quantum number

$$G = |K \pm l|, \tag{14}$$

considered by Watson [15]. Since both the G and $|K_y|$ labels are defined (mod 3), they provide an equivalent classification scheme. It is important to note that, unlike for $l=0$ where $|K_y|=G=|K|$, for $l>0$ there are two possible $|K_y|$ or G values for each K. Thus $|K_y|$ (or G) is an additional quantum number needed to supplement the D_3 and parity labels for a complete classification of the oblate top states. As an example, in E vibrations of the type $(\nu_1,\nu_2^{l=1})$ the two L_E^- levels with $K=3$ are distinguished by $|K_y|=5$ $(G=2)$ and $|K_y|=1$ $(G=4)$.

From the above discussion it is evident that the last two terms in Eq. (10) commute with the Hamiltonian of Eq. (3) and thus correspond to *exact* symmetries. Their eigenvalues $\kappa_3 L(L+1)+\kappa_4 K_y^2$ are similar in form to those of a symmetric top. All rotational states with $K\neq 0$ are split in two, with different $|K_y|$ assignments in accord with Eqs. (12) and (13). The splitting between $+l$ and $-l$ levels is $8\kappa_4 lK$, i.e., increases linearly with K. The κ_1 and κ_2 terms in Eq. (10) do not commute with the intrinsic Hamiltonian of Eq. (7). 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.

The one- and two-body u(7) Hamiltonian presented so far does not exhibit l-type doubling and consequently its calculated A_1 and A_2 levels occur in degenerate doublets. This degeneracy can be lifted with the inclusion of higher-order terms that break the $|K_y|$ symmetry. An example of such a three-body term is considered below. A similar situation is encountered in Watson's effective Hamiltonian [15], whose major terms are diagonal in the quantum number G, and small higher-order correction terms (with $\Delta G=6$) are important for the splitting of the (A_1,A_2) doublets.

C. Applications

Among the different features in the proposed u(7) spectrum-generating algebra, as compared to the $u_1(4)\otimes u_2(4)$ scheme, is the exact account of the point symmetry. This is particularly important for degenerate vibrations present in symmetric top X_3 molecules. With that in mind, we apply the present formalism to the vibrational spectrum of H_3^+. This molecule, with a triangular equilibrium shape, has been studied extensively [16] and can serve as a test ground for different spectrum-generating algebras. It was shown [4,12] that the u(4)⊗u(4) model encounters some difficulties in the description of the vibrational spectrum of H_3^+ [2]. Our goal here is to examine to what extent these difficulties arise from the lack of an exact treatment of the molecular point-group symmetry. For that purpose we use a simple u(7) Hamiltonian

$$H=H_{\rm int}(\xi_1,\xi_2,R^2)+\kappa_4\hat{K}_y\cdot\hat{K}_y+\zeta\, T^\dagger\cdot\tilde{T}, \tag{15}$$

where $H_{\rm int}$ is given in Eq. (7) and $T^\dagger=(\pi_1^\dagger\cdot\pi_1^\dagger-\pi_2^\dagger\cdot\pi_2^\dagger)\times\pi_2^\dagger+2(\pi_1^\dagger\cdot\pi_2^\dagger)\pi_1^\dagger$. The parameters are determined from a fit to the estimated band origins in H_3^+ [17]. In the fit we minimize $\Sigma_i w_i\,[E_i(\text{calc})-E_i]^2$ with weights $w_i=1.0$ for the two fundamentals (the only band origins known from experiment) and $w_i=0.1$ for the other levels. As shown in Table I, the u(7) calculation shows a significant improvement over the $u_1(4)\otimes u_2(4)$ fit, thus highlighting the importance of incorporating the discrete point-group symmetry in the algebraic description. It is clear, however, that the simple u(7) Hamiltonian (15) used here is not sufficient to reach the accuracy of *ab initio* calculations. Adding more interactions (e.g., rotation-vibration terms and/or additional higher-order terms in the algebraic Hamiltonian) can improve the spectroscopic accuracy of the fit at the expense of more parameters. The need for such terms is expected in view of the known large rotation-vibration couplings in H_3^+, the non-Born-Oppenheimer corrections in the H_3^+ potential [18], and the presence of higher-order terms in *ab initio* potential surfaces (31 terms [17]).

