

A SYMMETRY ADAPTED APPROACH TO VIBRATIONAL EXCITATIONS IN ATOMIC CLUSTERS

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Abstract

An algebraic method especially suited to describe strongly anharmonic vibrational spectra in molecules may be an appropriate framework to study vibrational spectra of Na_n^+ clusters, where nearly flat potential energy surfaces and the appearance of close lying isomers have been reported. As an illustration we describe the model and apply it to the Be_4 , H_3^+ , Be_3 and Na_3^+ clusters.

INTRODUCTION

The study of metallic clusters has been mainly concerned with the electronic properties of these systems. It has been suggested, however, that in analogy to the way crystalline structure determines the optical response and metallic properties in solid-state physics, the geometric structure may play a significant role in the case of cluster physics [1, 2]. Small finite size systems present special problems which cannot directly be dealt with by means of the methods applied to the bulk. Nuclear theorists, on the other hand, have much experience dealing with “the many body problem” and the application of these methods to clusters is already leading to significant contributions to their understanding. These techniques, however, usually ignore the position of atomic nuclei [3]. In [1, 2] ab initio calculations for

Na_n^+ ($n = 2 - 9, 11, 21$) clusters at low temperature are reported, which allow the assignment of specific cluster geometries by comparing the theoretical results with experimental optical depletion spectra for these systems. While for dimers and trimers the rovibrational spectra lead to a precise determination of internuclear distances and ground-state potential energy surfaces (P.E.S.), up to now the resolution of the vibronic structure for $n \geq 4$ is not enough to carry out a theoretical analysis that would confirm the results of ref. [2] and give information on the P.E.S. for the heavier clusters [4]. Even if the rovibrational data become available in the near future, the calculations of [2] imply that the corresponding potential surfaces are in general quite flat and thus one expects anharmonic effects to be significant. Also, in a number of cases close lying isomeric structures are found [2]. Since the usual molecular physics calculations are well suited for deep minima and not for “soft” molecules, it is important to consider alternative models in order to analyse the experimental results. In this paper we describe a new model which was designed to incorporate anharmonic behavior from the outset and which has been applied to a number of molecules, including the Na_3^+ cluster [5]-[8]. We illustrate the method with applications to some D_{3h} molecules and clusters and to the Be_4 cluster.

THE $U(2)$ VIBRON MODEL

The model is based on the isomorphism of the $U(2)$ Lie algebra and the one dimensional Morse oscillator, whose eigenstates can be associated with $U(2) \supset SO(2)$ states [9]. In the framework of the model the total number of bosons N is fixed by the potential shape and the eigenvalue m of the $SO(2)$ generator J_z , takes the values $m = \pm N/2, \pm(N-2)/2, \dots$. The Morse spectrum is reproduced twice and consequently for these applications the m -values must be restricted to be positive. In terms of the $U(2)$ algebra, the Morse Hamiltonian has the algebraic realization

$$\hat{H} = A(\mathbf{J}^2 - J_z^2) \quad . \quad (1)$$

with eigenvalues

$$E_M = AN[(v + 1/2) - v^2/N] \quad , \quad (2)$$

where the label $v = j - m$ denotes the number of quanta in the oscillator. The parameters N and A appearing in (2) are related with the usual harmonic and anharmonic constants ω_e and $x_e\omega_e$ used in spectroscopy [10]. We now consider the $U_i(2) \supset SU_i(2) \supset SO_i(2)$ algebra, generated by the set $\{\hat{G}_i\} \equiv \{\hat{N}_i, \hat{J}_{+,i}, \hat{J}_{-,i}, \hat{J}_{0,i}\}$, satisfying the commutation relations

$$[\hat{J}_{0,i}, \hat{J}_{\pm,i}] = \pm \hat{J}_{\pm,i} \quad , \quad [\hat{J}_{+,i}, \hat{J}_{-,i}] = 2\hat{J}_{0,i} \quad , \quad [\hat{N}_i, \hat{J}_{\mu,i}] = 0 \quad , \quad (3)$$

with $\mu = \pm, 0$. For the symmetric irreducible representation $[N_i, 0]$ of $U_i(2)$ one can show that the Casimir operator is given by [8] $\vec{J}_i^2 = \hat{N}_i(\hat{N}_i + 2)/4$, from which follows the identification $j_i = N_i/2$.

