Algebraic approach to molecular rotation-vibration spectra. II. Triatomic molecules

van Roosmalen, O. S.; Iachello, F.; Levine, R. D.; Dieperink, A. E. L.

Algebraic approach to molecular rotation-vibration spectra. II. Triatomic molecules

O. S. van Roosmalen, F. Iachello, R. D. Levine, and A. E. L. Dieperink

Algebraic approach to molecular rotation-vibration spectra. II. Triatomic molecules

O. S. van Roosmalen

Kernfysisch Versneller Instituut, Rijksuniversiteit Groningen, The Netherlands,
Institute for Theoretical Physics, University of California, Santa Barbara, California 93106,
and W. K. Kellogg Radiation Laboratory 106—38, California Institute of Technology, Pasadena,
California 91125[a]

F. Iachello

Wright Nuclear Structure Laboratory, Yale University, New Haven, Connecticut 06511[b]
and Kernfysisch Versneller Instituut, Rijksuniversiteit Groningen, The Netherlands

R. D. Levine

The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University, Jerusalem 91904, Israel

A. E. L. Dieperink

Kernfysisch Versneller Instituut, Rijksuniversiteit Groningen, The Netherlands

The algebraic approach to molecular rotation-vibration spectra introduced in a previous article is extended from di- to tri- and polyatomic molecules. The spectrum generating algebra appropriate to triatomic molecules $U(4) \otimes U(4)$ is explicitly constructed. Its dynamical symmetries and their relation to rigid, nonrigid, linear, and nonlinear structures are discussed. Applications to the spectra of HCN, CO_2, and H_3^+ are considered. In particular, it is shown that the algebraic description can account for the Fermi resonances occurring in CO_2. Some remarks are made on the spectrum generating algebras appropriate to polyatomic molecules.

I. INTRODUCTION

In a previous article[1] (in the following referred to as I), two of us have suggested an algebraic approach to molecular rotation-vibration spectra and considered the particular case of diatomic molecules. In that article, it was suggested that the algebraic approach may lead to considerable simplifications over the usual approaches (Dunham expansion and potential approach) in the treatment of two problems.

(i) The description of tri- and polyatomic molecules.

(ii) The calculation of transition probabilities in laser excitation[2] and atom—molecule and molecule—molecule collisions.[3]

In this article we consider the first problem and construct explicitly the spectrum generating algebra (SGA) $U(4) \otimes U(4)$, appropriate to triatomic molecules. Although this algebra may be capable of describing both rigid and nonrigid[4] (van der Waals[5]) molecules, we shall concentrate our attention to linear and nonlinear molecules with a rigid character. Furthermore, we shall consider only energy spectra and defer a discussion of transition probabilities to a subsequent investigation.

In addition to presenting the formalism appropriate to triatomic molecules, our main purpose is to show that the algebraic approach is capable of providing, with little effort, a fair quantitative description of the observed spectra. We thus consider in detail applications

of the algebraic approach to the description of the spectra of HCN, CO_2, and H_3^+. In particular, we show that this approach can account even for fine details of the observed spectra, such as the Fermi resonances in CO_2.

The spectrum generating algebra $U(4) \otimes U(4)$ can be further generalized to more complex molecules. In the last section of this article we describe how this can be achieved. A preliminary, brief, version of some of the work presented here has already appeared.[6] Some details have also been discussed by one of us separately.[7]

II. VIBRON MODEL FOR TRIATOMIC MOLECULES

Spectra of diatomic molecules were generated in I by introducing a set of boson creation $b_\alpha^\dagger$ and annihilation b_α operators $\alpha = 1, \ldots, 4$. These operators satisfy Bose commutation relations [Eq. (2.1) of I] and provide a basis

$$B: \quad b_\alpha^\dagger \ldots b_{\alpha'}^\dagger |0\rangle , \qquad (2.1)$$

in which the Hamiltonian H can be diagonalized. The construction of the basis B is simplified by the use of group theory, since the N boson states [Eq. (2.1)] span the totally symmetric irreducible representation $[N]$ of the group $U(4)$, equivalent to a Young tableau with N squares in a row. This group is generated by the $4^2 = 16$ operators

$$G_{\alpha\alpha'} = b_\alpha^\dagger b_{\alpha'} . \qquad (2.2)$$

In order to construct states with good angular momentum, the four boson operators $b_\alpha^\dagger$ were divided

---

[a] Present address.
[b] Permanent address.

into a scalar, called $\sigma^\dagger$ and a vector, called $\pi_\mu^\dagger$ ($\mu = +1$, $0, -1$), such that the corresponding one boson states had angular momentum J and parity P,

$$\sigma^\dagger |0\rangle : J^P = 0^\dagger \ ,$$

$$\pi_\mu^\dagger |0\rangle : J^P = 1^- \ .$$

(2.3)

The π and σ bosons were called *vibrons*. Spectra of diatomic molecules were obtained by diagonalizing the model Hamiltonian H, constructed using the generators (2.2), within an irreducible representation $[N]$ of $U(4)$. This representation was thus assumed to span the Hilbert space of the bound (and quasibound) rotational-vibrational states (finite in number) of the molecule in a given electronic configuration.

A. Boson operators and group structure for triatomic molecules

In order to construct the spectrum generating algebra appropriate to triatomic molecules we proceed as in I. A triatomic molecule has six internal degrees of freedom, that can be taken as the two vectors r_1 and r_2, specifying the interatomic distances (Fig. 1). Thus, here one has twice as many degrees of freedom as in diatomic molecules, where the internal degrees of freedom are characterized by only one vector r. In analogy with I, we suggest that the spectrum generating algebra appropriate to triatomic molecules is formed by the direct product of two $U(4)$ groups, that we denote by $U^{(1)}(4) \otimes U^{(2)}(4)$. This is because addition of degrees of freedom, described by a group G, can be achieved by taking the direct product $G \otimes G$. Correspondingly, we introduce two types of boson operators $b_{i\alpha}^\dagger$, $b_{i\alpha}$; $i = 1, 2$; $\alpha = 1, 2, 3, 4$. Operators with different index i commute

$$[b_{1\alpha}, b_{2\alpha'}^\dagger] = 0, \quad [b_{1\alpha}, b_{2\alpha'}] = 0,$$

$$[b_{2\alpha}, b_{1\alpha'}^\dagger] = 0, \quad [b_{2\alpha}^\dagger, b_{1\alpha'}^\dagger] = 0 \ ,$$

(2.4)

while operators with the same index satisfy Bose commutation relations

$$[b_{i\alpha}, b_{i\alpha'}^\dagger] = \delta_{\alpha\alpha'}, \quad [b_{i\alpha}, b_{i\alpha'}] = 0,$$

$$[b_{i\alpha}^\dagger, b_{i\alpha'}^\dagger] = 0, \quad i = 1, 2 \ .$$

(2.5)

Basis states are now of the form

$$B' : b_{1\alpha}^\dagger \ldots b_{1\alpha'}^\dagger \cdot b_{2\beta}^\dagger \ldots b_{2\beta'}^\dagger |0\rangle \ ,$$

(2.6)

and span the product representation $[N_1] \otimes [N_2]$ of $U^{(1)}(4) \otimes U^{(2)}(4)$, where N_1 and N_2 are the number of bosons (vibrons) of type 1 and 2, respectively. The group $U^{(1)}(4) \otimes U^{(2)}(4)$ is generated by the $2 \times 4^2 = 32$ operators

$$G_{1\alpha\alpha'} = b_{1\alpha}^\dagger b_{1\alpha'}, \quad G_{2\beta\beta'} = b_{2\beta}^\dagger b_{2\beta'} \ .$$

(2.7)

All operators are expanded in terms of the generators (2.7). For example, the Hamiltonian H may be written as

$$H = H_1 + H_2 + H_{12} \ ,$$

(2.8)

with

$$H_i = h_{i0} + \sum_{\alpha\alpha'} \epsilon_{i\alpha\alpha'} G_{i\alpha\alpha'}$$

$$+ \frac{1}{2} \sum_{\alpha\alpha'\beta\beta'} u_{i\alpha\alpha'\beta\beta'} G_{i\alpha\alpha'} G_{i\beta\beta'} + \cdots; \quad i = 1, 2 \ ,$$
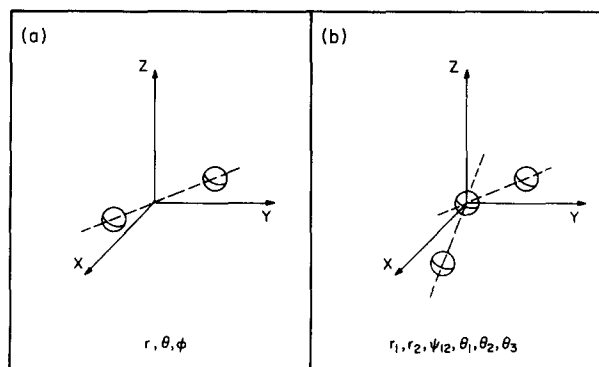
FIG. 1. Schematic representation of the geometric structure of a triatomic molecule.

$$V_{12} = \sum_{\alpha\alpha'\beta\beta'} w_{\alpha\alpha'\beta\beta'} G_{1\alpha\alpha'} G_{2\beta\beta'} + \cdots \ .$$

(2.9)

Since H conserves, by construction, both N_1 and N_2, it can be diagonalized within the basis (2.6).

As in I, it is convenient to assign to the boson operators $b_{1\alpha}^\dagger$, $b_{2\alpha}^\dagger$ definite transformation properties under rotations and inversions. We thus introduce σ and π vibrons of type 1 and 2, with

$$\sigma_1^\dagger, \sigma_2^\dagger : J^P = 0^\dagger \ ,$$

$$\pi_{1\mu}^\dagger, \pi_{2\mu}^\dagger, \quad \mu = -1, 0 + 1 : J^P = 1^- \ .$$

(2.10)

The commutation relations of the vibron operators (2.10) follow from Eqs. (2.4) and (2.5) above. In I, it was suggested that the vectorlike nature $J^P = 1^-$ of the π vibrons was related to the dipole character of the degrees of freedom of a diatomic molecule. Similarly here, the vectorlike nature of the two types of π vibrons π_1 and π_2 can be viewed as corresponding to the dipole character of the normal coordinates of a triatomic molecule.

B. Calculation of spectra

In calculating the spectrum of a given triatomic molecule, one begins by specifying the Hamiltonian H. Since this Hamiltonian must be rotation and reflection invariant, it is convenient to introduce boson annihilation operators that transform appropriately under rotations

$$\tilde{\sigma}_i = \sigma_i, \quad \tilde{\pi}_{i\mu} = (-)^\mu \pi_{i,-\mu}, \quad i = 1, 2 \ .$$

(2.11)

This notation is slightly different than in I and it has been introduced here in order to make phases in the computer program described below simpler to deal with. The tensor product of two operators $t_{l,\mu}$ and $t_{l',\mu'}$ will still be denoted as in I,

$$[t_l \times t_{l'}]_\kappa^{(k)} = \sum_{\mu,\mu'} \langle l\mu l'\mu' | k\kappa\rangle t_{l,\mu} t_{l',\mu'} \ ,$$

(2.12)

but, occasionally, we will also introduce curly brackets to denote the same angular momentum coupling.

Retaining only up to quadratic terms in the generators and using the conservation of vibron numbers

$$N_i = \sigma_i^\dagger \sigma_i + \sum_\mu \pi_{i\mu}^\dagger \pi_{i\mu}, \quad i = 1, 2 \ ,$$

(2.13)

i.e.,

$$[H,N_1]=[H,N_2]=0 ,$$ (2.14)

we can write the most general Hamiltonian (2.9) as

$$H_i = h'_{i0} + e'^{(1)}_{i1}[\pi^\dagger_i \times \tilde{\pi}_i]^{(0)}_0 + e'^{(2)}_{i1}\{[\pi^\dagger_i \times \pi^\dagger_i]^{(0)} \times [\tilde{\pi}_i \times \tilde{\pi}_i]^{(0)}]\}^{(0)}_0 + e'^{(2)}_{i2}\{[\pi^\dagger_i \times \pi^\dagger_i]^{(2)} \times [\tilde{\pi}_i \times \tilde{\pi}_i]^{(2)}]\}^{(0)}_0$$
$$+ e'^{(2)}_{i3}\{[\pi^\dagger_i \times \pi^\dagger_i]^{(0)} \times [\tilde{\sigma}_i \times \tilde{\sigma}_i]^{(0)} + [\sigma^\dagger_i \times \sigma^\dagger_i]^{(0)} \times [\tilde{\pi}_i \times \tilde{\pi}_i]^{(0)}\}^{(0)}_0 ; \quad i=1,2,$$ (2.15)

and

$$V_{12} = f^{(1,1)}_1\{[\pi^\dagger_1 \times \pi^\dagger_2]^{(0)} \times [\tilde{\sigma}_1 \times \tilde{\sigma}_2]^{(0)} + [\sigma^\dagger_1 \times \sigma^\dagger_2]^{(0)} \times [\tilde{\pi}_1 \times \tilde{\pi}_2]^{(0)}\}^{(0)}_0 + f^{(1,1)}_2\{[\pi^\dagger_1 \times \sigma^\dagger_2]^{(1)} \times [\tilde{\pi}_2 \times \tilde{\sigma}_1]^{(1)}$$
$$+ [\pi^\dagger_2 \times \sigma^\dagger_1]^{(1)} \times [\tilde{\pi}_1 \times \tilde{\sigma}_2]^{(1)}\}^{(0)}_0 + f^{(1,1)}_3\{[\pi^\dagger_1 \times \pi^\dagger_2]^{(0)} \times [\tilde{\pi}_1 \times \tilde{\pi}_2]^{(0)}\}^{(0)}_0 + f^{(1,1)}_4\{[\pi^\dagger_1 \times \pi^\dagger_2]^{(1)}$$
$$\times [\tilde{\pi}_1 \times \tilde{\pi}_2]^{(1)}\}^{(0)}_0 + f^{(1,1)}_5\{[\pi^\dagger_1 \times \pi^\dagger_2]^{(2)} \times [\tilde{\pi}_1 \times \tilde{\pi}_2]^{(2)}\}^{(0)}_0 .$$ (2.16)

The Hamiltonian (2.15)–(2.16) is written in normal ordered form, i.e., all creation operators to the left of all annihilation operators.

An alternative way of rewriting the Hamiltonian H is by introducing operators with definite tensor properties under rotations

$$n_{i\sigma} = [\sigma^\dagger_i \times \tilde{\sigma}_i]^{(0)}_0 = \sigma^\dagger_i \sigma_i ,$$

$$n_{i\pi} = -\sqrt{3}[\pi^\dagger_i \times \tilde{\pi}_i]^{(0)}_0 = \sum_\mu \pi^\dagger_{i\mu}\pi_{i\mu} ,$$

$$J^{(1)}_{i\mu} = \sqrt{2}[\pi^\dagger_i \times \tilde{\pi}_i]^{(1)}_\mu ,$$

$$D^{(1)}_{i\mu} = [\pi^\dagger_i \times \tilde{\sigma}_i + \sigma^\dagger_i \times \tilde{\pi}_i]^{(1)}_\mu ,$$ (2.17)

$$R^{(1)}_{i\mu} = i[\pi^\dagger_i \times \tilde{\sigma}_i - \sigma^\dagger_i \times \tilde{\pi}_i]^{(1)}_\mu ,$$

$$Q^{(2)}_{i\mu} = [\pi^\dagger_i \times \tilde{\pi}_i]^{(2)}_\mu .$$

Here $n_{i\sigma}$, $n_{i\pi}$ are number operators for σ and π vibrons, $J^{(1)}_{i\mu}$ is the angular momentum operator, $D^{(1)}_{i\mu}$ and $R^{(1)}_{i\mu}$ are the two dipole operators, and $Q^{(2)}_{i\mu}$ is the quadrupole operator of system i. The Hamiltonian (2.15)–(2.16) can now be written as

$$H_i = h'_{i0} + e''^{(1)}_{i1} n_{i\pi} + e''^{(2)}_{i1} n^2_{i\pi} + e''^{(2)}_{i2} J^{(1)}_i \cdot J^{(1)}_i$$
$$+ e''^{(2)}_{i3} D^{(1)}_i \cdot D^{(1)}_i ; \quad i=1,2 ,$$ (2.18)

and

$$V_{12} = f'^{(1,1)}_1 D^{(1)}_1 \cdot D^{(1)}_2 + f'^{(1,1)}_2 R^{(1)}_1 \cdot R^{(1)}_2$$
$$+ f'^{(1,1)}_3 n_{1\pi} \cdot n_{2\pi} + f'^{(1,1)}_4 J^{(1)}_1 \cdot J^{(1)}_2 + f'^{(1,1)}_5 Q^{(2)}_1 \cdot Q^{(2)}_2 .$$ (2.19)

The dots in Eqs. (2.18) and (2.19) denote scalar products

$$T_i \cdot T_j = \sum_\mu (-)^\mu T^{(l)}_{i\mu} T^{(l)}_{j,-\mu} .$$ (2.20)

The relation between the coefficients in Eqs. (2.15), (2.16), and Eqs. (2.18) and (2.19) is

$$h_{0i} = N_i e''^{(2)}_{i3} + h''_{0i} ,$$

$$e'^{(1)}_{i1} = -\sqrt{3} e''^{(1)}_{i1} - \sqrt{3} e''^{(2)}_{i1} - 2\sqrt{3} e''^{(2)}_{i2} - 2\sqrt{3}(N_i - 1)e''^{(2)}_{i3} ,$$

$$e'^{(2)}_{i1} = e''^{(2)}_{i1} - 2e''^{(2)}_{i2} - 2e''^{(2)}_{i3} ,$$

$$e'^{(2)}_{i2} = \sqrt{5} e''^{(2)}_{i1} + \sqrt{5} e''^{(2)}_{i2} - 2\sqrt{5} e''^{(2)}_{i3} ,$$ (2.21)

$$e'^{(2)}_{i3} = -\sqrt{3} e''^{(2)}_{i3} ,$$

and

$$f^{(1,1)}_1 = -\sqrt{3} f'^{(1,1)}_1 - \sqrt{3} f'^{(1,1)}_2 ,$$

$$f^{(1,1)}_2 = -\sqrt{3} f'^{(1,1)}_1 + \sqrt{3} f'^{(1,1)}_2 ,$$

$$f^{(1,1)}_3 = f'^{(1,1)}_3 - 2f'^{(1,1)}_4 + \tfrac{5}{3} f'^{(1,1)}_5 ,$$ (2.22)

$$f^{(1,1)}_4 = \sqrt{3} f'^{(1,1)}_3 - \sqrt{3} f'^{(1,1)}_1 - \tfrac{5}{6} f'^{(1,1)}_5 ,$$

$$f^{(1,1)}_5 = \sqrt{5} f'^{(1,1)}_3 + \sqrt{5} f'^{(1,1)}_4 + \tfrac{1}{6} f'^{(1,1)}_5 .$$

The calculation of the rotation-vibration spectrum of a given molecule is done by diagonalizing the Hamiltonian $H = H_1 + H_2 + V_{12}$ in an appropriate basis. However, before describing details of this diagonalization, we prefer to discuss dynamical symmetries of the Hamiltonian H. The study of these dynamical symmetries facilitates the solution of the corresponding eigenvalue problem.