TABLE I. H_3^+ band origins in cm^{-1}.

				u(4)⊗u(4)[c]	
(ν_1,ν_2^l)	t	DMT[a]	u(7)[b]	I	II
$(0,0^0)$	A_1	0	0	0	0
$(0,1^1)$	E	2521	2522	2506	2506
$(1,0^0)$	A_1	3178	3184	3181	3174
$(0,2^0)$	A_1	4778	4770	4928	4929
$(0,2^2)$	E	4998	5007	4928	4929
$(1,1^1)$	E	5554	5543	5603	5597
$(2,0^0)$	A_1	6262	6233	6233	6243
$(0,3^1)$	E	7006	7019	7266	7269
$(0,3^3)$	A_1	7283	7276	7266	7269
$(0,3^3)$	A_2	7493	7492	7266	7269

[a] From [17].

[b] Calculated with $N=40$, $R^2=1.65$, $\xi_1=12.3$ cm^{-1}, $\xi_2=21.3$ cm^{-1}, $\kappa_4=-14.8$ cm^{-1}, and $\zeta=-0.38$ cm^{-1}.

[c] From [2].

V. SUMMARY AND CONCLUSIONS

In this work we have introduced a u(7) spectrum-generating algebra for the description of triatomic molecules. Particular emphasis was put on the ability of the model to adequately treat degenerate vibrations as they occur in oblate top X_3 molecules, by imposing the discrete point-group symmetry on the Hamiltonian. A normal mode analysis revealed that the characteristic pattern of fundamental vibrations of a symmetric bent X_3 molecule is recovered in this model. Algebraic terms affecting the vibrations, rotations, and their coupling have been identified. The u(7) algebra provides a quantum number $|K_y|$ (the analog of the quantum number G), needed for a complete classification of oblate top states. Although we have focused the discussion on oblate top X_3 molecules, the u(7) model can be applied to any triatomic molecule, both linear and bent. In each case the results of a normal mode analysis are in agreement with those dictated by the relevant point group [4]. All these features of the u(7) model are necessary ingredients for a proper description of rotations and vibrations in triatomic molecules.

We have compared the present model with two other algebraic approaches. The main difference between the models lies in the choice of the model space. In the u(7) model the distribution of quanta among the two dipole degrees of freedom is determined dynamically by the Hamiltonian, whereas in the u(4)⊗u(4) model [or its simplified u(2)⊗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 different ingredient that enables an exact treatment of the point-group symmetry and a proper description of degenerate vibrations. Unlike in the $u_1(4) \otimes u_2(4)$ case, in the u(7) scheme there is no need to use nonanalytic (absolute value) interaction terms to describe bent molecules. On the other hand, the u(7) algebra does not have a $so(4) \otimes so(4)$ dynamical symmetry, which leads to considerable simplification in the u(4)⊗u(4) description of linear molecules. In a fit to the band origins of $H_3{}^+$ we showed that a simple u(7) Hamiltonian with the proper point-group symmetry improves considerably the previous $u_1(4) \otimes u_2(4)$ description of triangular X_3 molecules.

Refinements of the simple u(7) Hamiltonian are needed to achieve spectroscopic accuracy. The choice of rotation-vibration terms and of additional higher-order algebraic terms may be guided by examining corresponding terms in Watson's effective Hamiltonian. The inherent simplicity in algebraic methods is potentially important for polyatomic molecules, where *ab initio* calculations are difficult to perform. A first step in this direction would be to extend the current procedure to larger molecules, resulting in a spectrum-generating algebra of $u(3n-2)$ as a candidate for a spectrum-generating algebra for vibrations and rotations in n-atomic molecules with prescribed point-group symmetries. Work along these lines, as well as on the rotational aspects of these models, is in progress and will be reported separately.

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