In the algebraic approach each relevant interatomic interaction is associated with a $U_i(2)$ algebra [5, 6]. As a first example, we consider the Be_4 cluster, which has a tetrahedral shape. \mathcal{D}_{3h} molecules can be similarly treated. In the Be_4 case there are six $U_i(2)$ algebras involved ($i = 1, \dots, 6$). The operators in the model are expressed in terms of the generators of these algebras, and the symmetry requirements of the tetrahedral group \mathcal{T}_d can be readily imposed [6, 11]. The local operators $\{\hat{G}_i\}$ acting on bond i can be projected to any of the fundamental irreps $\Gamma = A_1, E$ and F_2 . Using the $\hat{J}_{\mu,i}$ generators (3) we obtain the \mathcal{T}_d tensors

$$\hat{T}_{\mu,\gamma}^\Gamma = \sum_{i=1}^6 \alpha_{\gamma,i}^\Gamma \hat{J}_{\mu,i}, \quad (4)$$

where $\mu = \pm, 0$ and γ denotes the component of Γ . The expansion coefficients are the same as those given in the one phonon wave functions [7]. The Hamiltonian operator can be constructed by repeated couplings of these tensors to a total symmetry A_1 , since it must commute with all operations in \mathcal{T}_d . This is accomplished by means of the \mathcal{T}_d -Clebsch-Gordan coefficients [6, 11, 12].

All calculations can be carried out in a symmetry-adapted basis, which is projected from the local basis

$$\begin{array}{ccccccc} U_1(2) & \otimes & \cdots & \otimes & U_6(2) & \supset & SO_1(2) & \otimes & \cdots & \otimes & SO_6(2) & \supset & SO(2) \\ \downarrow & & & & \downarrow & & \downarrow & & & & \downarrow & & \downarrow \\ | [N_1] & , & \cdots & , & [N_6] & ; & v_1 & , & \cdots & , & v_6 & ; & V \end{array} \quad (5)$$

in which each anharmonic oscillator is well defined. By symmetry considerations, $N_i = N$ for the six oscillators, v_i , denotes the number of quanta in bond i and $V = \sum_i v_i$ is the total number of quanta [13, 8]. The local basis states for each oscillator are usually written as $|N_i, v_i\rangle$, where $v_i = (N_i - 2m_i)/2 = 0, 1, \dots [N_i/2]$ denotes the number of oscillator quanta in the i -th oscillator. The phonon states $|^V \phi_\gamma^\Gamma\rangle$ can be constructed using the Clebsch-Gordan coefficients of \mathcal{T}_d [6, 11]. Since all operators are expressed in terms of powers of the $U_i(2)$ generators, their matrix elements can be easily evaluated in closed form. The symmetry-adapted operators (11) and states [7] are the building blocks of the model.

We now proceed to explicitly construct the Be_4 Hamiltonian. For interactions that are at most quadratic in the generators the procedure yields

$$\hat{H}_0 = \omega_1 \hat{\mathcal{H}}_{A_1} + \omega_2 \hat{\mathcal{H}}_E + \omega_3 \hat{\mathcal{H}}_{F_2} + b_2 \hat{\mathcal{V}}_E + b_3 \hat{\mathcal{V}}_{F_2}, \quad (6)$$

with

$$\begin{aligned} \hat{\mathcal{H}}_\Gamma &= \frac{1}{2N} \sum_\gamma \left(\hat{T}_{-, \gamma}^\Gamma \hat{T}_{+, \gamma}^\Gamma + \hat{T}_{+, \gamma}^\Gamma \hat{T}_{-, \gamma}^\Gamma \right) \\ \hat{\mathcal{V}}_\Gamma &= \frac{1}{N} \sum_\gamma \hat{T}_{0, \gamma}^\Gamma \hat{T}_{0, \gamma}^\Gamma, \end{aligned} \quad (7)$$