We also note at this point that stopping the expansion of the Hamiltonian H at terms which are bilinear in the generators $G_{\alpha\beta}$ as in Eqs. (2.15) and (2.16) does not imply that higher order terms cannot be incorporated (indeed they can) or that they are necessarily small or of limited physical significance. For example, without higher order terms, it is not possible to account for the Darling–Dennison coupling that will be mentioned in Sec. V C. The truncation to bilinear terms is done here only for convenience and simplicity.

III. DYNAMICAL SYMMETRIES

As discussed in I, one of the major advantages of the algebraic approach is that it allows one to construct, in some special cases, analytic expressions for all observable quantities. These special cases correspond to dynamical symmetries of the Hamiltonian H. We now proceed to construct the dynamical symmetries appropriate to triatomic molecules by considering all possible subgroup chains of the dynamical group $U^{(1)}(4) \otimes U^{(2)}(4)$.

A. Subgroup chains of $U(4) \otimes U(4)$

The group structure of $U^{(1)}(4) \otimes U^{(2)}(4)$ is obviously much richer than that of $U(4)$. In its study, we begin by noting that each $U^{(i)}(4)$ group has two possible subgroup chains, given by Eq. (3.2) of I. The generators of the corresponding group can be written as

$$\{G_i\}_{O^{(i)}(4)} \equiv \{D^{(1)}_{i\mu}, J^{(1)}_{i\mu}\} ,$$

$$\{G_i\}_{U^{(i)}(3)} \equiv \{Q^{(2)}_{i\mu}, J^{(1)}_{i\mu}, n_{i\pi}\}, \quad i=1,2 .$$ (3.1)

Both groups, $0^{(i)}(4)$ and $U^{(i)}(3)$, contain the rotation groups $0^{(i)}(3)$ as subgroups. These have generators

$$\{G_i\}_{0^{(i)}(3)} \equiv \{J_{iu}^{(1)}\} , \tag{3.2}$$

and are, in turn, contained in $U^{(i)}(4)$, with generators

$$\{G_i\}_{U^{(i)}(4)} \equiv \{n_{i\sigma}, n_{i\tau}, J_{iu}^{(1)}, D_{iu}^{(1)}, R_{iu}^{(1)}, Q_{iu}^{(2)}\} . \tag{3.3}$$

We shall, in the following discussion, omit the groups $0^{(i)}(2)$, corresponding to rotations around an axis, since these do not play any role, unless the molecule is placed in an external field.

Since the generators of type 1 commute with those of type 2, the commutation relations appropriate to each group are conserved if one adds corresponding operators with different label 1, 2. For example, the operators

$$J_u^{(1)} = J_{1u}^{(1)} + J_{2u}^{(1)}, \quad \mu = -1, 0, +1 , \tag{3.4}$$

satisfy the same commutation relations as the operators $J_{iu}^{(1)}, i = 1, 2$. The operators (3.4) generate a subgroup of $0^{(1)}(3) \otimes 0^{(2)}(3)$ that we denote by $0(3)$, i.e.,

$$0^{(1)}(3) \otimes 0^{(2)}(3) \supset 0(3), \tag{3.5}$$

with

$$\{G\}_{0(3)} \equiv \{J_{1u}^{(1)} + J_{2u}^{(2)}\} . \tag{3.6}$$

Note that no other linear combination of $J_{1u}^{(1)}$ and $J_{2u}^{(1)}$ leads to commutation relations that are appropriate to $0(3)$, and that Eq. (3.4) represents the usual rule of adding angular momenta. Similarly, one can introduce $U(4)$, $U(3)$, and $0(4)$ groups, with generators

$$\begin{aligned} \{G\}_{U(4)} \equiv \{&n_{1\sigma} + n_{2\sigma}, n_{1\tau} + n_{2\tau}, J_{1u}^{(1)} + J_{2u}^{(1)}, \\ &D_{1u}^{(1)} + D_{2u}^{(1)}, R_{1u}^{(1)} + R_{1u}^{(1)}, Q_{1u}^{(2)} + Q_{2u}^{(2)}\} , \end{aligned} \tag{3.7}$$

$$\{G\}_{U(3)} \equiv \{n_{1\tau} + n_{2\tau}, J_{1u}^{(1)} + J_{2u}^{(1)}, Q_{1u}^{(2)} + Q_{2u}^{(2)}\} ,$$

$$\{G\}_{0(4)} \equiv \{D_1^{(1)} + D_2^{(1)}, J_1^{(1)} + J_2^{(1)}\} .$$

Possible chains of subgroups of $U^{(1)}(4) \otimes U^{(2)}(4)$ are then

$$U^{(1)}(4) \otimes U^{(2)}(4) \supset U^{(1)}(3) \otimes U^{(2)}(3) \supset 0^{(1)}(3) \otimes 0^{(2)}(3) \supset 0(3) , \quad \text{I a}$$

$$\supset U^{(1)}(3) \otimes 0^{(2)}(4) \supset 0^{(1)}(3) \otimes 0^{(2)}(3) \supset 0(3) , \quad \text{I b}$$

$$\supset 0^{(1)}(4) \otimes 0^{(2)}(4) \supset 0^{(1)}(3) \otimes 0^{(2)}(3) \supset 0(3) , \quad \text{I c}$$

$$\supset U^{(1)}(3) \otimes U^{(2)}(3) \supset U(3) \supset 0(3) , \quad \text{II a}$$

$$\supset U(4) \supset U(3) \supset 0(3) , \quad \text{II b}$$

$$\supset 0^{(1)}(4) \otimes 0^{(2)}(4) \supset 0(4) \supset 0(3) , \quad \text{III a}$$

$$\supset U(4) \supset 0(4) \supset 0(3) . \quad \text{III b} \tag{3.8}$$

When one considers coupled systems a further complication arises due to an existing automorphism among the generators of $U^{(i)}(4)$ that conserves the commutation relations. Consider, in fact, the following transformation:

$$\begin{aligned} \pi_{iu}^\dagger &\to \tilde{\pi}_{iu} , \\ \sigma_i^\dagger &\to \tilde{\sigma}_i , \\ \tilde{\pi}_{iu} &\to -\pi_{iu}^\dagger , \\ \tilde{\sigma}_i &\to \sigma_i^\dagger . \end{aligned} \tag{3.9}$$

This transformation does not affect the commutation

relations (2.4) and (2.5). As a result, the automorphism

$$\mathcal{A}_i(R_{iu}^{(1)}) \to R_{iu}^{(1)}, \quad \mathcal{A}_i(n_{i\tau}) = -n_{i\tau} ,$$

$$\mathcal{A}_i(n_{i\sigma}) = -n_{i\sigma}, \quad \mathcal{A}_i(Q_{iu}^{(2)}) = -Q_{iu}^{(2)} , \tag{3.10}$$

$$\mathcal{A}_i(D_{iu}^{(1)}) = D_{iu}^{(1)}, \quad \mathcal{A}_i(J_{iu}^{(1)}) = J_{iu}^{(1)} .$$

leaves invariant the commutation relations between generators. By adding now generators of type 1 and transformed generators of type 2, we obtain two new subgroups, that we denote by $U^*(4)$ and $U^*(3)$, with generators

$$\{G\}_{U^*(3)} \equiv \{n_{1\tau} - n_{2\tau}, J_{1u}^{(1)} + J_{2u}^{(1)}, Q_{1u}^{(2)} - Q_{2u}^{(2)}\} ,$$

$$\{G\}_{U^*(4)} \equiv \{n_{1\sigma} - n_{2\sigma}, n_{1\tau} - n_{2\tau}, J_{1u}^{(1)} + J_{2u}^{(2)}, \tag{3.11}$$

$$D_{iu}^{(1)} + D_{2u}^{(1)}, R_{1u}^{(1)} - R_{2u}^{(1)}, Q_{1u}^{(2)} - Q_{2u}^{(2)}\} .$$

Note that, because of the properties (3.10), no additional groups $0^*(4)$ and $0^*(3)$ are obtained.

Using the groups $U^*(4)$ and $U^*(3)$ one can obtain three more subgroup chains

$$U^{(1)}(4) \otimes \bar{U}^{(2)}(4) \supset U^{(1)}(3) \otimes \bar{U}^{(2)}(3) \supset U^*(3) \supset 0(3) , \quad \text{IV a}$$

$$\supset U^*(4) \supset U^*(3) \supset 0(3) , \quad \text{IV b}$$

$$\supset U^*(4) \supset 0(4) \supset 0(3) . \quad \text{III c} \tag{3.12}$$

In this equation we have denoted $\mathcal{A}_2 U^{(2)}(4)$ and $\mathcal{A}_2 U^{(2)}(3)$ by $\bar{U}^{(2)}(3)$. Since, however, $\mathcal{A}_2$ is an automorphism of the corresponding algebras, there is no effect on the generator content, i.e., the algebras are the same. The effect appears only in the state labeling problem as it will be discussed below.

The chains in Eqs. (3.8) and (3.12) exhaust all possibilities (up to isomorphisms). In I, the chain associated with the $0(4)$ group was related to rigid diatomic molecules, while that associated with the $U(3)$ group was related to nonrigid molecules, using the rigidity parameter γ introduced by Berry.[4] When considering triatomic molecules the situation is more complex, since one can have, in principle, both bonds rigid, one bond rigid and one nonrigid and both nonrigid. Furthermore, the molecule can be linear or nonlinear. We We have divided the group chains in Eqs. (3.8) and (3.12) into four classes I, II, III, and IV. Class III appears to describe molecules with both bonds rigid and it will be discussed in detail in this article. Class II and IV appear to describe three-body systems in which all bonds are nonrigid. Class I may be used to describe mixed situations.

B. Labeling of states

The first problem one encounters is using the group chains (3.8) and (3.12) in the labeling of states. In this subsection, we discuss the labeling of states for some of the group chains. We begin with chain I a. This chain is of importance if one wants to perform a complete diagonalization of the most general Hamiltonian H (2.18) and (2.19). Furthermore, it is closely related to the chain introduced by Kellman, Amar, and Berry[8] in their group theoretical treatment of nonrigid triatomic molecules.

The labeling of states in chains I a, is done along the same lines of I. States are labeled by

$$U^{(1)}(4) \otimes U^{(2)}(4) \supset U^{(1)}(3) \otimes U^{(2)}(3) \supset 0^{(1)}(3) \otimes 0^{(2)}(3) \supset 0(3) \supset 0(2)$$

$$|[N_1]\,, \quad [N_2]\,, \quad n_{1r}\,, \quad n_{2r}\,, \quad J_1\,, \quad J_2\,, \quad J\,, \quad M\rangle\,.$$

$$(3.13)$$

The ranges of the quantum numbers n_{1r}, n_{2r}, J_1, J_2 contained in each representation $[N_1],[N_2]$ of $U^{(1)}(4) \otimes U^{(2)}(4)$ are the same as in I. The quantum number J takes on the integer values

$$|J_1 - J_2| \le J \le |J_1 + J_2|\,, \tag{3.14}$$

and $-J \le M \le J$ as usual. In this and in the following sections we shall use the same symbol for an operator and its eigenvalue, unless explicitly stated. The basis states (3.13) are simply related to the states of I by

$$|[N_1],[N_2], n_{1r}, n_{2r}, J_1, J_2, J, M\rangle$$

$$= \sum_{M_1, M_2} \langle J_1 M_1 J_2 M_2 | J M\rangle\,|[N_1], n_{1r}, J_1, M_1\rangle\,|[N_2], n_{2r}, J_2, M_2\rangle, \tag{3.15}$$

where $\langle J_1 M_1 J_2 M_2 | J M\rangle$ is a Clebsch–Gordan coefficient. An explicit expression for the states $|N, n_r, J, M\rangle$ in terms of vibron operators can be obtained[9]

$$|[N], n_r, J, M\rangle = \sqrt{\frac{4\pi}{(n_r + J + 1)!\,!\,(n_r - J)!\,!\,(N - n_r)!}}$$

$$\times (\sigma^\dagger)^{N-n_r}(\pi^\dagger \cdot \pi^\dagger)^{1/2(n_r - J)}\,\mathcal{Y}_{JM}(\pi^\dagger)\,|0\rangle\,, \tag{3.16}$$

where $\mathcal{Y}_{JM}$ is the vector spherical harmonics. Matrix elements of all generators of $U(4)$ can easily be calculated in the basis (3.16) and are given in Table I. Using angular momentum recoupling techniques, matrix elements of the most general Hamiltonian (2.18)–(2.19) can be calculated and the corresponding matrix diagonalized in the space of fixed J.[10] However, for realistic values of the vibron numbers N_1 and N_2, the dimension of the matrices to diagonalize is very large (Table II). A complete diagonalization of the Hamiltonian H in the full space is thus of limited value and other, more appropriate, techniques must be used as discussed below.

TABLE I. $O(3)$ Reduced matrix elements of the generators of $U(4)$ in the $U(4) \supset U(3)$ basis.

$$\langle [N], n_r, J \| n_r \| [N], n_r, J\rangle = n_r [2J+1]^{1/2}$$

$$\langle [N], n_r, J \| J^{(1)} \| [N], n_r, J\rangle = [J(J+1)(2J+1)]^{1/2}$$

$$\langle [N], n_r - 1, J - 1 \| D^{(1)} \| [N], n_r, J\rangle = [J(n_r + J + 1)(N - n_r + 1)]^{1/2}$$

$$\langle [N], n_r - 1, J + 1 \| D^{(1)} \| [N], n_r, J\rangle = [(J+1)(n_r - J)(N - n_r + 1)]^{1/2}$$

$$\langle [N], n_r - 1, J - 1 \| R^{(1)} \| [N], n_r, J\rangle = -[J(n_r + J + 1)(N - n_r + 1)]^{1/2}$$

$$\langle [N], n_r - 1, J + 1 \| R^{(1)} \| [N], n_r, J\rangle = [(J+1)(n_r - J)(N - n_r + 1)]^{1/2}$$

$$\langle [N], n_r, J \| Q^{(2)} \| [N], n_r, J\rangle = -(2n_r + 3)\left[\frac{J(J+1)(2J+1)}{6(2J-1)(2J+3)}\right]^{1/2}$$

$$\langle [N], n_r, J + 2 \| Q^{(2)} \| [N], n_r, J\rangle = \left[\frac{(J+2)(J+1)(n_r + J + 3)(n_r - J)}{(2J+3)}\right]^{1/2}$$

TABLE II. Number of states of a given angular momentum and parity J^P that occur in the representation $[N] \otimes [N]$ of $U^{(1)}(4) \otimes U^{(2)}(4)$.

N \ J^P	0^+	1^+	1^-	2^+	2^-
6	44	28	68	84	44
10	146	110	250	330	190
30	2736	2480	5200	7440	4720
50	11726	11050	22750	33150	21450
100	88451	85850	174250	257550	169150

We now come to a discussion of the three group chains III a, III b, and III c that contain the group $O(4)$ as a subgroup. These chains appear to be appropriate for a treatment of rigid molecules.

The group chain III a is characterized by the quantum numbers

$$U^{(1)}(4) \otimes U^{(2)}(4) \supset 0^{(1)}(4) \otimes 0^{(2)}(4) \supset 0(4) \supset 0(3) \supset 0(2)$$

$$|[N_1]\,, \quad [N_2]\,, \quad (\omega_1, 0)\,, \quad (\omega_2, 0)\,, \quad (\tau_1, \tau_2)\,, \quad J^P, \quad M\rangle\,. \tag{3.17}$$

The values taken on by the quantum numbers ω_1 and ω_2 are the same as in I,

$$\omega_1 = N_1, N_1 - 2, \ldots, 1 \text{ or } 0 \text{ for } N_1 = \text{odd or even;} \tag{3.18}$$

$$\omega_2 = N_2, N_2 - 2, \ldots, 1 \text{ or } 0 \text{ for } N_2 = \text{odd or even}\,.$$

In general, representations of $O(4)$ are characterized by two quantum numbers. For totally symmetric representations, the second quantum number is always zero. This quantum number was omitted in I but it is explicitly written in Eq. (3.17). The values of the quantum numbers (τ_1, τ_2) characterizing the representations of the combined $O(4)$ group contained in the product $0^{(1)}(4) \otimes 0^{(2)}(4)$ are given by[11]

$$\tau_1 = \omega_1 + \omega_2 - \mu - \nu, \quad \tau_2 = \mu - \nu; \tag{3.19}$$

$$\mu = 0, 1, \ldots, \min(\omega_1, \omega_2), \quad \nu = 0, 1, \ldots, \mu\,.$$

The values of the quantum numbers J^P characterizing the representations of $O(3)$ contained in one representation (τ_1, τ_2) of $O(4)$ are given by

$$J^P = 0^+, 1^-, \ldots, (\tau_1^+ \text{ or } \tau_1^-), \text{ when } \tau_2 = 0 \text{ and } (\tau_1 = \text{even or odd}),$$

$$J^P = \tau_2^\pm, (\tau_2 + 1)^\pm, \ldots, \tau_1^\pm, \text{ when } \tau_2 \ne 0\,. \tag{3.20}$$

Finally, the values of M contained in each J are given by the usual rule $-J \le M \le J$. This chain was briefly discussed in Ref. 6.

