

Vibrational excitations of arsine in the framework of a local unitary group approach

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Abstract

A description of vibrational excitations of pyramidal molecules in terms of the unitary group approach $U(v+1)$ is presented. Based on the recent reformulation of this algebraic method the Hamiltonian is first expressed in the space of coordinates and momenta and thereafter translated into an algebraic realization in terms of the generators of the dynamical group $U_s(4) \times U_b(4)$, where s and b stand for stretching and bending degrees of freedom, respectively. Fermi and number interactions are considered in the stretching–bending contribution of the Hamiltonian. This new approach provides in natural form the connection between the spectroscopic parameters and force constants. The analysis of the vibrational excitations of arsine is presented.

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1. Introduction

In the last decades local mode models have provided an alternative way to study highly excited vibrational states of symmetrical molecules. Because significant differences in atomic masses and anharmonicity are correlated, local behavior is strongly manifested in systems containing hydrogen atoms, like for instance H_2O , AsH_3 , SbH_3 , C_2H_2 , SiH_2 and C_6H_6 [1–3]. The observed stretching vibrational energy level patterns with close degeneracies are typical of these molecules, a feature that is nicely explained with the simplest version of this theory, where the bond oscillators are coupled by bilinear kinetic and potential energy terms [4]. The basic idea of the local models consists in considering a set of non interacting oscillators as a zeroth order Hamiltonian in such a way that the strength of their coupling versus bond anharmonicities determines the local character of the spectra. Although this approach

was originally applied only to stretching modes, using Morse oscillators for the diagonal contribution and taking a harmonic approximation for the interaction matrix elements (harmonically coupled anharmonic oscillator model) [1,4], an extension to include the bending vibrations as valence angle oscillators was also developed [5]. In the latter case a direct product of functions is proposed as a basis, with Morse functions for the stretching degrees of freedom and harmonic oscillator functions for the bending modes. A more general approach may be possible in which Morse oscillators are considered for stretches and asymmetrical bond bends and Pöshel-Teller oscillators for symmetrical out-of-plane modes [6]. This treatment has the advantage that it allows to unify in an algebraic $\text{SU}(2)$ representation the vibrational description of molecules without losing the connection with the configuration space [7–11]. An alternative local approach to describe vibrational excitations is represented by algebraic methods based on the use of unitary dynamical groups [12,13].

The second quantization formalism [14] and factorization methods [15–17] have given rise to a wide variety of algebraic methods in different fields of physics and

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chemistry [18–21]. In particular, when the vibrational excitations are described in terms of a basis of harmonic oscillators the number operator representation has proved its usefulness to compute matrix elements as well as to establish relevant interactions in the construction of effective Hamiltonians in both local and normal representations [12,19,22]. In the framework of a local mode picture another possibility of description consists in considering Morse and/or Pöshel-Teller oscillators either algebraically or in configuration space. In any case the approach provides a basis defined by the eigenfunctions of the zeroth order Hamiltonian of independent oscillators. An alternative basis is provided by the $U(v+1)$ model, although in this case there is no clear potential associated with it.

The $U(v+1)$ model was proposed some time ago first in the context of the description of collective states of nuclei [23,24] and later on in the field of molecular physics [12,13]. In the latter case for a set of v equivalent oscillators the dynamical group becomes $U(v+1)$, while for several sets of equivalent oscillators the direct product of groups is taken as the dynamical group. Recently a connection between the unitary group approach and the traditional description in configuration space of vibrational excitations was proposed [25,26]. This new approach has the remarkable feature that it is possible to set up the $U(v+1)$ algebraic representation of any Hamiltonian in configuration space without ambiguities, allowing to obtain force constants and model dipole transition operators directly from dipole functions in coordinates [26]. Up to now the application of this approach has been restricted to the stretching modes of arsine, where force constants and dipole transitions were studied. An analysis of the stretching modes of arsine using the traditional $U(v+1)$ approach has also been presented [27]. In this contribution we proceed to establish the general description of pyramidal molecules where no tunneling motion is allowed. This approximation is justified for systems where no inversion splitting is observed, like arsine and stibine [28–30]. In order to evaluate this new approach we shall present a study of the complete overtone spectra of arsine in a close correspondence with previous analysis in configuration space, including the attainment of force constants.