The five interaction terms in Eq. (10) correspond to linear combinations of the ones obtained in lowest order in [6, 13]. However, it is necessary to include interactions which are related to the vibrational angular momenta associated with the degenerate modes E and F_2 . These kind of terms is absent in the former versions of the model [6, 13]. We now proceed to show how they can be obtained in the present model. In configuration space the vibrational angular momentum operator for the E mode is given by [14]

$$\hat{l}^{A_2} = -i \left(q_1^E \frac{\partial}{\partial q_2^E} - q_2^E \frac{\partial}{\partial q_1^E} \right), \quad (8)$$

where q_1^E and q_2^E are the normal coordinates associated to the E mode. This relation can be transformed to the algebraic space by means of the harmonic oscillator operators

$$b_\gamma^{\Gamma\dagger} = \frac{1}{\sqrt{2}} \left(q_\gamma^\Gamma - \frac{\partial}{\partial q_\gamma^\Gamma} \right), \quad b_\gamma^\Gamma = \frac{1}{\sqrt{2}} \left(q_\gamma^\Gamma + \frac{\partial}{\partial q_\gamma^\Gamma} \right), \quad (9)$$

to obtain

$$\hat{l}^{A_2} = -i \left(b_1^{E\dagger} b_2^E - b_2^{E\dagger} b_1^E \right). \quad (10)$$

Here $b_\gamma^E = \sum_i \alpha_{\gamma,i}^E b_i$, with a similar form for $b_\gamma^{\Gamma\dagger}$, while the $\alpha_{\gamma,i}^E$ can be read from (4). In order to find the algebraic expression for \hat{l}^{A_2} we first introduce a scale transformation in (11)

$$\bar{b}_i^\dagger \equiv \hat{J}_{-,i}/\sqrt{N_i}, \quad \bar{b}_i \equiv \hat{J}_{+,i}/\sqrt{N_i}. \quad (11)$$

The relevant commutator can be expressed as

$$[\bar{b}_i, \bar{b}_i^\dagger] = \frac{1}{N_i} [\hat{J}_{+,i}, \hat{J}_{-,i}] = \frac{1}{N_i} 2\hat{J}_{0,i} = 1 - \frac{2\hat{v}_i}{N_i}, \quad (12)$$

where

$$\hat{v}_i = \frac{\hat{N}_i}{2} - \hat{J}_{0,i}. \quad (13)$$

The other two commutators in (11) are not modified by (11). In the harmonic limit, which is defined by $N_i \rightarrow \infty$, Eq. (12) reduces to the standard boson commutator $[\bar{b}_i, \bar{b}_i^\dagger] = 1$. This limit corresponds to a contraction of $SU(2)$ to the Weyl algebra and can be used to obtain a geometric interpretation of the algebraic operators in terms of those in configuration space. In the opposite sense, Eq. (5) provides a procedure to construct the anharmonic representation of harmonic operators through the correspondence $b_i^\dagger \rightarrow \bar{b}_i^\dagger = \hat{J}_{-,i}/\sqrt{N_i}$ and $b_i \rightarrow \bar{b}_i = \hat{J}_{+,i}/\sqrt{N_i}$. Applying this method to the vibrational angular momentum (4) we find

$$\hat{l}^{A_2} = -\frac{i}{N} \left(\hat{J}_{-,1}^E \hat{J}_{+,2}^E - \hat{J}_{-,2}^E \hat{J}_{+,1}^E \right). \quad (14)$$

Table 1: Vibrational excitations of Be_4 using the algebraic Hamiltonian with parameters given in the text. The *ab initio* ($N \rightarrow \infty$) spectrum is generated with the parameters from [15]. The energies are given in cm^{-1} .