A second group chain containing $O(4)$ as a subgroup is III b. States here are characterized by the quantum numbers

$$U^{(1)}(4) \otimes U^{(2)}(4) \supset U(4) \supset 0(4) \supset 0(3) \supset 0(2)$$

$$|[N_1]\,, \quad [N_2]\,, \quad [N_1 + N_2 - n, n]\,, (\tau_1, \tau_2)\,, \quad J^P, \quad M\rangle\,. \tag{3.21}$$

The values of n can be obtained by using the usual rules for the product of Young tableaux[12]

$$
\underbrace{\Box\Box\ldots\Box}_{N_1} \otimes \underbrace{\Box\Box\ldots\Box}_{N_2} = \sum_n \overbrace{\Box\Box\ldots\Box\Box}^{N_1 \quad N_2-n} \qquad (3.22)
$$

This gives

$$
n = 0, 1, \ldots, \min(N_1, N_2) . \qquad (3.23)
$$

$$
\begin{array}{ccccccc}
U^{(1)}(4) \otimes \bar{U}^{(2)}(4) & \supset & U^*(4) & \supset & O(4) \supset O(3) \supset O(2) \\
\downarrow \quad\quad \downarrow & & \downarrow & & \downarrow \quad\quad \downarrow \quad\quad \downarrow
\end{array}
$$

$$
|[N_1], \; [N_2, N_2, N_2], \; [N_1 + N_2 - n^*, N_2, N_2, n^*], \; (\tau_1, \tau_2), \quad J^P, \quad M\rangle. \qquad (3.24)
$$

Since $\bar{U}^{(2)}(4)$ is related to $U^{(2)}(4)$ by the transformation (3.9), vibron operators of type 2 transform according to the conjugate fundamental representation $[1,1,1]$ instead of $[1]$ of $\bar{U}^{(2)}(4)$. States of vibron type 2 are thus labeled by $[N_2, N_2, N_2]$ in Eq. (3.24). This property gives rise to branching rules for the product $U^{(1)}(4) \otimes \bar{U}^{(2)}(4) \supset U^*(4)$ that are very different from those in Eq. (3.21). The values of n^* can be obtained by using again the rules for multiplying Young tableaux

$$
\underbrace{\Box\Box\ldots\Box}_{N_1} \otimes \underbrace{\begin{array}{c}\Box\Box\ldots\Box \\ \Box\Box\ldots\Box \\ \Box\Box\ldots\Box\end{array}}_{N_2} = \sum_{n^*} \overbrace{\begin{array}{c}\Box\Box\ldots\Box \quad \Box\Box\ldots\Box\Box \\ \Box\Box\ldots\Box \\ \underbrace{\Box\Box}_{n^*}\end{array}}^{N_2 \quad N_1 - n^*} . \qquad (3.25)
$$

These rules give

$$
n^* = 0, 1, \ldots, \min(N_1, N_2) . \qquad (3.26)
$$

The reduction from $U^*(4)$ to $O(4)$, from $O(4)$ to $O(3)$ and from $O(3)$ to $O(2)$ is then the same as above.

C. Energy eigenvalues for linear molecules

The three chains IIIa, IIIb, and IIIc allow one to construct analytic solutions to the eigenvalue problem for H appropriate to rigid molecules. This occurs whenever H can be written in terms only of invariant operators (Casimir operators) of one chain. We begin by considering chain IIIa. In this case, the Hamiltonian H can be written, up to two-body terms, as

The further reduction from $U(4)$ to $O(4)$ is rather complex and it will not be discussed here. Some examples of this reduction are given in Ref. 13. The reduction from $O(4)$ to $O(3)$ is given by Eq. (3.20) above, and that from $O(3)$ to $O(2)$ is given by the usual rule $-J \le M \le J$.

The third and last chain containing $O(4)$ as a subgroup is IIIc. States in this chain are characterized by the quantum numbers

$$
H^{(a)} = F + A_1 \mathcal{C}_2(O^1 4) + A_2 \mathcal{C}_2(O^2 4) + B \mathcal{C}_2(O4) + C \mathcal{C}_2(O3) . \qquad (3.27)
$$

In terms of the dipole $\mathbf{D}_1, \mathbf{D}_2$ and angular momentum $\mathbf{J}_1, \mathbf{J}_2$, operators of Eq. (2.17), the explicit form of $H^{(a)}$ is

$$
H^{(a)} = F + (A_1 + B)\mathbf{D}_1 \cdot \mathbf{D}_1 + (A_1 + B + C)\mathbf{J}_1 \cdot \mathbf{J}_1 + (A_2 + B)\mathbf{D}_2 \cdot \mathbf{D}_2
$$
$$
+ (A_2 + B + C)\mathbf{J}_2 \cdot \mathbf{J}_2 + 2B\,\mathbf{D}_1 \cdot \mathbf{D}_2 + 2(B + C)\mathbf{J}_1 \cdot \mathbf{J}_2 , \qquad (3.28)
$$

where we have used the expressions (3.7) of I for the Casimir invariants of $O(4)$ and $O(3)$:

$$
\mathcal{C}_2(O4) = \mathbf{D} \cdot \mathbf{D} + \mathbf{J} \cdot \mathbf{J}, \quad \mathcal{C}_2(O3) = \mathbf{J} \cdot \mathbf{J} . \qquad (3.29)
$$

The Hamiltonian $H^{(a)}$ can be diagonalized in the basis IIIa. Its eigenvalues are simply given by

$$
E^{(a)}(N_1, N_2, \omega_1, \omega_2, \tau_1, \tau_2, J^P, M) = F + A_1\omega_1(\omega_1 + 2)
$$
$$
+ B[\tau_1(\tau_1 + 2) + \tau_2^2] + C J(J + 1) . \qquad (3.30)
$$

In obtaining Eq. (3.30) we have made use of the explicit form of the eigenvalues of the Casimir operators in the appropriate basis.[11] In order to see the structure of the spectrum corresponding to Eq. (3.30), it is convenient to introduce the quantum numbers $v_1, v_2^{l_2}, v_3$, related to $\omega_1, \omega_2, \tau_1$, and τ_2 by

$$
\omega_1 = N_1 - 2v_1 ,
$$
$$
\omega_2 = N_2 - 2v_3 ,
$$
$$
\tau_1 = N_1 + N_2 - 2v_1 - v_2 - 2v , \qquad (3.31)
$$
$$
\tau_2 = l_2 .
$$

The eigenvalue formula (3.30) can then be rewritten as

$$
E(N_1, N_2, v_1, v_2^{l_2}, v_3, J^P, M) = F' - [4B(N_1 + N_2 + 4) + 4A_1(N_1 + 2)](v_1 + 1/2) + 4(A_1 + B)(v_1 + 1/2)^2 - 2B(N_1 + N_2 + 4)
$$
$$
\times (v_2 + 1) + B(v_2 + 1)^2 + B\,l_2^2 - [4B(N_1 + N_2 + 4) + 4A_2(N_2 + 2)](v_3 + 1/2) + 4(A_2 + B)(v_3 + 1/2)^2 + 8B(v_1 + 1/2)
$$
$$
\times (v_3 + 1/2) + 4B(v_3 + 1/2)(v_2 + 1) + 4B(v_1 + 1/2)(v_2 + 1) + C J(J + 1) . \qquad (3.32)
$$

where F' depends on F, N_1, N_2, A_1, A_2, B. Equation (3.32) describes the spectrum of a rigid linear triatomic molecule. In order to see that, we first note that, due to the branching rules (3.20), the angular momentum content of each vibrational band in Eq. (3.32) is precisely the same as that of a rigid linear triatomic molecule in which $\tau_2 = l_2$ is the projection of the angular momentum along an intrinsic axis,[14] Fig. 2. We also note that Eq. (3.32) is the same as the Dunham expansion of the energy levels of a rigid linear triatomic molecule[14]

$$
E(v_1, v_2^{l_2}, v_3, J) = E_0 + \alpha_2(v_1 + 1/2) + \alpha_2(v_2 + 1) + \alpha_3(v_3 + 1/2) + \chi_{11}(v_1 + 1/2)^2 + \chi_{22}(v_2 + 1)^2 + g_{22}\,l_2^2
$$
$$
+ \chi_{33}(v_3 + 1/2)^2 + \chi_{12}(v_1 + 1/2)(v_2 + 1) + \chi_{13}(v_1 + 1/2)(v_3 + 1/2) + \chi_{23}(v_2 + 1)(v_3 + 1/2) + \cdots . \qquad (3.33)
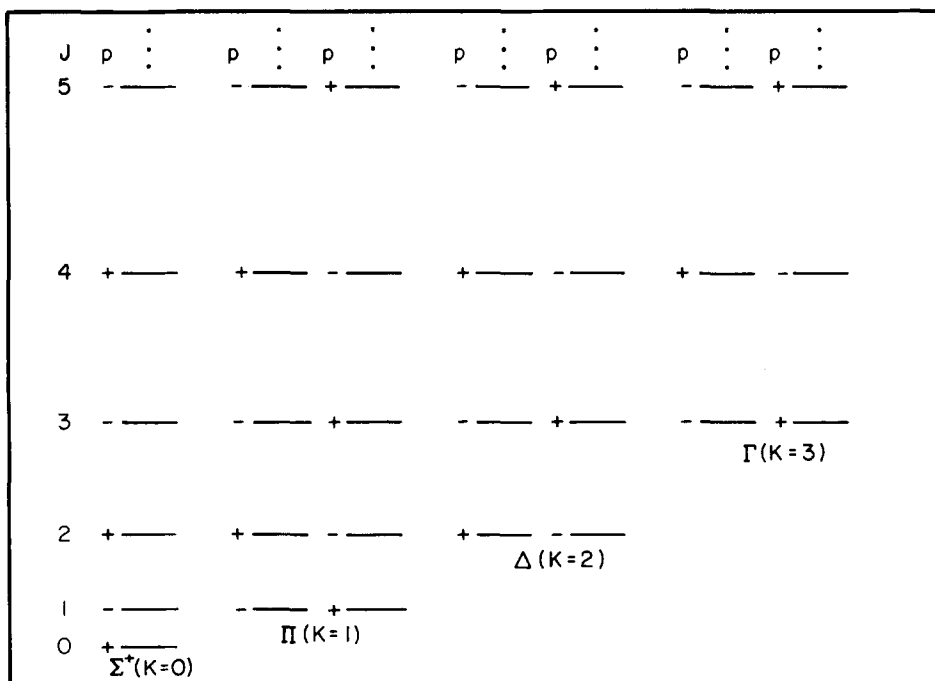$$

FIG. 2. Rotational levels in various species of vibrational levels of rigid linear triatomic molecules.

The quantum numbers v_1, v_2 and v_3 describe normal vibrations (see for instance Fig. 3). An example of the corresponding spectrum is shown in Fig. 4. It is interesting to identify the representations of the various groups in the chain (3.17) in the spectrum of Fig. 4. All states in the figure belong to the same representation $[6] \otimes [4]$ of $U^{(1)}(4) \otimes U^{(2)}(4)$. All bending modes on top of a fixed stretching quantum number belong to a representation of $0^{(1)}(4) \otimes 0^{(2)}(4)$. Finally, each vibrational state is the bandhead of a representation of the combined 0(4) group. This representation contains all the rotational excitations.

Because of the relations (3.31), one can see that the vibron numbers N_1 and N_2 are related to the maximum number of bound vibrational states for the normal modes v_1 and v_3. These numbers can thus, in principle, be determined by studying the vibrational spectra near the dissociation limits. It is interesting to note that, since each $U(4) \supset 0(4)$ chain can be associated with a three-dimensional Morse oscillator, as discussed in I, the group chain III a can be associated with the problem of
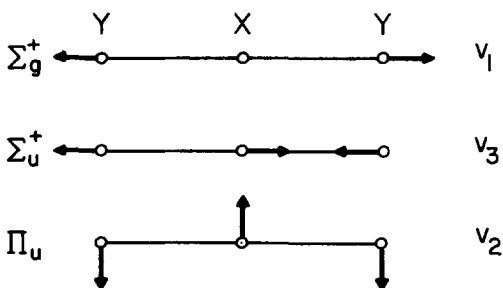
FIG. 3. Schematic representation of the normal vibrations of a linear XY_2 molecule.

two coupled three-dimensional Morse oscillators. From the identification (3.31) for the chain III a it is also clear that the vibron types 1 and 2 should be interpreted in this case as normal modes in the molecule.

Although Eq. (3.32) describes, to a good approximation, the energy levels of a rigid linear triatomic molecule, it has several limitations. For example, since the coefficient B of the l_2^2 term is related to that of the $(v_2 + 1)$ and $(v_2 + 1)^2$ terms, which must be negative, only negative values of this coefficient are obtained. Furthermore, the coefficient C of the $J(J+1)$ term is independent of $v_1, v_2^{l_2}, v_3$. All these limitations can be removed in the algebraic approach, either by retaining the dynamic symmetry III a and introducing higher order terms in the Casimir invariants, or by breaking the symmetry. An example of the latter approach will be discussed in Sec. IV.

We next discuss the chain III b. In this case, we must consider the Hamiltonian

$$H^{(b)} = F + A_1 \mathcal{C}_1(U4) + A_2 \mathcal{C}_2(U4) + B \, \mathcal{C}_2(04) + C \, \mathcal{C}_2(03). \quad (3.34)$$

Since $\mathcal{C}_1(U4)$ has eigenvalues given by $N_1 + N_2$, which is constant within a given representation of $U^{(1)}(4) \otimes U^{(2)}(4)$, we can absorb it in F. Furthermore, it is convenient to use, instead of $\mathcal{C}_2(U4)$, the operator $\mathfrak{M}$, called the Majorana operator, related to $\mathcal{C}_2(U4)$ by

$$\mathcal{C}_2(U4) = (3/4)(N_1 + N_2)(N_1 + N_2 + 4) - 2\mathfrak{M} . \quad (3.35)$$

This operator has a simple expression in terms of creation and annihilation operators

$$\mathfrak{M} = [\pi_1^\dagger \times \sigma_2^\dagger - \sigma_1^\dagger \times \pi_2^\dagger]^{(1)} \cdot [\tilde{\pi}_1 \times \tilde{\sigma}_2 - \tilde{\sigma}_1 \times \tilde{\pi}_2]^{(1)}$$
$$+ 2[\pi_1^\dagger \times \pi_2^\dagger]^{(1)} \cdot [\tilde{\pi}_1 \times \tilde{\pi}_2]^{(1)} . \quad (3.36)$$

The Hamiltonian

$$H^{(b)} = F' + A\mathfrak{M} + B \, \mathcal{C}_2(04) + C \, \mathcal{C}_2(03) \quad (3.37)$$

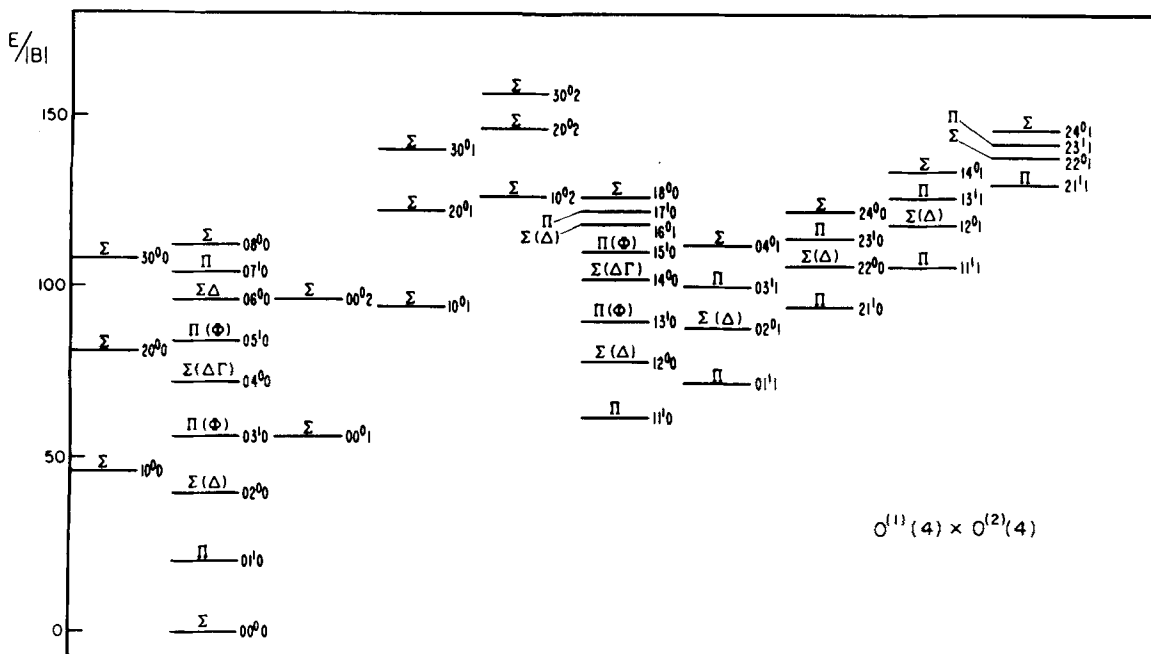FIG. 4. Schematic representation of a spectrum with $0^{(1)}(4) \otimes 0^{(2)}(4)$ symmetry III a. The energy levels are calculated using Eq. (3.32) with $N_1 = 6$, $N_2 = 4$, $A_2 = 0.25 B$, $A_2 = B$, and B negative. The spectrum is plotted in dimensionless units $E / |B|$. The vibrational quantum numbers v_1, $v_2^{l_2}$, v_3 are shown next to the levels and the species Σ, Π, ... above them. Only the energies of the lowest species Σ and Π are plotted. The higher species Δ, Φ, Γ, contained in each vibrational level are indicated in parenthesis, but their energy, which is slightly different from that of the Σ and Π species, is not plotted.