This paper is organized as follows. A summary of the new formulation of the $U(v+1)$ model is briefly presented in Section 2. Section 3 is devoted to establish the general model to describe the vibrational excitations of pyramidal molecules. The analysis of the results obtained for arsine is discussed in Section 4. Finally, our summary and conclusions are given in Section 5.

2. A summary of the $U(v+1)$ approach to vibrational excitations

In this section we present a summary of the $U(v+1)$ model according to the new reformulation presented in Ref. [25,26]. Let us start considering v equivalent oscillators. Associated with the i -th oscillator we have bosonic

creation \hat{a}_i^\dagger and annihilation \hat{a}_i operators. An additional \hat{s} boson is added with the constraint that the total number of bosons \hat{N} is constant. In this model the state vectors associated to a local mode description consist of a set of $v+1$ independent harmonic oscillators. Explicitly the basis is given by [25]

$$|[N], n; n_1, n_2, \dots, n_v\rangle = \frac{1}{\sqrt{(N-n)! \prod_j^v n_j!}} (\hat{s}^\dagger)^{N-n} \times \prod_i^v (\hat{a}_i^\dagger)^{n_i} |0\rangle, \quad (1)$$

which is characterized by the total number of quanta N , whose corresponding operator is given by

$$\hat{N} = \hat{n} + \hat{n}_s, \quad (2)$$

with

$$\hat{n} = \sum_{i=1}^v \hat{a}_i^\dagger \hat{a}_i; \quad \hat{n}_s = \hat{s}^\dagger \hat{s}. \quad (3)$$

The addition of the boson \hat{s} together with the fact that the representation $[N]$ is fixed, makes the unitary group $U(v+1)$ a dynamical group for the set of v oscillators.

From the generators of the unitary group $U(v+1)$ the following operators are introduced [25,26]

$$\hat{b}_i^\dagger \equiv \frac{\hat{s} \hat{a}_i^\dagger}{\sqrt{N}}; \quad \hat{b}_i \equiv \frac{\hat{s}^\dagger \hat{a}_i}{\sqrt{N}}, \quad (4)$$

with commutation relations

$$[\hat{b}_i, \hat{b}_j^\dagger] = \delta_{ij} - \frac{1}{N} [\hat{n} \delta_{ij} + \hat{a}_j^\dagger \hat{a}_i]; \quad [\hat{b}_i^\dagger, \hat{b}_j^\dagger] = [\hat{b}_i, \hat{b}_j] = 0, \quad (5)$$

which may be identified with the angular momentum commutation relations [31]. The action of these operators over the kets (1) is the following

$$\hat{b}_i^\dagger |[N], n; n_1, n_2, \dots, n_v\rangle = \sqrt{(n_i+1) \left(1 - \frac{n}{N}\right)} |[N], n+1; n_1, \dots, n_i+1, \dots, n_v\rangle, \quad (6a)$$

$$\hat{b}_i |[N], n; n_1, n_2, \dots, n_v\rangle = \sqrt{n_i \left(1 - \frac{n-1}{N}\right)} |[N], n-1; n_1, \dots, n_i-1, \dots, n_v\rangle, \quad (6b)$$

while for the operators $\hat{a}_i^\dagger(\hat{a}_i)$

$$\hat{a}_i^\dagger |[N], n; n_1, n_2, \dots, n_v\rangle = \sqrt{(n_i+1)} |[N], n+1; n_1, \dots, n_i+1, \dots, n_v\rangle, \quad (7a)$$

$$\hat{a}_i |[N], n; n_1, n_2, \dots, n_v\rangle = \sqrt{n_i} |[N], n-1; n_1, \dots, n_i-1, \dots, n_v\rangle. \quad (7b)$$

In the harmonic limit the operators $\hat{b}_i^\dagger(\hat{b}_i)$ go to $\hat{a}_i^\dagger(\hat{a}_i)$, with the usual bosonic commutation relations [25,26].

When α sets of equivalent oscillators are present in the vibrational description, a $u(v+1)$ algebra is introduced

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