V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio $N \rightarrow \infty$	Present $N = 44$	V	$(\nu_1, \nu_2^m, \nu_3^l)$	Γ	Ab initio $N \rightarrow \infty$	Present $N = 44$
1	$(1, 0^0, 0^0)$	A_1	638.6	637.0	3	$(1, 0^0, 2^0)$	A_1	2106.8	2105.6
	$(0, 1^1, 0^0)$	E	453.6	455.0		$(1, 0^0, 2^2)$	E	2000.1	1999.8
2	$(0, 0^0, 1^1)$	F_2	681.9	678.2		F_2	F_2	2056.8	2052.8
	$(2, 0^0, 0^0)$	A_1	1271.0	1269.2		$(0, 3^1, 0^0)$	E	1341.3	1343.7
	$(1, 1^1, 0^0)$	E	1087.1	1087.0		$(0, 3^3, 0^0)$	A_1	1355.5	1352.5
	$(1, 0^0, 1^1)$	F_2	1312.6	1308.3		A_2	A_2	1355.5	1354.4
	$(0, 2^0, 0^0)$	A_1	898.3	901.4		$(0, 2^{0,2}, 1^1)$	F_2	1565.5	1565.7
	$(0, 2^2, 0^0)$	E	905.4	906.1		F_2	F_2	1584.4	1583.1
	$(0, 1^1, 1^1)$	F_1	1126.7	1125.1		$(0, 2^2, 1^1)$	F_1	1578.5	1578.0
		F_2	1135.5	1134.1		$(0, 1^1, 2^{0,2})$	E	1821.4	1821.6
		A_1	1484.0	1483.0		E	E	1929.5	1929.0
		E	1377.3	1373.9		$(0, 1^1, 2^2)$	A_2	1813.3	1813.1
3		F_2	1434.1	1429.6		A_1	A_1	1830.8	1831.7
	$(3, 0^0, 0^0)$	A_1	1897.0	1896.7		F_2	F_2	1874.4	1873.2
	$(2, 1^1, 0^0)$	E	1714.3	1714.3		F_1	F_1	1883.2	1883.0
	$(2, 0^0, 1^1)$	F_2	1937.0	1933.7		$(0, 0^0, 3^{1,3})$	F_2	2136.5	2134.2
	$(1, 2^0, 0^0)$	A_1	1526.6	1529.2		F_2	F_2	2327.3	2326.9
	$(1, 2^2, 0^0)$	E	1533.7	1532.8		$(0, 0^0, 3^3)$	F_1	2199.8	2197.1
	$(1, 1^1, 1^1)$	F_1	1752.2	1749.7		A_1	A_1	2256.5	2254.4
		F_2	1761.0	1759.8					

For the vibrational angular momentum $\hat{l}_\gamma^{F_1}$ associated with the F_2 mode we find a similar expression.

We can now use our model to fit the spectroscopic data of several polyatomic molecules. In the case of Be_4 the energy spectrum was analyzed by *ab initio* methods in [15], where force-field constants corresponding to an expansion of the potential up to fourth order in the normal coordinates and momenta were evaluated. We have generated the *ab initio* spectrum up to three phonons using the analysis in [14]. For the algebraic Hamiltonian we take [7]

$$\begin{aligned}
 \hat{H} = & \omega_1 \hat{\mathcal{H}}_{A_1} + \omega_2 \hat{\mathcal{H}}_E + \omega_3 \hat{\mathcal{H}}_{F_2} + X_{33} \left(\hat{\mathcal{H}}_{F_2} \right)^2 + X_{12} \left(\hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_E \right) \\
 & + X_{13} \left(\hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_{F_2} \right) + g_{33} \sum_{\gamma} \hat{l}_\gamma^{F_1} \hat{l}_\gamma^{F_1} + t_{33} \hat{\mathcal{O}}_{33} + t_{23} \hat{\mathcal{O}}_{23} . \quad (15)
 \end{aligned}$$

The terms $\hat{\mathcal{O}}_{33}$ and $\hat{\mathcal{O}}_{23}$ represent the algebraic form of the corresponding interactions in [14] which are responsible for the splitting of the vibrational levels in the $(\nu_1, \nu_2^m, \nu_3^l) = (0, 0^0, 2^2)$ and the $(0, 1^1, 1^1)$ overtones.

Table 2: Least-square energy fit for the vibrational excitations of H_3^+ , Be_3 and Na_3^+ . The energy differences $\Delta E = E_{th} - E_{exp}$ are given in cm^{-1} .