is diagonal in the basis III b, with eigenvalues

$$E^{(b)}(N_1, N_2, n, \tau_1, \tau_2, J^P, M)$$

$$= F' + A[(N_1 + N_2)n - n(n - 1)]$$

$$+ B[\tau_1(\tau_1 + 2) + v_2^2] + CJ(J + 1), \qquad (3.38)$$

where we have used the expectation value of the operator $\mathfrak{M}$, obtained using the expectation value of $\mathcal{C}_2(U4)$ given in Ref. 13,

$$\langle \mathfrak{M} \rangle = (N_1 + N_2)n - n(n - 1) . \qquad (3.39)$$

Again, it is convenient to introduce the quantum numbers $v_1, v_2^{l_2}, v_3$ related to n, τ_1, τ_2 by

$$n = v_2 + v_3 ,$$

$$\tau_1 = N_1 + N_2 - 2v_1 - 2v_3 - v_2^2 , \qquad (3.40)$$

$$\tau_2 = l_2 .$$

Equation (3.37) can then be recast in the form of a Dunham expansion

$$E(N_1, N_2, v_1, v_2^{l_2}, v_3, J^P, M) = F'' - 4B(N_1 + N_2 + 4)(V_1 + 1/2) + 4B(v_1 + 1/2)^2 + (A - 2B)(N_1 + N_2 + 4)(v_2 + 1) - (A - B)(v_2 + 1)^2$$

$$+ Bl_2^2 + (A - 4B)(N_1 + N_2 + 4)(v_3 + 1/2) - (A - 4B)(v_3 + 1/2)^2 + 4B(v_1 + 1/2)(v_2 + 1) - (2A - 4B)(v_3 + 1/2)(v_2 + 1)$$

$$+ 8B(v_1 + 1/2)(v_3 + 1/2) + CJ(J + 1) . \qquad (3.41)$$

The corresponding spectrum is shown in Fig. 5. The main difference between this spectrum and that corresponding to the chain III a is that Eq. (3.21) does not provide us with as many quantum numbers as Eq. (3.17) (missing label). As a result, it is not possible to adjust in Eq. (3.41) independently the energies of the three vibrational modes. Other differences are that Eq. (3.41) depends only on the total vibron number $N_1 + N_2$ (although this is not true for the branching rules) and that $H^{(b)}$ is invariant under interchange of vibrons of type 1 and 2. Hence the states (3.21) can also be characterized by the eigenvalues of a discrete operator P_{12} that interchanges vibrons of type 1 and 2. These are given by $P(-)^r$. Because of the points discussed above, the chain III b is not appropriate for a description of the most general rigid linear triatomic molecule, although it may describe some special cases.

The third and last chain containing the group O(4) is III c. Here again, we must consider the Hamiltonian

$$H^{(c)} = F + A_1^* \, \mathcal{C}_1(U^*4) + A_2^* \, \mathcal{C}_2(U^*4) + B \, \mathcal{C}_2(04) + C \, \mathcal{C}_2(03) . \qquad (3.42)$$

For the same reasons as in the discussion following Eq. (3.34) we prefer to introduce the Majorana operator $\mathfrak{M}^*$. This operator is related to $\mathfrak{M}$ by

$$\mathfrak{M}^* = (1/2)\mathcal{C}_2(0^14) + (1/2)\mathcal{C}_2(0^24) - (1/2)\mathcal{C}_2(04) - \mathfrak{M} , \qquad (3.43)$$

and, within the states of the chain III c has eigenvalues[13]

FIG. 5. Schematic representation of a spectrum with $U(4)$ symmetry IIIb. The energy levels are calculated using Eq. (3.41) with $N_1 = 6$, $N_2 = 4$, $A = -1.5 B$, and B negative. The notation is the same as in Fig. 4.

$$\langle \mathfrak{M} \rangle = -N_1 N_2 + n^*(N_1 + N_2) - n^*(n^* - 3) \ . \tag{3.44}$$

The Hamiltonian

$$H^{(c)} = F' + A^* \mathfrak{M}^* + B \, \mathfrak{C}_2(04) + C \, \mathfrak{C}_2(03) \tag{3.45}$$

is then diagonal in the basis IIIc with eigenvalues

$$E^{(c)}(N_1, N_2, n^*, \tau_1, \tau_2, J^P, M) = F' + A^* [-N_1 N_2 + n^*(N_1 + N_2) - n^*(n^* - 3)] + B[\tau_1(\tau_1 + 2) + \tau_2^2] + CJ(J + 1) \ . \tag{3.46}$$

Introducing the quantum numbers

$$n^* = v_3 \ , \qquad \tau_1 = N_1 + N_2 - 2v_1 - v_2 - 2v_3 \ , \qquad \tau_2 = l_2 \ , \tag{3.47}$$
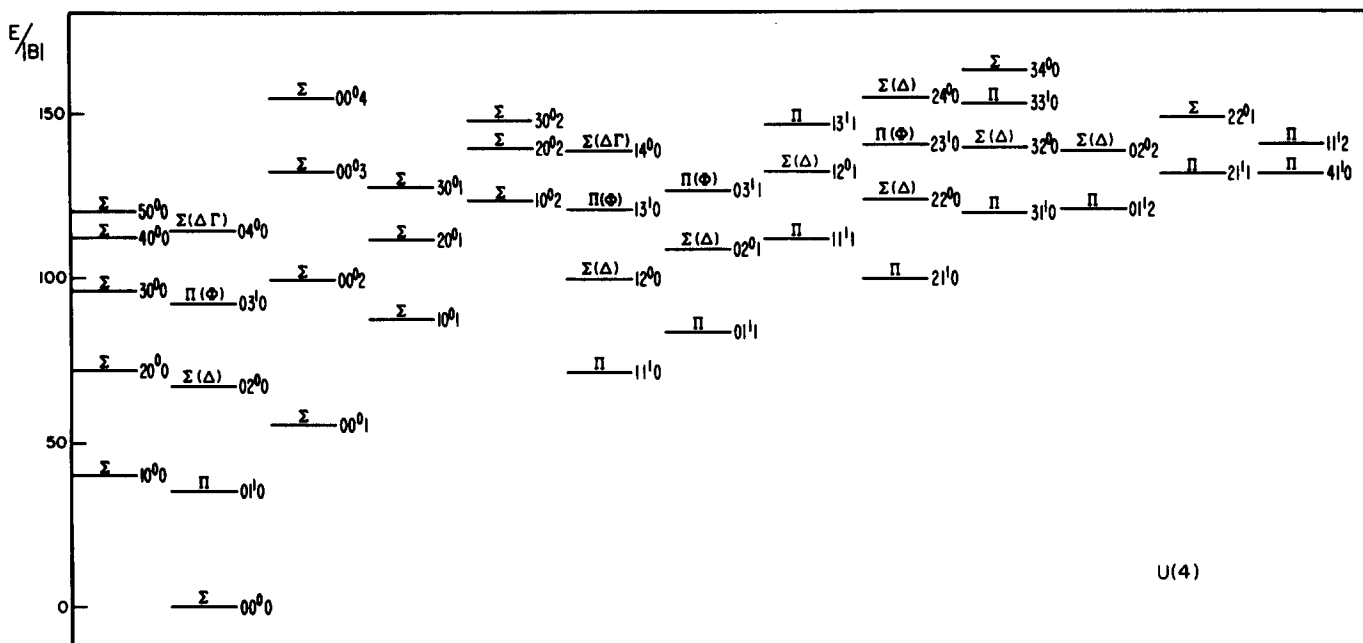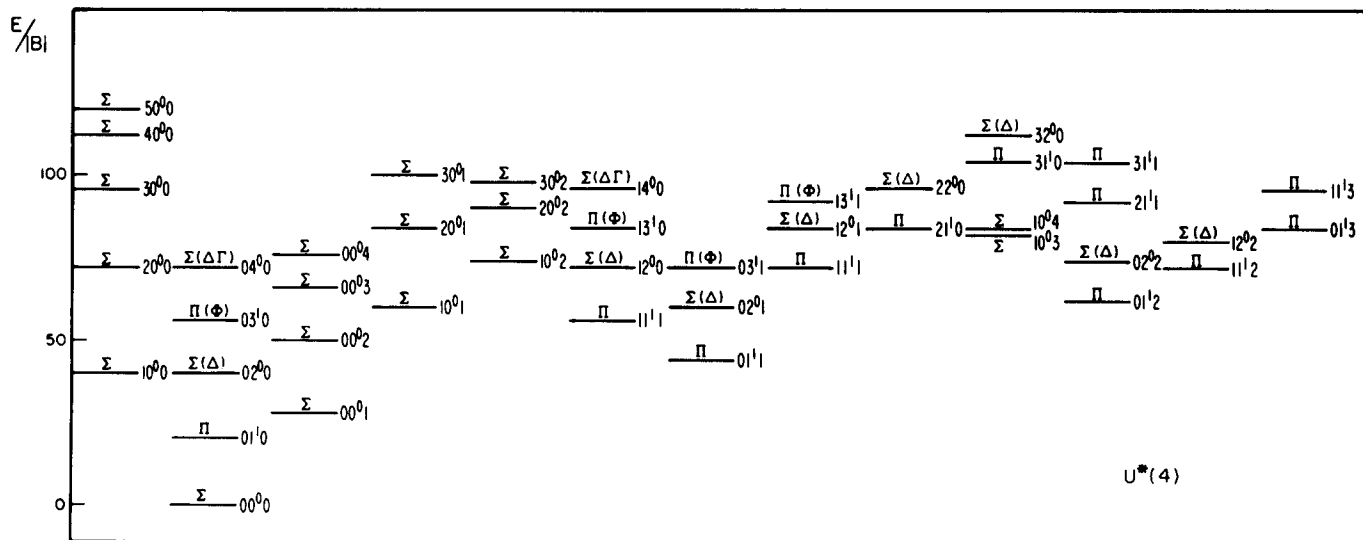
Eq. (3.46) can be rewritten as a Dunham expansion

FIG. 6. Schematic representation of a spectrum with $U^*(4)$ symmetry IIIc. The energy levels are calculated using Eq. (3.48) with $N_1 = 6$, $N_2 = 4$, $A^* = B$, and B negative. The notation is the same as in Fig. 4.

$$E(N_1, N_2, v_1, v_2^{l_2}, v_3, J^P, M) = F'' - 4B(N_1 + N_2 + 4)(v_1 + 1/2) + 4B(v_1 + 1/2)^2 - 2B(N_1 + N_2 + 4)(v_2 + 1) + B(v_2 + 1)^2$$
$$+ Bl_2^2 + (A^* - 4B)(N_1 + N_2 + 4)(v_3 + 1/2) - (A^* - 4B)(v_3 + 1/2)^2 + 4B(v_1 + 1/2)(v_2 + 1)$$
$$+ 4B(v_2 + 1)(v_3 + 1/2) + 8B(v_1 + 1/2)(v_3 + 1/2) + CJ(J+1) . \tag{3.48}$$

The corresponding spectrum is shown in Fig. 6. As in the case of the chain IIIb, because of a missing label, it is not possible to independently adjust here the three vibrational frequencies. Thus, this chain is not suited to describe the most general situation. In addition, the Hamiltonian $H^{(c)}$ is invariant under interchange of vibron types 1 and 2.

D. Energy eigenvalues for nonlinear molecules

The most important difference between a linear and a nonlinear molecule is in its rotational spectrum. While for each vibrational state v_1, $v_2^{l_2}$, v_3 only values of the projection K of the angular momentum along the figure axis occur with

$$K = l_2 = v_2, v_2 - 2, \ldots, 0 \text{ or } 1 , \tag{3.49}$$

(see Fig. 2), in the nonlinear case all values of $K = 0$, 1, ... appear, in each vibrational state v_1, v_2, v_3. Hence, each vibrational excitation contains all the rotational states of Fig. 2.

Starting with the Hamiltonian (2.18) and (2.19), it does not appear to be possible to construct spectra with the appropriate rotational degeneracies. However, a simple extension of this Hamiltonian allows one to construct spectra that display the degenercies appropriate to bent molecules. The Hamiltonian (2.18) and (2.19) was constructed by expanding it into products of boson operators with the constraint that H be a scalar. This excluded terms of the type $\mathbf{J}_1 \cdot \mathbf{D}_1$, since these terms are pseudoscalars. However, one could consider adding to the Hamiltonian terms of the type $|\mathbf{J}_1 \cdot \mathbf{D}_1|$. The absolute value sign changes these terms from pseudoscalar to scalar. We thus consider a class of more general Hamiltonians of the form

$$H_i' = H_i + g_{ii}^{(2)} |J_i^{(1)} \cdot D_i^{(1)}| ; \quad i = 1, 2 ,$$
$$V_{12}' = V_{12} + g_1'^{(1,1)} |J_1^{(1)} \cdot D_2^{(1)} + D_1^{(1)} \cdot J_2^{(1)}| \tag{3.50}$$
$$+ g_2'^{(1,1)} |J_1^{(1)} \cdot R_2^{(1)} + R_1^{(1)} \cdot J_2^{(1)}| .$$

The study of dynamic symmetries presented in the previous subsection can now be repeated with these additional terms. We begin by considering the chain III a. The most general Hamiltonian with this dynamic symmetry can now be written

$$H'^{(a)} = F + A_1 \, \mathfrak{C}_2(0^1 4) + A_2 \, \mathfrak{C}_2(0^2 4)$$
$$+ B \, \mathfrak{C}_2(04) + B' \, \overline{\mathfrak{C}}_2(04) + C \, \mathfrak{C}_2(03) . \tag{3.51}$$

In Eq. (3.51) a new Casimir invariant has appeared:

$$\overline{\mathfrak{C}}_2(04) = |\mathbf{D} \cdot \mathbf{J}| . \tag{3.52}$$

Its eigenvalues are given by

$$\langle \overline{\mathfrak{C}}_2(04) \rangle = (\tau_1 + 1)\tau_2 . \tag{3.53}$$

This operator is simply related to the second Casimir invariant of O(4):

$$\mathfrak{C}_2'(04) = \mathbf{D} \cdot \mathbf{J} \tag{3.54}$$

by the absolute sign. $\mathfrak{C}_2'(04)$ could not have been used directly, since it is a pseudoscalar, and thus has both positive and negative eigenvalues within one representation of O(4):

$$\langle \mathfrak{C}_2'(04) \rangle = \pm (\tau_1 + 1)\tau_2 . \tag{3.55}$$

Note that $\overline{\mathfrak{C}}_2(04)$ is not an analytic function of the generators. The absolute value is defined as the absolute value of the diagonal elements in the basis of eigenstates. Examples of dynamic symmetries defined by nonanalytic functions of the invariants are known, e.g., in atomic physics.[15]

The energy eigenvalues corresponding to Eq. (3.51) are given by

$$E'^{(a)}(N_1, N_2, \omega_1, \omega_2, \tau_1, \tau_2, J^P, M)$$
$$= F + A_1 \, \omega_1(\omega_1 + 2) + A_2 \, \omega_2(\omega_2 + 2)$$
$$+ B[\tau_1(\tau_1 + 2) + \tau_2^2] + B'(\tau_1 + 1)\tau_2 + CJ(J+1) . \tag{3.56}$$

In the special case $B' = 2B$, this reduces to

$$E'^{(a)}(N_1, N_2, \omega_1, \omega_2, \tau_1, \tau_2, J^P, M) = F + A_1 \, \omega_1(\omega_1 + 2)$$
$$+ A_2 \, \omega_2(\omega_2 + 2) + B(\tau_1 + \tau_2)(\tau_1 + \tau_2 + 2) + CJ(J+1) . \tag{3.57}$$

It is convenient to introduce the quantum numbers v_1, v_2, v_3, K through

$$\omega_1 = N_1 - 2v_1 ,$$
$$\omega_2 = N_2 - 2v_3 ,$$
$$\tau_1 = N_1 + N_2 - 2v_1 - 2v_2 - 2v_3 - K , \tag{3.58}$$
$$\tau_2 = K .$$

This introduction is suggested by the correlation diagram[16] relating energy levels in linear and bent molecules (Fig. 7). Here one sees that

$$2v_2^{bent} \rightarrow v_2^{linear} - l_2 ,$$
$$K \rightarrow l_2 . \tag{3.59}$$

Introducing Eq. (3.58) in Eq. (3.57) leads to the Dunham expansion for a rigid triatomic molecule

$$E(N_1, N_2, v_1, v_2, v_3, K, J^P, M) = F' - [4B(N_1 + N_2 + 4) + 4A_1(N_1 + 2)](v_1 + 1/2) + 4(A_1 + B)(v_1 + 1/2)^2$$
$$- 4B(N_1 + N_2 + 4)(v_2 + 1/2) + 4B(v_2 + 1/2)^2 - [4B(N_1 + N_2 + 4) + 4A_2(N_2 + 2)](v_3 + 1/2)$$
$$+ 4(A_2 + B)(v_3 + 1/2)^2 + 8B(v_1 + 1/2)(v_2 + 1/2)$$
$$+ 8B(v_1 + 1/2)(v_3 + 1/2) + 8B(v_2 + 1/2)(v_3 + 1/2) + CJ(J+1) . \tag{3.60}$$
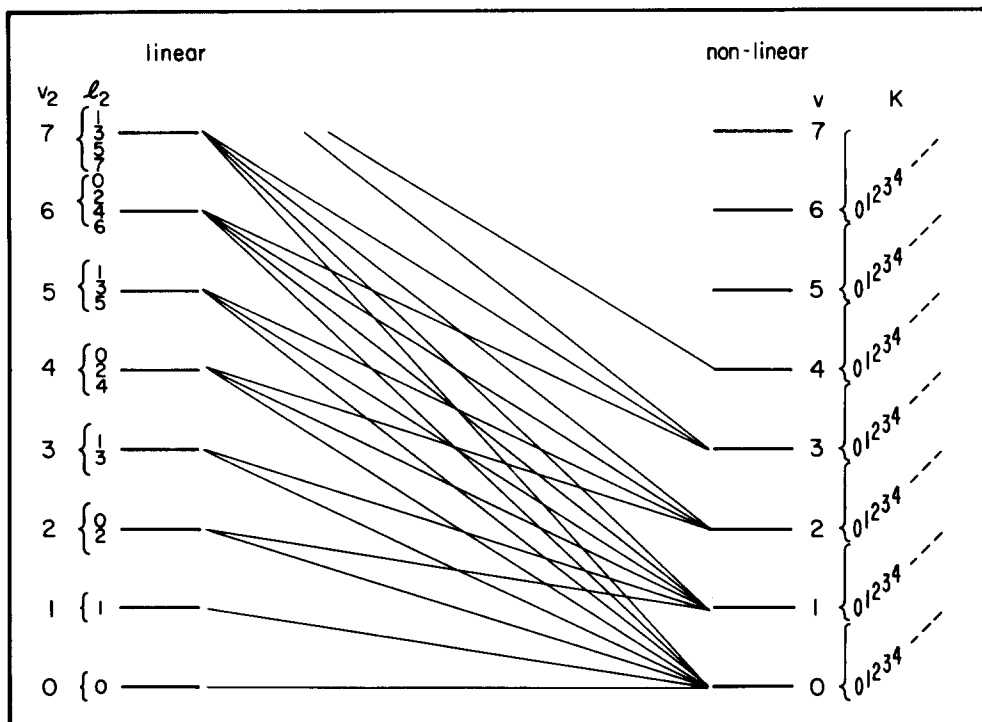
FIG. 7. Correlation diagram for the rotation-vibration spectra of linear and nonlinear triatomic molecules.

Since Eq. (3.60) does not depend on K, it actually describes spherical tops. Relaxing the condition $B' = 2B$ and adding higher order terms introduces K dependence. This allows one to treat symmetric tops and asymmetric tops. The spectrum corresponding to Eq. (3.60) is shown in Fig. 8.

We consider next the chain III b. Since, in this case, the O(4) representations $(N - \tau_2, \tau_2)$, $\tau_2 = 0, 1, \ldots$ are not contained in a single representation of $U(4)$ it is not possible to obtain an energy spectrum with degeneracies appropriate to bent molecules.

Finally, we consider the chain III c. In this case it is possible to obtain spectra with the correct rotational structure. We thus write the Hamiltonian

$$H'^{(c)} = F' + A^* \mathfrak{M}^* + B\,\mathbb{C}_2(04) + B'\,\overline{\mathbb{C}}_2(04) + C\,\mathbb{C}_2(03) \ . \tag{3.61}$$

The energy eigenvalues corresponding to Eq. (3.61), in the special case $B' = 2B$, are given by

$$E'^{(c)}(N_1, N_2, n^*, \tau_1, \tau_2, J^P, M) = F' + A^*[-N_1 N_2 + n^*(N_1 + N_2) - n^*(n^* - 3)] + B[(\tau_1 + \tau_2)(\tau_1 + \tau_2 + 2)] + CJ(J+1) \ . \tag{3.62}$$
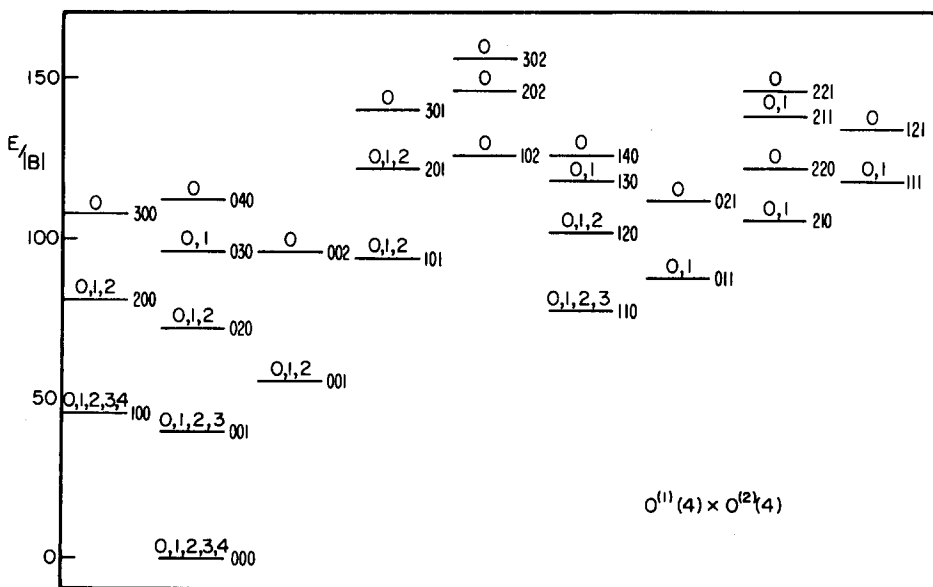
FIG. 8. Schematic representation of a spectrum with $0^{(1)}(4) \otimes 0^{(2)}(4)$ symmetry in the nonlinear case. The energy levels are calculated using Eq. (3.60) with $N_1 = 6$, $N_2 = 4$, $A_1 = 0.25B$, $A_2 = B$, and B negative. The vibrational quantum numbers v_1, v_2, v_3 are indicated next to the levels and the occurring values of K above them.
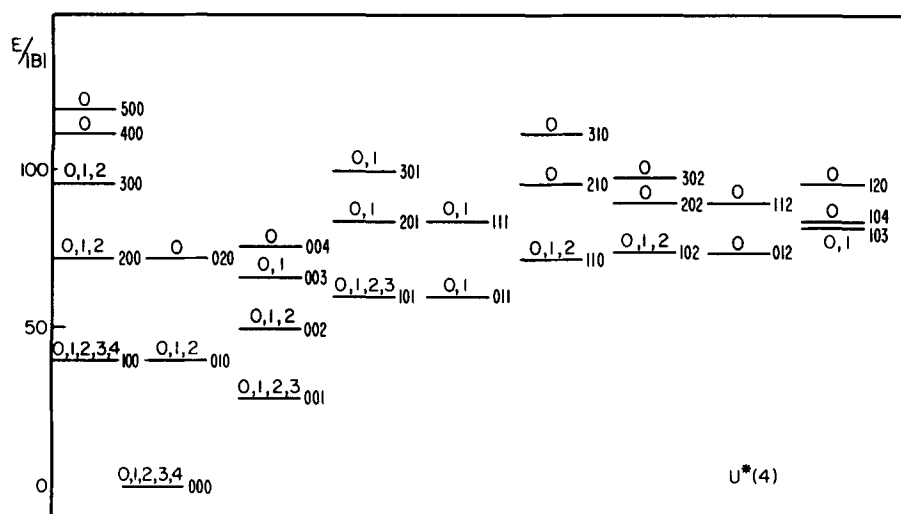
FIG. 9. Schematic representation of a spectrum with U^* (4) symmetry in the nonlinear case. The energy levels are calculated using Eq. (3.64) with $N_1 = 6$, $N_2 = 4$, $A^* = B$, and B negative. The notation is the same as in Fig. 8.

Introducing now the quantum numbers

$$n^* = v_3 \ , \qquad \tau_1 = N_1 + N_2 - 2v_1 - 2v_2 - 2v_3 - K \ , \qquad \tau_2 = K \ , \tag{3.63}$$

one can recast Eq. (3.62) in the form

$$E(N_1, N_2, v_1, v_2, v_3, K, J^P, M) = F'' - 4B(N_1 + N_2 + 4)(v_1 + 1/2) + 4B(v_1 + 1/2)^2 - 4B(N_1 + N_2 + 4)(v_2 + 1/2)$$

$$+ 4B(v_2 + 1/2)^2 - (4B - A^*)(N_1 + N_2 + 4)(v_3 + 1/2) + (4B - A^*)(v_3 + 1/2)^2 \tag{3.64}$$

$$+ 8B(v_1 + 1/2)(v_2 + 1/2) + 8B(v_2 + 1/2)(v_3 + 1/2) + 8B(v_1 + 1/2)(v_3 + 1/2) + CJ(J + 1) \ .$$

Equation (3.64) is similar to Eq. (3.60) but with two vibrational modes degenerate. The corresponding spectrum is shown in Fig. 9. Remarks similar to those following Eq. (3.48) apply here too.

In concluding this section we remark that the O(4) group discussed here is not related to that used to describe triangular configurations in Ref. 8. The O(4) group used in Ref. 8 arises from the degeneracy group of the spherical top[17] and an O(4) representation contains all states with the same J and different values of M and K. In the present approach, the O(4) representations contain all possible rotational levels in the same band. It would be interesting to study the connection between the two approaches.

IV. VIBRATIONAL SPECTRA OF RIGID MOLECULES

The dynamic symmetries discussed in Sec. III provide a zeroth order description of the energy spectra of triatomic molecules. In order to improve this description one can add terms of higher order in the Casimir invariants $\mathcal{C}$ of the appropriate groups and/or introduce symmetry breaking terms. In this section, we study the latter approach. This study can be done by returning to the most general Hamiltonian (2.18)–(2.19) and diagonalizing it numerically. A good basis for this diagonalization is given by the group chain I a [Eq. (3.13)]. As mentioned above, a computer code[10] has been written for this purpose. However, for large values of the vibron numbers N_1 and N_2 the dimension of the matrices to diagonalize is very large. A simpler diagonalization can be performed if one insists that the molecule is rigid. In that case one can assume that the O(4) dynamical symmetry is preserved and one can diagonalize H within the subspace of states carrying the same representation labels (τ_1, τ_2) of O(4). This is analogous to diagonalizing a rotationally invariant Hamiltonian in the space of states characterized by the same angular momentum J. Since the Hamiltonian H has, in this case, only off-diagonal matrix elements within a subspace of states with $2v_1 + v_2 + 2v_3 = $ constant, $l_2 = $ constant [see Eqs. (3.31), (3.40), (3.47), (3.58), and (3.63)], the corresponding matrices have relatively small dimensions (at least for small values of the vibrational quantum numbers v_1, v_2, and v_3). An appropriate basis for this diagonalization is provided by one of the three chains III a, III b, and III c. Of them, the most convenient appears to be the chain III a. Thus, a computer program has been written to diagonalize the most general O(4) Hamiltonian in this basis.[18]

A. Model Hamiltonian and matrix elements

The most general O(4) Hamiltonian can be constructed with the Casimir invariants of all the groups appearing in the group lattice

$$U^{(1)}(4) \otimes U^{(2)}(4) \overset{\displaystyle \nearrow O^{(1)}(4) \otimes O^{(2)}(4) \searrow}{\underset{\displaystyle \searrow U^*(4) \nearrow}{\longrightarrow \quad U(4) \quad \longrightarrow}} O(4) \supset O(3) \supset O(2) \ . \tag{4.1}$$

Since the quadratic Casimir invairant of $U^*(4)$ is related to those of $U(4)$, $0^{(1)}(4)$, and $0^{(2)}(4)$ by Eq. (3.43), we need not introduce it. We can therefore write the most general 0(4) invariant Hamiltonian as

$$H = F + A_1 \mathcal{C}_2(0^14) + A_2 \mathcal{C}_2(0^24) + B \mathcal{C}_2(04) + B' \overline{\mathcal{C}}_2(04) + A \mathfrak{M} .$$

(4.2)

If $A = 0$, we then have the dynamic symmetry III a; if $A_1 = A_2 = 0$, we have the dynamic symmetry III b, and if $A_1 = A_2 = A^*/2$, $A = -A^*$, we have the dynamic symmetry III c.

In the basis III a all terms except that containing the Majorana operator $\mathfrak{M}$ are diagonal. We thus need to construct only matrix elements of this operator. This construction is done in Appendix B. Once the matrix elements are calculated, the corresponding matrix can be diagonalized. Before presenting results of the numerical diagonalization, we study the case in which the coefficient A in Eq. (4.2) is small and thus we can use perturbation theory. In the basis III a labeled by v_1, $v_2^{l_2}$, v_3 [Eq. (3.31)], the diatonal matrix elements of the Majorana operator are given, up to terms of the order $1/N_1$ and $1/N_2$, by

$$\langle N_1, N_2, v_1, v_2^{l_2}, v_3 | \mathfrak{M} | N_1, N_2, v_1, v_2^{l_2}, v_3 \rangle$$

$$= (N_1 + N_2 + 1)v_2 - (1/4)\left(4 + \frac{N_2}{N_1} + \frac{N_1}{N_2}\right)v_2^2 + (1/4)\left(\frac{N_2}{N_1} + \frac{N_1}{N_2}\right)l_2^2 + N_2\left(1 + \frac{1}{N_1}\right)v_1 + N_1\left(1 + \frac{1}{N_2}\right)v_3 - \left(1 - \frac{N_2}{N_1}\right)v_1 v_2 - \left(1 - \frac{N_1}{N_2}\right)v_2 v_3 .$$

(4.3)

The vibrational energy levels of a linear triatomic molecule are given, up to first order in perturbation theory, by

$$E(N_1, N_2, v_1, v_2^{l_2}, v_3, J^P, M) = F' - [4B_1(N_1 + N_2 + 4) + 4A_1(N_1 + 2) - A(N_2 + 1)](v_1 + 1/2) + 4(A_1 + B_1)(v_1 + 1/2)^2$$

$$- [2B_1(N_1 + N_2 + 4) - A(N_1 + N_2 + 4)](v_2 + 1) + \left[B_1 - \left(1 + \frac{N_2}{4N_1} + \frac{N_1}{4N_2}\right)\right](v_2 + 1)^2 + \left[B_1 + \frac{A}{4}\left(\frac{N_2}{N_1} + \frac{N_1}{N_2}\right)\right]l_2^2$$

$$- [4B_1(N_1 + N_2 + 4) + 4A_2(N_2 + 2) - A(1 + N_1)](v_3 + 1/2) + 4(A_2 + B_1)(v_3 + 1/2)^2 + 8B_1(v_1 + 1/2)(v_3 + 1/2)$$

$$+ \left[4B_1 - A\left(1 - \frac{N_1}{N_2}\right)\right](v_3 + 1/2)(v_2 + 1) + \left[4B_1 - A\left(1 - \frac{N_2}{N_1}\right)\right](v_1 + 1/2)(v_2 + 1) + CJ(J + 1) ,$$

(4.4)

and thus in terms of only four parameters A_1, A_2, B_1, A, in addition to the vibron numbers N_1, N_2.

An interesting situation occurs when two vibrational modes are accidentally degenerate. One expects then the presence of resonances. An example is the approximate degeneracy of the states $v_1 + u$, $v_2 - 2u$, v_3, with u integer. This situation occurs in CO_2 as discussed below.

In this case, first order perturbation theory cannot be used and one must diagonalize H among the degenerate states. The matrix elements of $\mathfrak{M}$, up to order $1/N_1$ and $1/N_2$, between the different degenerate states are given by

$$\langle N_1, N_2, v_1, v_2^{l_2}, v_3 | \mathfrak{M} | N_1, N_2, v_1 - 1, (v_2 + 2)^{l_2}, v_3 \rangle$$

$$= -\frac{(N_1 + N_2 + 4)}{2(N_1 + 2)^{1/2}} v_1^{1/2}[(v_2 + 2)^2 - l_2^2]^{1/2}\left\{1 - \left[\frac{4}{(N_1 + N_2 + 4)} - \frac{3}{2(N_1 + 2)}\right]v_1 \right.$$

$$\left. - \left[\frac{1}{(N_1 + N_2 + 4)} + \frac{1}{2(N_1 + 2)} + \frac{1}{2(N_2 + 2)}\right](v_2 + 2) - \left[\frac{4}{(N_1 + N_2 + 4)} + \frac{2}{(N_2 + 2)}\right](v_3 + 1/2)\right\} .$$

(4.5)

These matrix elements are similar to those used to discuss the Fermi resonance in CO_2 in the potential approach.[19]

Perturbative techniques are also of importance for the treatment of small contributions coming from terms in the Hamiltonian H that are outside the group lattice (4.1).

V. APPLICATION TO REALISTIC SPECTRA

In this section we investigate the extent to which the simple Hamiltonian H of Eq. (4.2) can describe experimental spectra. For linear molecules, we set $B' = 0$. Thus H contains four parameters A_1, A_2, B, and A, in addition to the vibron numbers N_1 and N_2. The parameter F does not play any role since it sets only the zero of the energy scale that we take to coincide with the energy of the ground states. In all cases discussed below, a least mean square fit to the data was obtained using a

Simplex method[20] in combination with the program VIBRON. Such a method provides only local minima. Our best fit to the data was obtained by varying the initial guess. A fair description of all energies, including the highly excited ones, for which there is an increasing interest,[21,22] was considered to be more important than a very accurate description of the low-lying states. Hence, all energy levels were given equal weight.