V	(ν_1, ν_2^l)	Γ	H_3^+ ΔE	Be_3 ΔE	Na_3^+ ΔE
1	$(0, 1^1)$	E	-1.55	0.51	0.93
	$(1, 0^0)$	A_1	0.42	0.02	1.95
2	$(0, 2^0)$	A_1	7.48	-0.74	0.37
	$(0, 2^2)$	E	-5.69	0.17	0.84
	$(1, 1^1)$	E	-0.61	0.82	1.68
	$(2, 0^0)$	A_1	-0.11	-0.04	1.26
3	$(0, 3^1)$	E	-4.46	-2.05	-1.19
	$(0, 3^3)$	A_1	3.18	-1.23	-0.34
	$(0, 3^3)$	A_2	2.44	0.61	-0.33
	$(1, 2^0)$	A_1	0.66	1.90	-0.01
	$(1, 2^2)$	E	-5.00	-1.36	0.34
	$(2, 1^1)$	E	4.07	0.79	-0.19
	$(3, 0^0)$	A_1	-1.23	-1.66	-2.06
r.m.s.			5.84	1.35	1.33
Parameters			8	4	4

Note that the Be_4 Hamiltonian (15) preserves the total number of quanta V . This is a good approximation for this case according to the analysis of [14, 15], but it is known that Fermi resonances can occur for certain molecules when the fundamental mode frequencies are such that (V, V') states with $V \neq V'$ are close in energy. These interactions can be introduced in the Hamiltonian by means of a polyad analysis [16]. For \mathcal{D}_{3h} molecules we can follow an analogous procedure, namely, we can construct the \mathcal{D}_{3h} symmetry-adapted operators and states corresponding to (4) and [7] and carry out the building up procedure to construct the Hamiltonian and higher phonon states, using in this case the appropriate projection operators and Clebsch-Gordan coefficients [6, 11].

EXAMPLES

We now present the results of our least-square fits to the energy spectra of Be_4 , Be_3 , Na_3^+ and H_3^+ . In Table 1 we show the fit to Be_4 using the Hamiltonian (15). The fit includes all levels up to $V = 4$ quanta and gives a r.m.s. deviation of 2.6

cm^{-1} , which can be considered of spectroscopic quality. In Table 1 we only show the results for the levels with $V \leq 3$. We point out that in [14, 15] several higher order interactions are present which we have neglected. Since our model can be put into a one to one correspondence with the configuration space calculations, it is in fact possible to improve the accuracy of the fit considerably, but we have used a simpler Hamiltonian than the one of [14, 15]. When no *ab initio* calculations are available (or feasible) the present approach can be used empirically, achieving increasingly good fits by the inclusion of higher order interactions [7]. In Table 2 we present fits to the spectra of Be_3 , Na_3^+ and H_3^+ up to three phonons. While remarkably accurate descriptions of the first two molecules can be achieved using a four-parameter Hamiltonian, we were forced to include four additional higher order terms in the H_3^+ Hamiltonian in order to properly describe this molecule. This is in accordance with the work of Carter and Meyer [17], who were forced to include twice as many terms in the potential energy surface for H_3^+ than for the Na_3^+ molecule. The H_3^+ ion is a very “soft” molecule which, due to the light mass of its atomic constituents carries out large amplitude oscillations from its equilibrium positions [17]. This may also be the case for the potentials associated to metallic clusters [2].

SUMMARY

In this paper we have studied the vibrational excitations of several molecules and clusters in a symmetry-adapted algebraic model. These studies suggest that the symmetry-adapted algebraic model provides a numerically efficient tool to study molecular vibrations with high precision. The main difference with other methods is the use of symmetry-adapted tensors in the construction of the Hamiltonian. In this approach, the anharmonicity can be introduced from the outset, interactions can be constructed in a systematic way, each term has a direct physical interpretation, and spurious modes can be eliminated exactly [16]. It is important to further explore the scope and applicability of the present approach, and in particular study the vibrational spectra in metallic clusters, including the appearance of isomeric shapes with different point symmetries.

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