A. HCN

Using the energies of the vibrational excitations of the electronic ground state of HCN listed in Refs. 22 and 23, we have performed several least square fits. The results are given in Table III. In the fits I, II, and III only the experimental data on Σ states were taken into account. The reason for considering only those states is that the order of the $\Sigma, \Delta, \dots$ and $\Pi, \Phi, \dots$ species in a given vibrational excitation cannot be ad-

TABLE III. Observed (Refs. 23 and 24) and calculated energies (cm⁻¹) of the vibrational states of HCN. In fits I, II, and III only Σ Σ states were included. The average deviation δ is defined in Eq. (5.4). The Hamiltonian used in the calculations is given in Eq. (4.2) with $B' = 0$. Columns II and V show the effect of keeping N_1 and N_2 fixed and columns III and VI show that the introduction of the Majorana term $A\mathfrak{M}$ gives only a slight improvement.

v_1	$v_2^{l_2}$	v_3	Obs.	I	II	III	IV	V	VI	Obs.−Calc. VI
0	2^0	0	1 411.43	1 406.49	1 406.61	1 409.68	1 413.30	1 413.28	1 414.86	−3.43
1	0^0	0	2 096.85	2 102.37	2 102.67	2 099.51	2 104.63	2 104.48	2 102.74	−5.89
0	0^0	1	3 311.48	3 301.32	3 299.69	3 299.79	3 299.38	3 299.59	3 298.65	12.83
0	4^0	0	2 802.85	2 798.19	2 798.48	2 804.97	2 811.46	2 811.44	2 816.03	−13.18
1	2^0	0	3 501.13	3 494.07	3 494.54	3 494.35	3 502.79	3 502.64	3 502.14	−0.01
2	0^0	0	4 173.07	4 180.26	4 180.93	4 174.69	4 184.22	4 183.97	4 180.61	−7.54
0	2^0	1	4 684.32	4 693.01	4 691.57	4 694.46	4 697.54	4 697.76	4 697.36	−13.02
1	0^0	1	5 393.70	5 388.90	5 387.63	5 384.47	5 388.87	5 388.96	5 385.97	7.73
0	0^0	2	6 519.61	6 506.45	6 504.10	6 504.58	6 503.50	6 503.80	6 502.77	16.83
2	2^0	0	5 571.89	5 557.17	5.558.08	5 554.68	5 567.24	5 567.01	5 564.54	7.35
1	2^0	1	6 761.33	6 765.80	6 764.78	6 764.29	6 771.89	6 772.00	6 769.20	−7.87
1	0^0	2	8 585.57	8 579.23	8 577.31	8 574.43	8 577.86	8 578.05	8 574.65	10.92
0	0^0	3	9 627.02	9 615.39	9 613.23	9 614.37	9 612.37	9 612.63	9 612.37	14.65
1	2^0	2	9 914.41	9 941.34	9 939.73	9 939.21	9 945.75	9 945.98	9 941.66	−27.25
1	0^0	3	11 674.46	11 673.38	11 671.71	11 669.39	11 671.59	11 671.76	11 668.82	5.64
0	0^0	4	12 635.90	12 628.14	12 627.06	12 629.15	12 625.99	12 626.07	12 627.45	8.45
0	0^0	5	15 551.94	15 544.71	15 545.62	15 548.93	15 544.35	15 544.13	15 547.99	3.95
3	0^0	3	15 710.53	15 715.92	15 715.48	15 706.47	15 714.92	15 715.06	15 707.22	3.31
2	0^0	4	16 674.21	16 690.06	16 690.17	16 685.22	16 689.12	16 689.11	16 684.69	−10.48
1	0^0	5	17 550.39	17 573.11	17 574.64	17 574.29	17 573.30	17 573.03	27 573.61	−23.22
0	0^0	6	18 377.01	18 365.08	18 368.88	18 373.69	18 367.46	18 366.80	18 373.99	3.02
5	0^0	2	16 640.31	16 625.53	16 626.18	16 634.79	16 624.91	16 625.14	16 636.95	3.36
0	1^1	0	711.98				706.65	706.64	707.07	4.91
0	3^1	0	2113.46				2112.38	2112.36	2115.09	−1.63
1	1^1	0	2 805.58				2 803.71	2 803.56	2 802.07	3.51
0	1^1	1	4 004.17				3 998.46	3 998.67	3 997.60	6.57
1	3^1	0	4 201.29				4 194.30	4 194.16	4 194.63	6.66
2	1^1	0	4 878.27				4 875.73	4 875.49	4 872.21	6.06
0	3^1	1	5 366.86				5 389.05	5 389.28	5 389.50	−22.64
1	1^1	1	6 083.35				6 080.38	6 080.48	6 077.19	6.16
0	1^1	2	7 194.75				7 195.01	7 195.33	7 193.58	−0.83
0	2^2	0	1 426.53				1 405.73	1 405.72	1 406.57	19.96
0	4^2	0	2 818.16				2 803.89	2 803.88	2 807.75	10.41
1	2^2	0	3 516.88				3 495.22	3 495.08	3 493.84	23.04
0	2^2	1	4 699.21				4 689.97	4 690.20	4 689.00	10.21

Parameters

		I	II	III	IV	V	VI	
N_1		143.599	144ᵃ	144ᵃ	139.659	140ᵃ	140ᵃ	
N_2		46.559	47ᵃ	47ᵃ	47.083	47ᵃ	47ᵃ	
A_1		−1.212	−1.208	−1.178	−1.238	−1.234	−1.148	
A_2		−10.174	−10.070	−10.012	−10.015	−10.034	−9.852	
B		−1.849	−1.841	−1.862	−1.892	−1.889	−1.960	
A		0ᵃ	0ᵃ	−0.033	0ᵃ	0ᵃ	−0.140	
Average deviation δ		11.633	11.939	11.002	12.344	12.345	11.712	

ᵃNot varied in the least mean square search.

justed with the simple Hamiltonian (4.2). Higher order terms should be added. For example, a term like $(J \cdot D)^2$ would correct for the discrepancy. This term does not affect Σ states.

In order to obtain an estimate of the values of N_1 and N_2, we performed two fits (I and IV), using the analytic formula (3.32) for the $0^{(1)}(4) \otimes 0^{(2)}(4)$ dynamic symmetry. This allowed us to treat N_1 and N_2 as real parameters instead of integers. Subsequently, we performed a new search, keeping N_1 and N_2 fixed to the integers closest

to the real values obtained previously. Several remarks on the values of N_1 and N_2 can be made. As discussed in Sec. III and in I, N_1 and N_2 are related to the number of vibrational bands, and hence to the dissociation energy [obtained using $D(\mathrm{HC-N})^{16}$ and $D(\mathrm{HC})^{24}$]

$$D_0(\mathrm{H-C-N}) = 106 \times 10^3 \text{ cm}^{-1} . \tag{5.1}$$

A remarkable feature of the values of N_1 and N_2 shown in Table III, is that they are very close to the values that one would obtain by considering the diatomic mole-
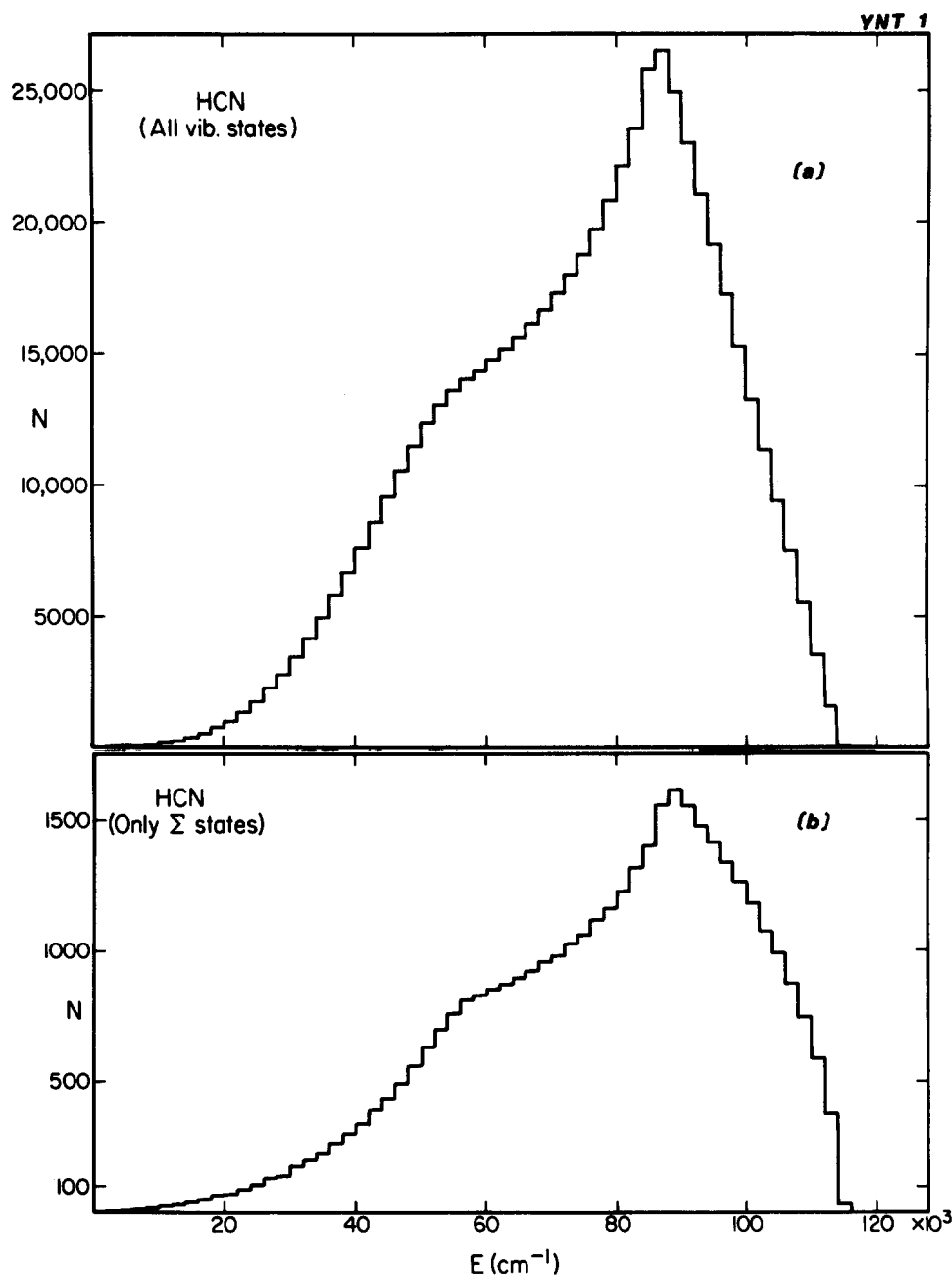
FIG. 10. The density of vibra-
tional states in the vibron descrip-
tion of HCN ($N_1 = 140$, $N_2 = 47$) as
a function of the excitation energy;
(a) all states, (b) only Σ states.

cules CH and CN separately. Using Eq. (3.10) of I, it
follows that for CN[24]

$$N + 2 \simeq \frac{\omega_e}{\omega_e \chi_e} = \frac{2068.7}{13.134} \simeq 158 , \qquad (5.2)$$

and for CH[24]

$$N + 2 \simeq \frac{\omega_e}{\omega_e \chi_e} = \frac{2859.1}{63.3} \simeq 45 , \qquad (5.3)$$

where we have used the usual spectroscopic notation ω_e,
$\omega_e \chi_e$, for the coefficients of the $(v + 1/2)$ and $(v + 1/2)^2$
terms. The close correspondence between Eqs. (5.2)
and (5.3) and the values obtained in our fit 144 and 47
appears to be related to the fact that the HCN molecule
exhibits normal vibrational modes which are very nearly
localized in the CN and CH bonds.[25]

From Table III one can see that hardly any improve-
ment in the fit is obtained by adding the Majorana term
(fits III and VI). We thus conclude that HCN can be con-
sidered as a good example of a dynamic $0^{(1)}(4) \otimes 0^{(2)}(4)$
symmetry in molecular spectra. The corresponding
description employs five parameters N_1, N_2, A_1, A_2,
and B and it gives an average deviation of

$$\delta = \sqrt{\frac{1}{\nu} \sum_{i=1}^{\nu} (E_{\exp i} - E_{\text{calc} i})^2} = 12 \text{ cm}^{-1} , \qquad (5.4)$$

where ν is the number of data point.

Once a fit has been obtained, several other properties
can be calculated. As an example, we show the density
of states as a function of excitation energy (Fig. 10).
The calculated states extend above the dissociation en-
ergies[24]

TABLE IV. Observed (Refs. 14 and 19) and calculated energies (cm^{-1}) of the vibrational states of CO_2. The Hamiltonian used in the calculation is given in Eq. (4.2) with $B' = 0$. The average deviation δ is defined in Eq. (5.4). States in Fermi resonance are in brackets.

v_1	$v_2^{l_2}$	v_3	Obs.	I	II	III	Obs-Calc III
0	2^0	0 }	1 285.41	1 290.69	1 289.97	1 289.28	-3.87
1	0^0	0 }	1 388.19	1 390.89	1 390.80	1 390.34	-2.15
0	0^0	1	2 349.16	2 338.80	1 339.53	2 339.58	9.58
0	0^0	1 }	3 612.84	3 613.80	3 613.59	3 613.26	-0.42
1	0^0	1 }	3 714.78	3 713.59	3 713.96	3 713.92	0.86
0	4^0	1 }	4 853.63	4 862.69	4 861.83	4 861.51	-7.88
1	2^0	1 }	4 977.81	4 976.54	4 976.84	4 976.71	1.10
2	0^0	1 }	5 099.61	5 104.49	5 104.98	5 104.91	-5.30
0	0^0	3	6 972.49	6 956.20	6 956.91	6 956.70	15.79
0	6^0	1 }	6 075.93	6 084.36	6 082.88	6 082.55	-6.62
1	4^0	1 }	6 227.88	6 288.02	6 228.85	6 229.36	-1.48
2	2^0	1 }	6 347.81	6 346.62	6 347.95	6 348.40	-0.59
3	0^0	1 }	6 503.05	6 506.72	6 507.72	6 507.51	-4.46
0	2^0	3 }	8 192.62	8 199.81	8 199.16	8 199.17	-6.55
1	0^0	3 }	8 294.01	8 298.82	8 298.66	8 299.05	-5.04
0	0^0	5	11 496.85	11 493.28	11 492.01	11 491.08	5.77
0	1^1	0	667.38	674.51	674.35	674.39	-7.01
0	3^1	0 }	1 932.47	1 940.83	1 939.88	1 939.17	-6.70
1	1^1	0 }	2 076.50	2 081.17	2 081.10	2 080.54	-4.04
0	3^1	1 }	4 247.71	4 255.67	4 255.13	4 254.97	-7.26
1	1^1	1 }	4 390.63	4 395.60	4 395.87	4 395.93	-5.30
0	1^1	2	5 316.09	5 315.53	5 316.09	5 316.53	-0.44
0	1^1	3	7 602.85	7 605.93	7 606.12	7 606.58	-3.73
0	7^1	1	6 688.54	6 691.33	6 689.52	6 689.15	-0.61
1	5^1	1	6 893.91	6 862.97	6 863.40	6 863.83	30.08
2	3^1	1	7 024.03	7 021.45	7 022.79	7 023.20	0.83
3	1^1	1	7 204.22	7 203.33	7 204.64	7 204.33	-0.11
0	2^2	0	1 335.13	1 343.40	1 343.08	1 343.16	-8.03
0	4^2	1	4 888.00	4 896.54	4 895.67	4 895.69	-7.69
1	2^2	1	5 061.78	5 067.38	5 067.51	5 067.70	-5.92
0	2^2	2	5 960.08	5 967.88	5 968.05	5 968.95	-8.87
0	3^3	0	2 003.28	2 006.66	2 006.18	2 006.31	-3.03
0	5^5	0	3 341.80	3 316.33	3 315.54	3 315.75	26.05

Parameters

	I	II	III
N_1	150^a	160^a	170^a
N_2	90^a	80^a	70^a
A_1	0.479	0.032	-0.166
A_2	2.373	2.168	2.130
B	-2.870	-2.547	-2.414
A	-2.930	-2.338	-2.017
Average deviation δ	9.208	9.025	8.974

[a]Not varied in the least mean square search.

$$D_0(\text{H}-\text{CN}) = 43 \times 10^3 \ cm^{-1} \qquad (5.5)$$

and

$$D_0(\text{HC}-\text{N}) = 78 \times 10^3 \ cm^{-1} . \qquad (5.6)$$

We know of no other approach where (at least, semi-quantitative) estimates of the density of quasibound vibrational states can be so readily obtained. Such quasibound vibrational states (which appear as bound states in the present formalism) decay by vibrational energy redistribution, i.e., by vibrational predissociation.[26] They are analogous but not identical to the rotational predissociating states discussed in I. Such states can be detected both spectroscopically and in collision experiments (see the discussion of H_3^+ below).

B. CO_2

The CO_2 molecule differs from HCN in several respects. First, the vibrational modes in CO_2 are known to be nonlocal. Second, CO_2 exhibits Fermi resonances among the symmetric stretching and bending vibrations. These differences are reflected in the different values of the parameters we obtain in the fits.

TABLE V. $0(4) \otimes 0(4)$ components in some vibrational state of CO_2 (fit II of Table IV).

v_1	$v_2^{l_2}$	v_3	E_{calc} (cm⁻¹)	$(N_1, 0) \otimes (N_2, 0)$	$(N_1 - 2, 0) \otimes (N_2, 0)$	$(N_1, 0) \otimes (N_2 - 2, 0)$
0	2^0	0	1289.97	-0.5897	-0.1850	0.7862
1	0^0	0	1390.80	0.8053	-0.2078	0.5552
0	0^0	1	2339.53	-0.0606	-0.9605	-0.2715

We began with a search for the optimum values of N_1 and N_2. It turns out that the quality of the fits is almost independent from $N_1 + N_2$. We thus fixed $N_1 + N_2$ using a different criterion, namely that the highest calculated state had an energy approximately equal to[19]

$$D_0(O-C-O) = 133 \times 10^3 \text{ cm}^{-1} \ . \quad (5.7)$$

This gives $N_1 + N_2 \simeq 240$. Table IV gives the results of fits for several values of N_1 and N_2. The best fit is obtained when $N_1 \simeq 2N_2$.

In order to describe the energies of the levels which are in Fermi resonance, we found it necessary to introduce a relatively large Majorana term. One can see from Table IV that with this Majorana term one is able to account quite well for the energies of the multiplets in resonance (connected by lines in the table). It is interesting to analyze the wave functions obtained from these fits. In Table V, we list the components of the wave functions of three states in the $0^{(1)}(4) \otimes 0^{(2)}(4)$ basis. One can see that the asymmetric stretching vibration $(0\,0^0 1)$ is almost purely (92%) obtained from the configuration $(N_1 - 2, 0) \otimes (N_2, 0)$, whereas the symmetric stretching $(1 0^0 0)$ and bending $(0 2^0 0)$ modes (which are in resonance) are obtained from strongly mixed $0^{(1)}(4) \otimes 0^{(2)}(4)$ configurations. This is consistent with a normal mode interpretation of type 1 and type 2 vibrons since the mode which is not affected by the Fermi resonance is almost purely an excitation of system 1 [as one can see by comparing the configuration $(N_1 - 2, 0) \otimes (N_2, 0)$ with the ground state configuration $(N_1, 0) \otimes (N_2, 0)$]. In the previous subsection, we remarked that a description of the vibrational spectrum of HCN with an $0^{(1)}(4) \otimes 0^{(2)}(4)$ dynamical symmetry leads, by construction, to an interpretation of the vibrons as normal modes. However, in contrast with CO_2, the normal modes in HCN are very nearly local, due to the specific properties of that molecule (the small mass of the H atom). In conclusion, we have obtained a single description of the energy levels of CO_2 in terms of six parameters A_1, A_2, B, A, N_1, and N_2, with an average deviation of $\delta \approx 9$ cm⁻¹.

C. H_3^+

In order to illustrate how the algebraic approach can be used for a description of nonlinear molecules, we consider the molecule H_3^+. This molecule has a triangular equilibrium shape and recently some measurements of its rotation-vibration spectrum have been performed.[27,28] In Table VI we show fits to the vibrational energy levels obtained in *ab initio* calculations.[29] The experimental data are not extensive enough to allow us to perform a direct fit. The fits in Table VI are done as-

suming either an unbroken $0^{(1)}(4) \otimes 0^{(2)}(4)$ symmetry including the operator $\overline{C}_2(04)$ as described in Sec. III D or an unbroken $U^*(4)$ symmetry. In the former case, there are five parameters describing the vibrational spectra A_1, A_2, B, N_1, and N_2 [Eq. (3.60)]. In the special case of H_3^+, because of the additional symmetry of this molecule, one must put $N_1 = N_2$ and $A_1 = 0$ (if the degenerate modes are labeled by v_1 and v_2). This leaves three parameters A_2, B, and $N_1 = N_2 = (N/2)$. Furthermore, since there is not enough information available on the high energy part of the spectrum, we kept $N_1 = N_2 = 30$ fixed. Although the fits describe qualitatively the spectra, they show large deviations (±100 cm⁻¹) from the "experimental" results. In particular, the fits are unable to account for the couplings between states with v_1, v_2, v_3, and $v_1 \pm 2$, v_2, $v_3 \mp 2$ as it occurs in H_3^+. These couplings occur where the first excited state of the symmetric and antisymmetric normal modes belong to different symmetry species but have comparable frequencies. They were first pointed out by Darling and Dennison[30] for H_2O. A more recent example is ozone.[31] It appears, that, in contrast to the case of Fermi resonances as discussed earlier, couplings between anhar-

TABLE VI. Calculated energies (cm⁻¹) of the vibrational states in H_3^+ compared with *ab initio* results (Ref. 29). The Hamiltonian used is given in Eq. (4.2). The average deviation δ is defined in Eq. (5.4).

v_1	v_2	v_3	*Ab initio*	I	II
1	0	0	2515.99	2505.73	2506.49
0	1	0	2516.17	2505.73	2506.49
0	0	1	3185.32	3180.98	3174.29
2	0	0	4799.19	4927.93	4929.42
0	2	0	5000.26	4927.93	4929.42
1	1	0	5007.99	4927.93	4929.42
1	0	1	5567.62	5603.18	5597.22
0	1	1	5568.00	5603.18	5597.22
0	0	2	6267.77	6233.42	6243.48

Parameters		
N_1	30ᵃ	30ᵃ
N_2	30ᵃ	30ᵃ
A_1	0ᵃ	$-A/2$
A_2	-5.627	$-A/2$
B	-10.440	-15.829
B'	$2B$	$2B - A$
A	0ᵃ	-10.771
Average deviation δ	59.750	58.477

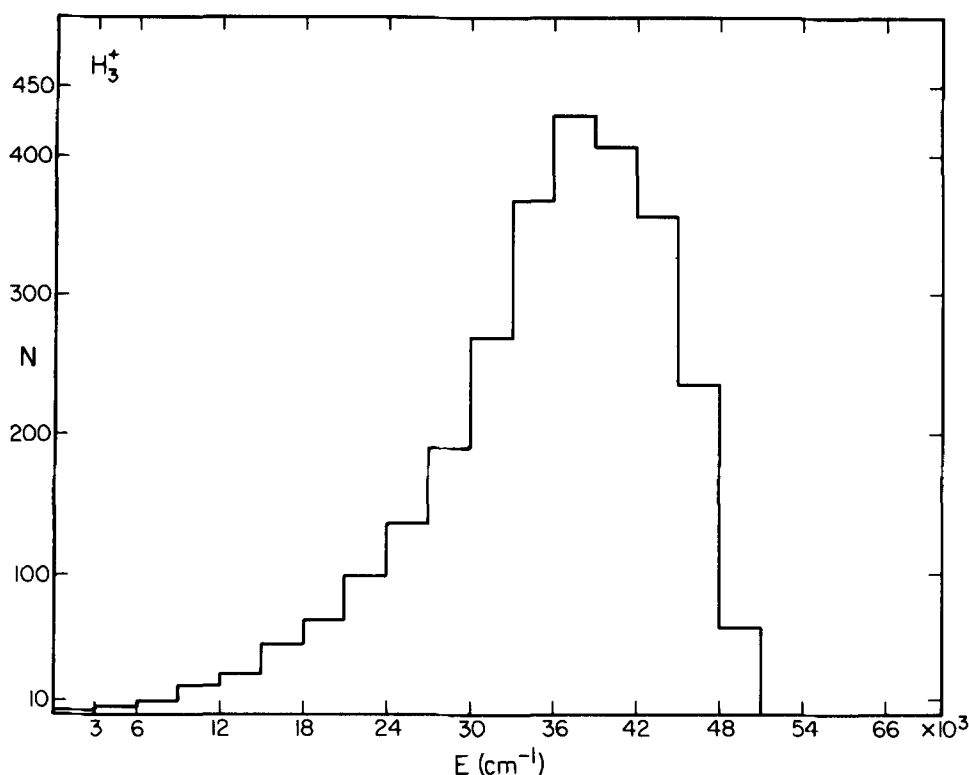ᵃNot varied in the least mean square search.

FIG. 11. The density of vibrational states in the vibron description of H_3^+ ($N_1 = N_2 = 30$) as a function of the excitation energy.

monic overtones cannot be described by an interaction, which is, at most, bilinear in the generators Eqs. (2.15) and (2.16). In order to treat these situations one must return to the most general Hamiltonian Eq. (2.9) and add higher order terms. The same conclusions apply to the $U^*(4)$ symmetry.

Furthermore, because of the particular nature of the triangular configurations, reflected in the algebraic approach in the choice $B' = 2B$ [Eq. (3.57)] any perturbation introduced by operators that break the $0^{(1)}(4) \otimes 0^{(2)}(4)$ symmetry will necessarily couple the vibrational and rotational degrees of freedom.

Finally, we have also calculated the density of states corresponding to this case, as shown in Fig. 11. The quasibound states (above the dissociation limit) of this figure, will be detected as "complexes" in proton-H_2 collisions.[32] It is therefore worth noting that the density of such states declines quite rapidly with energy. This feature (noted also for other systems) conforms to our general expectations that at higher energies molecular collisions tend to be direct even in the presence of a deep well.[33] It emerges from Figs. 10 and 11 that the transition from a compound to a direct mechanism is over at a collision energy which is about equal to the well depth.

We conclude this section by remarking once more that while we have achieved an excellent description of rigid linear molecules within the framework of an algebraic approach with a Hamiltonian, which is, at most, quadratic in the generators, this has not been the case for rigid nonlinear molecules. Work to include higher order terms is presently in progress.

VI. EXTENSION TO LARGER MOLECULES

On the basis of a simple counting of the number of degrees of freedom, one expects that rotation-vibration spectra of $(k + 1)$ atomic molecules can be described in terms of the group structure

$$U^{(1)}(4) \otimes U^{(2)}(4) \otimes \cdots \otimes U^{(k)}(4) . \qquad (6.1)$$

In order to illustrate how this proceeds in practice we consider the case of tetra-atomic molecules ($k = 3$). The corresponding boson space consists of k sets of σ and π vibrons, distinguished by an appropriate label. We shall not give a complete account of all the group chains that can be constructed. They can be found by generalizing the arguments leading to Eq. (3.8). We shall discuss only one chain which is a generalization of the chain III a.

States in this chain are characterized by the quantum numbers

$$
\begin{vmatrix}
U^{(1)}(4) \otimes U^{(2)}(4) \otimes U^{(3)}(4) \supset 0^{(1)}(4) \otimes 0^{(2)}(4) \otimes 0^{(3)}(4) \\
\quad\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow \qquad\quad \downarrow \qquad\quad \downarrow \\
[N_1] \qquad\quad [N_1] \qquad\quad [N_3] \qquad (\omega_1, 0) \quad (\omega_2, 0) \quad (\omega_3, 0) \\
\\
\supset 0^{(1+2)}(4) \otimes 0^{(3)}(4) \supset 0(4) \supset 0(3) \supset 0(2) \\
\qquad\downarrow \qquad\qquad\qquad\qquad\quad \downarrow \qquad\quad \downarrow \qquad\quad \downarrow \\
(\eta_1, \eta_2) \qquad\qquad\qquad (\tau_1, \tau_2) \quad J^P \qquad M
\end{vmatrix}
. \qquad (6.2)
$$

The $0^{(1+2)}(4)$ group is generated by the sum of generators of $0^{(1)}(4)$ and $0^{(2)}(4)$, as in Eq. (3.7). The total $0(4)$ group is obtained by adding the generators of $0^{(3)}(4)$. The values of (η_1, η_2) follow from the decomposition of the product $(\omega_1, 0) \otimes (\omega_2, 0)$ as in Eq. (3.19). The values
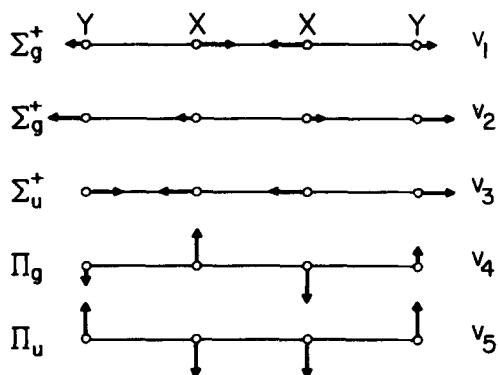
FIG. 12. Schematic representation of the normal vibrations of a linear X_2Y_2 molecule.

of (τ_1, τ_2) can be obtained from the product (η_1, η_2) $\otimes (\omega_3, 0)$.[11] They will not be given here explicitly. Note that the representation $(\tau_1, \tau_2 = 0)$ always occurs twice if $\eta_2 \neq 0$, once with a positive parity bandhead and once with a negative one.

By using arguments similar to those discussed in Sec. III, one can obtain the energy spectrum corresponding to the dynamic symmetry III a in linear rigid tetra-atomic molecules

$$E^{(a)}(N_1, N_2, N_3, \omega_1, \omega_2, \omega_3, \eta_1, \eta_2, \tau_1, \tau_2, J^P, M)$$

$$= F + A_1 \omega_1(\omega_1 + 2) + A_2 \omega_2(\omega_2 + 2) + A_3 \omega_3(\omega_3 + 2)$$

$$+ B_1[\eta_1(\eta_1 + 2) + \eta_2^2] + B_2[\tau_1(\tau_1 + 2) + \tau_2^2] + CJ(J + 1) .$$
(6.3)

The group theoretical quantum numbers can be related to those of the three stretching and the two bending modes (Fig. 12) by

$$\omega_1 = N_1 - 2v_1 , \quad \omega_2 = N_2 - 2v_2 , \quad \omega_3 = N_3 - 2v_3 ,$$

$$\eta_1 = N_1 + N_2 - (2v_1 + 2v_2 + v_4) , \quad \eta_2 = l_4 ,$$
(6.4)

$$\tau_1 = N_1 + N_2 + N_3 - (2v_1 + 2v_2 + 2v_3 + v_4 + v_5) , \quad \tau_2 = l_4 + l_5 .$$

Since the behavior of the stretching modes is relatively simple, we consider here only bending modes, and set $v_1 = v_2 = v_3 = 0$, $N_1 = N_2 = N_3 = (N/3)$. Then, the energy eigenvalues (6.3) can be rewritten as
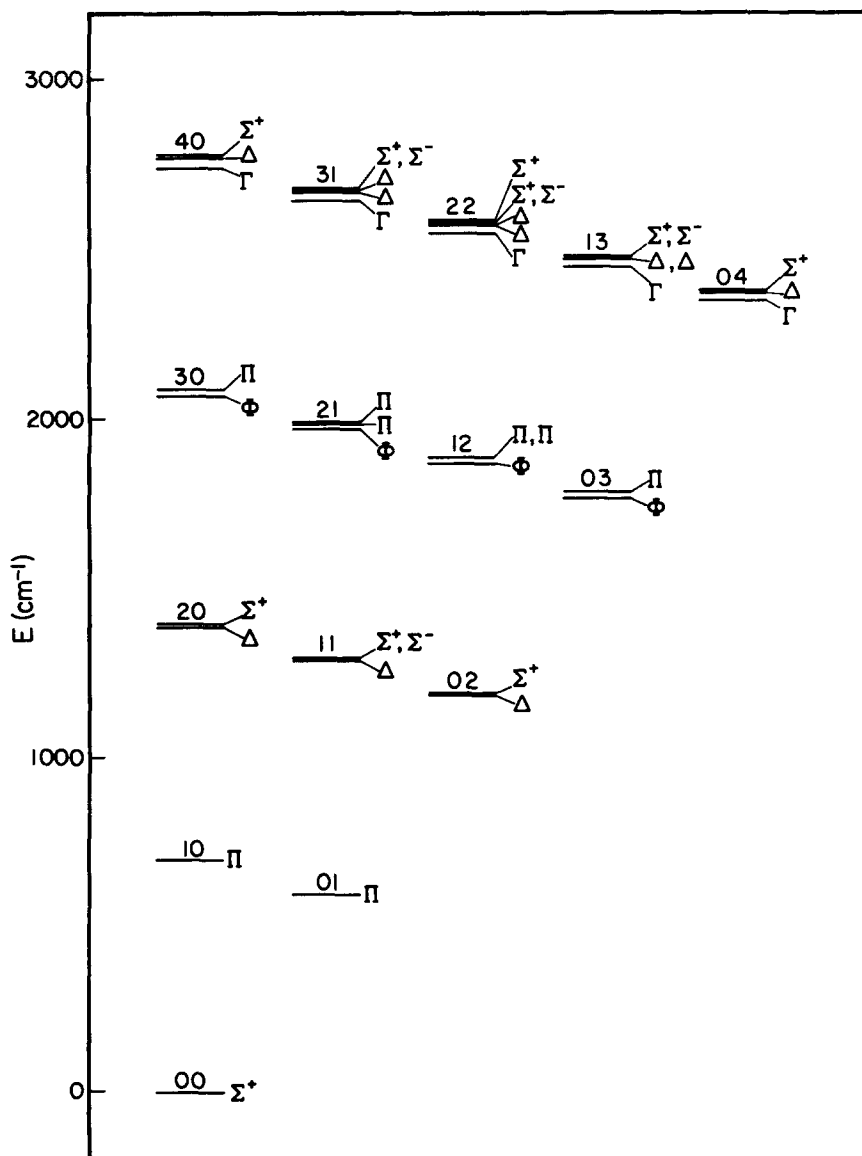

FIG. 13. Schematic representation of a spectrum of a linear tetra-atomic molecule with $0^{(1)}(4) \otimes 0^{(2)}(4) \otimes 0^{(3)}(4)$ symmetry. The energy levels are calculated using Eq. (6.5) with $N_1 = N_2 = N_3 = 50$, $B_1 = 0.5$, $B_2 = 2.0$ cm^{-1}. These values are appropriate to C_2H_2. Only a portion of the spectrum of the bending vibrations is shown.

$$E(N_1, N_2, N_3, v_1 = 0, v_2 = 0, v_3 = 0, v_4^{l_4}, v_5^{l_5}, J^P, M)$$

$$= F' - \frac{N}{3}(4B_1 + 6B_2)v_4 + (B_1 + B_2)v_4(v_4 - 2) + (B_1 + B_2)l_4^2$$

$$- 2NB_2v_5 + B_2v_5(v_5 - 2) + B_2l_5^2 - 2B_2v_4v_5 + 2B_2l_4l_5 .$$

$$(6.5)$$

The corresponding energy levels are shown in Fig. 13 with values of N, B_1, and B_2 appropriate to C_2H_2. Again, it appears that the $0^{(1)}(4) \otimes 0^{(2)}(4) \otimes 0^{(3)}(4)$ symmetry describes quite well the vibrational levels of rigid linear tetra-atomic molecules.

VII. CONCLUSIONS

We have presented here an algebraic description of rotation-vibration spectra of triatomic molecules. In particular, we have concentrated our attention to rigid linear and nonlinear molecules and shown that an algebraic Hamiltonian with, at most, two-body vibron interactions can well account for the observed properties of rigid linear molecules, including fine details such as Fermi resonances. For nonlinear, triangular molecules, this is no longer the case and higher order terms must be added. Work in this direction is in progress and it will be presented in a subsequent publication.

One of the main advantages of the algebraic approach is that, in addition to providing a quantitative description of the excitation spectra in terms of few parameters, it allows one to calculate all other properties. An example was shown in Fig. 10. Others include the calculation of the excitation probabilities in collisions and laser excitations. Finally, because of its group structure, the vibron model provides an excellent arena in which one can study the relation between classical and quantal behavior of molecules,[34] intermolecular energy transfer,[35] classical chaos,[36] and shape phase transitions.[37]

APPENDIX

Matrix elements of operators in the $0(4)$ basis can be calculated using the isomorphism $0(4) \approx SU(2) \otimes SU(2)$. The group chain $U(4) \supset SU(2) \otimes SU(2)$ was studied in detail by Hecht and Pang.[13] In this Appendix, we relate their notation to ours, so that matrix elements of any operator can be calculated analytically.

TABLE VII. Relations between the $U(4)$ generators (2.17) and the $SU(2) \otimes SU(2)$ tensors $T^{[211]}_{(s,m_s)(t,m_t)}$. N is the total vibron number $N = n_\pi + n_\sigma$.

$$2n_\pi - \frac{3}{2}N = \sqrt{3} \sum_m \langle 1, m, 1, -m \mid 0, 0 \rangle T^{[211]}_{(1,m)(1,-m)}$$

$$J_m^{(1)} = T^{[211]}_{(1,m)(0,0)} + T^{[211]}_{(0,0)(1,m)}$$

$$D_m^{(1)} = T^{[211]}_{(1,m)(0,0)} - T^{[211]}_{(0,0)(1,m)}$$

$$R_m^{(1)} = \sqrt{2} \sum_m \langle 1, m-m', 1, m' \mid 1, m \rangle T^{[211]}_{(1,m-m')(1,m')}$$

$$Q_m^{(2)} = \sum_{m'} \langle 1, m-m', 1, m' \mid 2, m \rangle T^{[211]}_{(1,m-m')(1,m')}$$

A. The single $U(4)$ case

The generators of $0(4)$:

$$\{G\}_{0(4)} = \{D_\mu^{(1)}, J_\mu^{(1)}\} \tag{A1}$$

are related to those of $SU(2) \otimes SU(2)$ by

$$S_\mu^{(1)} = (1/2)(J_\mu^{(1)} + D_\mu^{(1)}) , \quad T_\mu^{(1)} = (1/2)(J_\mu^{(1)} - D_\mu^{(1)}) . \tag{A2}$$

We consider three group chains with basis states labeled by

$$\begin{array}{cccc} U(4) \supset 0(4) \supset 0(3) \supset 0(2) \\ \downarrow & \downarrow & \downarrow & \downarrow \\ |[f] & (\rho, \tau) & J^P & M \rangle \end{array} , \tag{A3}$$

$$\begin{array}{ccccc} U(4) \supset SU(2) \otimes SU(2) \supset SU(2) \supset 0(2) \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ |[f] & s & t & J^P & M \rangle \end{array} , \tag{A4}$$

$$\begin{array}{ccccc} U(4) \supset SU(2) \otimes SU(2) \supset 0(2) \otimes 0(2) \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ |[f] & s & t & m_s & m_t \rangle \end{array} . \tag{A5}$$

For notational purposes, it is convenient to group together $\{s, t\}$ in Eq. (A4) and $(s, m_s)(t, m_t)$ in Eq. (A5). Furthermore, in these equations $[f]$ denotes the Young tableau of $U(4)$, $[f] \equiv [f_1, f_2, f_3, f_4]$.

For diatomic molecules, $[f] \equiv [N, 0, 0, 0] \equiv [N]$, but we consider here the most general case. The labels ρ, τ and s, t are related by

$$\rho = (s + t) , \quad \tau = (s - t) . \tag{A6}$$

Tensors in Eqs. (A4) and (A5) are related by

$$T^{[f]}_{(s,t)JM} = \sum_{m_s, m_t} \langle sm_s tm_t \mid JM \rangle T^{[f]}_{(sm_s)(tm_t)} , \tag{A7}$$

where $\langle sm_s tm_t \mid JM \rangle$ is a Clebsch–Gordan coefficient. The relation between these tensors and those defined in Eq. (2.16) is given in Table VII. $0(4)$-reduced matrix elements of generators of $U(4)$ can now be defined by making use of the Wigner–Eckart theorem for $0(4)$,

$$\langle [f](s''m_s'')(t''m_t'') \mid T^{[211]}_{(sm_s)(tm_t)} \mid [f](s'm_s')(t'm_t') \rangle$$

$$= [(2s'' + 1)(2t'' + 1)]^{-1/2} \langle s'm_s' sm_s \mid s''m_s'' \rangle \langle t'm_t' tm_t \mid t''m_t'' \rangle \langle [f]\{s'', t''\} \| T^{[211]}_{(s,t)} \| [f]\{s', t'\} \rangle_{0(4)} . \tag{A8}$$

TABLE VIII. 0(4) reduced matrix elements of the $U(4)$ generators (Ref. 13).

s'	t'	s''	t''	$[(2s+1)(2t+1)]^{-1/2}\langle[N]\{s,t\}\| T\{^{211}_{\bullet\bullet}\}_{t''}\|[N]\{s',t'\}\rangle_{0(4)}$
$s+1$	$s+1$	1	1	$-\left[\dfrac{(2s+3)(N-2s)(N+4+2s)}{4(2s+1)}\right]^{1/2}$
s	s	1	1	$-\dfrac{(N+2)}{2}$
$s-1$	$s-1$	1	1	$-\left[\dfrac{(2s-1)(N+2-2s)(N+2+2s)}{4(2s+1)}\right]^{1/2}$
s	s	1	0	$[s(s+1)]^{1/2}$
s	s	0	1	$[s(s+1)]^{1/2}$

The relation between 0(3)- and 0(4)-reduced matrix elements is

$$\langle[f]\{s'',t''\}J''\| T^{[211]}_{\{s,t\}}\|[f]\{s',t'\}J'\rangle_{0(3)}$$

$$=[(2J''+1)(2J'+1)(2J+1)]^{1/2}\begin{Bmatrix} s'' & t'' & J'' \\ s' & t' & J' \\ s & t & J \end{Bmatrix}\langle[f]\{s'',t''\}\| T^{[211]}_{\{s,t\}}\|[f]\{s',t'\}\rangle_{0(4)}, \tag{A9}$$

where the curly bracket denotes a 9-j symbol. These equations enable us to calculate 0(3)-reduced matrix elements of operators in the 0(4) basis. Using the results of Hecht and Pang,[13] given in Table VIII, we can calculate the 0(3)-reduced matrix elements shown in Table IX.

B. The coupled $U^{(1)}(4)\otimes U^{(2)}(4)$ case

The results of Appendix A can be used to calculate matrix elements of operators in the coupled case. As an example, we calculate matrix elements of the Majorana operator (3.36) in the $0^{(1)}(4)\otimes 0^{(2)}(4)\supset 0(4)$ basis. This operator can be rewritten as

$$\mathfrak{M}=-\sum_{J}(-)^{J}(T_{1}{}^{[211]}_{\{1,1\}J}\cdot T_{2}{}^{[211]}_{\{1,1\}J})+\tfrac{3}{4}N_{1}N_{2}-1/4[\mathcal{C}_{2}(04)-\mathcal{C}_{2}(0^{1}4)-\mathcal{C}_{2}(0^{2}4)]. \tag{B1}$$

Note that the tensors $T^{[211]}_{\{s,t\}J}$ acquire now an additional label (1 or 2) to distinguish vibron operators of type 1 or 2. The only nondiagonal term in Eq. (B1) has matrix elements

$$\left\langle[N_{1}],[N_{2}],(\omega_{1},0),(\omega_{2},0),(\tau_{1},\tau_{2})\left|\sum_{J}(-)^{J}(T_{1}{}^{[211]}_{\{1,1\}J}\cdot T_{2}{}^{[211]}_{\{1,1\}J})\right|[N_{1}],[N_{2}],(\omega'_{1},0),(\omega'_{2},0),(\tau_{1},\tau_{2})\right\rangle$$

$$=(-)^{\omega_{2}+\omega'_{1}+\tau_{1}}\begin{Bmatrix}\omega_{1}/2 & \omega_{2}/2 & (\tau_{1}+\tau_{2})/2 \\ \omega'_{2}/2 & \omega'_{1}/2 & 1\end{Bmatrix}\begin{Bmatrix}\omega_{1}/2 & \omega_{2}/2 & (\tau_{1}-\tau_{2})/2 \\ \omega'_{2}/2 & \omega'_{1}/2 & 1\end{Bmatrix}$$

$$\times\langle[N_{1}],\{\omega_{1}/2,\omega_{1}/2\}\| T_{1}{}^{[211]}_{\{1,1\}}\|[N_{1}],\{\omega'_{1}/2,\omega'_{1}/2\}\rangle_{0(4)}\langle[N_{2}],\{\omega_{2}/2,\omega_{2}/2\}\| T_{2}{}^{[211]}_{\{1,1\}}\|[N_{2}],\{\omega'_{2}/2,\omega'_{2}/2\}\rangle_{0(4)}, \tag{B2}$$

where the curly bracket denotes 6-j symbols and we have considered only totally symmetric representations $[N_{1}]$ and $[N_{2}]$. From (B2), inserting the appropriate values of the 6-j symbols, one can obtain the results quoted in Sec. IV,

TABLE IX. 0(3) reduced matrix elements of some generators in the 0(4) basis.

$$\langle[N],(\rho,0),J\|n_{\tau}\|[N],(\rho,0),J\rangle_{0(3)}=(2J+1)^{1/2}\left[\frac{N-1}{2}+\frac{J(J+1)(N+2)}{2\rho(\rho+2)}\right]$$

$$\langle[N],(\rho,0),J+1\|D^{(1)}\|[N],(\rho,0),J\rangle_{0(3)}=[(\rho+J+2)(J+1)(\rho-J)]^{1/2}$$

$$\langle[N],(\rho,0),J+1\|R^{(1)}\|[N],(\rho,0),J\rangle_{0(3)}=\frac{(N+2)(J+1)}{\rho(\rho+2)}[(\rho+J+2)(J+1)(\rho-J)]^{1/2}$$

$$\langle[N],(\rho+2,0),J+1\|R^{(1)}\|[N],(\rho,0),J\rangle_{0(3)}=-\frac{1}{2(\rho+2)}\times\left[\frac{(J+1)(\rho+J+2)(\rho+J+3)(\rho+J+4)(\rho+1-J)(N-\rho)(N+\rho+4)}{(\rho+1)(\rho+3)}\right]^{1/2}$$

$$\langle[N],(\rho-2,0),J+1\|R^{(1)}\|[N],(\rho,0),J\rangle_{0(3)}=-\frac{1}{2\rho}\times\left[\frac{(J+1)(\rho+J+1)(\rho-J)(\rho-J-1)(\rho-J-2)(N-\rho+2)(N+\rho+2)}{(\rho-1)(\rho+1)}\right]^{1/2}.$$

$$\left\langle [N_1], [N_2], (\omega_1, 0), (\omega_2, 0), (\tau_1, \tau_2) \,\middle|\, \sum_j (-)^j \, T_{1\,\{1,1\}_j}^{[211]} \cdot T_{2\,\{1,1\}_j}^{[211]} \,\middle|\, [N_1], [N_2], (\omega_1, 0), (\omega_2, 0), (\tau_1, \tau_2) \right\rangle$$

$$= \frac{(N_1 + 2)(N_2 + 2)}{16\omega_1(\omega_1 + 2)\omega_2(\omega_2 + 2)} [\omega_1(\omega_1 + 2) + \omega_2(\omega_2 + 2) - (\tau_1 + \tau_2)(\tau_1 + \tau_2 + 2)][\omega_1(\omega_1 + 2) + \omega_2(\omega_2 + 2) - (\tau_1 - \tau_2)(\tau_1 - \tau_2 + 2)] ,$$

$$\text{(B3)}$$

and

$$\left\langle [N_1], [N_2], (\omega_1 - 2, 0), (\omega_2, 0), (\tau_1, \tau_2) \,\middle|\, \sum_j (-)^j \, T_{1\,\{1,1\}_j}^{[211]} \cdot T_{2\,\{1,1\}_j}^{[211]} \,\middle|\, [N_1], [N_2], (\omega_1, 0), (\omega_2, 0), (\tau_1, \tau_2) \right\rangle$$

$$= \frac{(N_2 + 2)}{32\omega_2(\omega_2 + 2)\omega_1(\omega_1^2 - 1)} \{ [(\tau_1 + \omega_1 + \omega_2 + 2)^2 - \tau_2^2][(\omega_1 + \omega_2 - \tau_1)^2 - \tau_2^2]$$

$$\times [(\tau_1 + \omega_1 - \omega_2)^2 - \tau_2^2][(\tau_1 + \omega_2 - \omega_1 + 2)^2 - \tau_2^2][\omega_1^2 - 1][(N_1 + 2)^2 - \omega_1^2] \}^{1/2} .$$

$$\text{(B4)}$$

[1] F. Iachello and R. D. Levine, J. Chem. Phys. **77**, 3046 (1982).

[2] See, for example, *Photoselective Chemistry*, edited by J. Jortner, R. D. Levine, and S. A. Rice (Wiley, New York, 1981).

[3] See, for example, *Atom–Molecule Collision Theory*, edited by R. B. Bernstein (Plenum, New York, 1979).

[4] See, for example, R. S. Berry, in *Quantum Dynamics of Molecules*, edited by R. G. Woolley (Plenum, New York, 1980).

[5] B. B. Carey and G. Ewing, Annu. Rev. Phys. Chem. **27**, 553 (1976).

[6] O. S. van Roosmalen, A. E. L. Dieperink, and F. Iachello, Chem. Phys. Lett. **85**, 32 (1982).

[7] O. S. van Roosmalen, Ph. D. thesis, University of Groningen, The Netherlands, 1982.

[8] M. E. Kellman and R. S. Berry, Chem. Phys. Lett. **42**, 327 (1976); F. Amar, M. E. Kellman, and R. S. Berry, J. Chem. Phys. **70**, 1973 (1979); M. E. Kellman, F. Amar, and R. S. Berry, *ibid.* **73**, 2387 (1980).

[9] M. Moshinsky (to be published).

[10] O. S. van Roosmalen, Computer Program ROTVIB II, University of Groningen, The Netherlands, 1982.

[11] B. G. Wybourne, *Classical Groups for Physicists* (Wiley, New York, 1974).

[12] M. Hammermesh, *Group Theory* (Addison–Wesley, Reading, Mass., 1962).

[13] K. T. Hecht and S. C. Pang, J. Math. Phys. **10**, 1572 (1969).

[14] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1950).

[15] C. Wulfman, Chem. Phys. Lett. **23**, 370 (1973).

[16] G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (van Nostrand, New York, 1950).

[17] R. Anderson, S. Kumei, and C. Wulfman, J. Math. Phys. **14**, 1527 (1973).

[18] O. van Roosmalen, Computer Program VIBRON, University of Groningen, The Netherlands, 1982.

[19] I. Suzuki, J. Mol. Spectrosc. **25**, 479 (1968).

[20] Y. M. Engel (private communication).

[21] I. Abram, A. deMartino, and R. Frey, J. Chem. Phys. **76**, 572 (1982).

[22] K. Lehmann, G. Scherer, and W. Klemperer, J. Chem. Phys. **77**, 2853 (1982).

[23] T. Nakhagawa and Y. Morino, Bull. Chem. Soc. Jpn. **42**, 2212 (1969).

[24] S. N. Suchard, *Spectroscopic Data, Part A* (Plenum, New York, 1975).

[25] I. Suzuki, M. A. Pariseau, and J. Overend, J. Chem. Phys. **44**, 3561 (1966).

[26] G. E. Ewing, in *Potential Energy Surfaces and Dynamic Calculations*, edited by D. G. Truhlar (Plenum, New York, 1981).

[27] T. Oka, Phys. Rev. Lett. **45**, 531 (1980).

[28] A. Carrington, J. Buttonshaw, and R. Kennedy, Mol. Phys. **45**, 753 (1982).

[29] G. D. Carney and R. N. Porter, J. Chem. Phys. **65**, 3547 (1976); Phys. Rev. Lett. **45**, 537 (1980).

[30] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

[31] I. Benjamin, R. D. Levine, and J. L. Kinsey, J. Phys. **87**, 727 (1983).

[32] D. Gerlich, U. Nowotny, Ch. Schlier, and E. Tehoy, Chem. Phys. **47**, 245 (1982); Ch. Schlier in *Energy Storage and Redistribution in Molecules*, edited by J. Hinze (Springer, Berlin, 1982).

[33] R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics* (Clarendon, Oxford, 1974), Chap. 6.

[34] D. W. Noid, M. L. Koezukowski, and R. A. Marcus, in *Quantum Mechanics in Mathematics, Chemistry, and Physics*, edited by K. E. Gustafson and W. P. Reinhardt (Plenum, New York, 1981); S. A. Rice in *Quantum Dynamics of Molecules*, edited by R. G. Woolley (Plenum, New York, 1980).

[35] S. A. Rice, Adv. Chem. Phys. **47**, 117 (1981); J. Jortner and B. Pullman, *Intramolecular Dynamics* (Reidel, Dordrecht, 1982).

[36] G. Casati and J. Ford, *Stochastic Behavior in Classical and Quantum Hamiltonian Systems, Lecture Notes in Physics* (Springer, Berlin, 1979), Vol. 93.

[37] O. S. van Roosmalen and A. E. L. Dieperink, Ann. Phys. (N. Y.) **139**, 198 (1982).