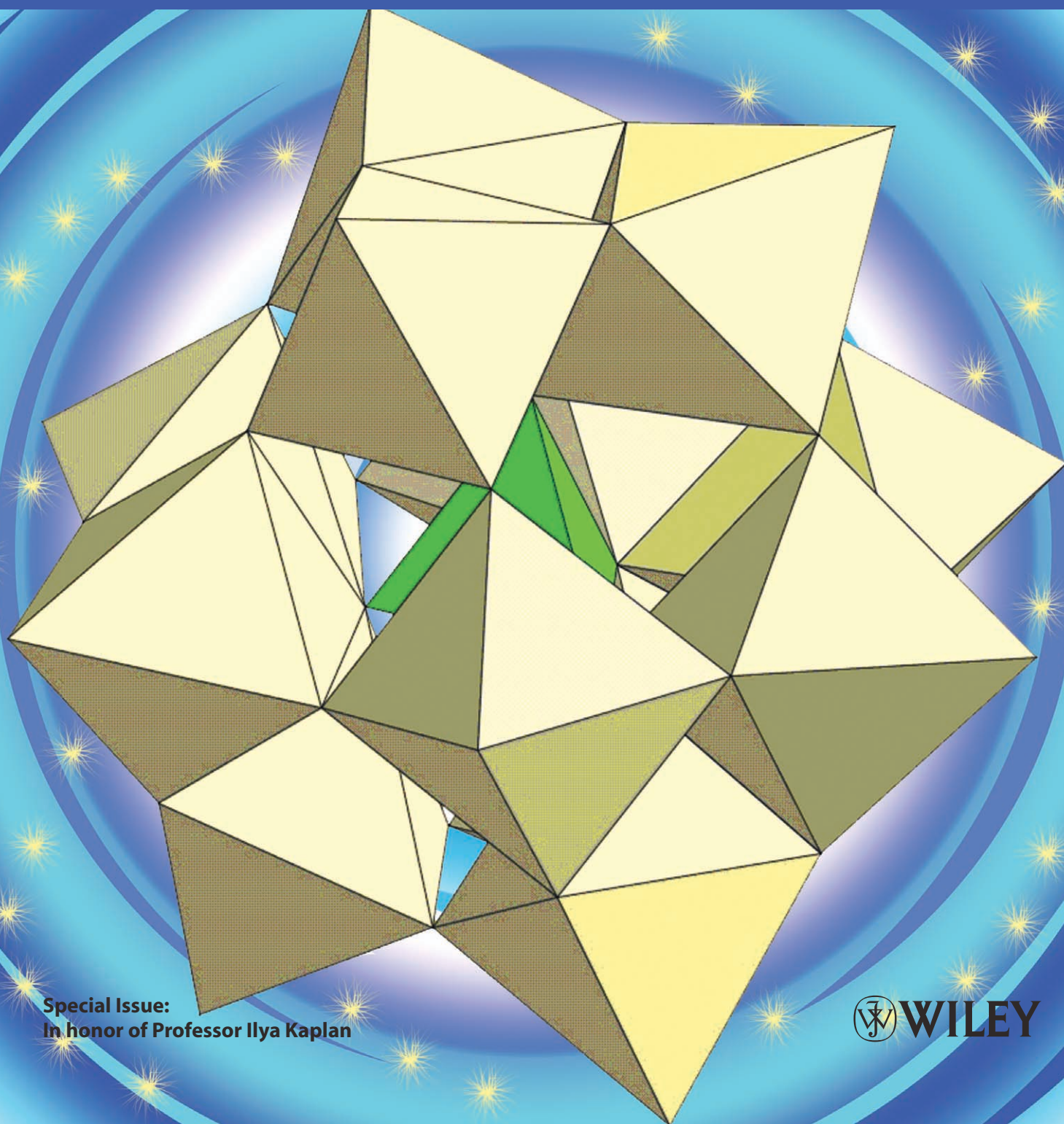


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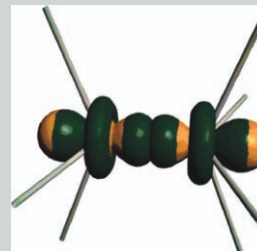
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The odd-electron molecular theory,  
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comparative consideration of  $sp^2$   
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An Analysis of Unsupported Triple  
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6 Transition Elements Based on the  
Combined Natural Orbitals for  
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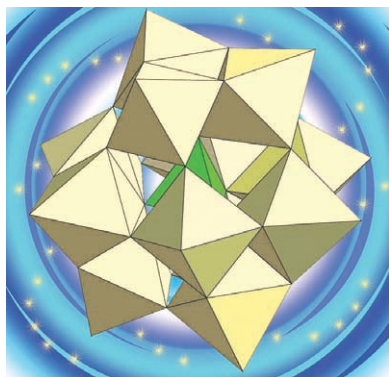


Assessing the Performance of  
Computational Methods for the  
Prediction of the Ground State  
Structure of a Cyclic Decapeptide

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The performance of a series of  
classical force fields is discussed to  
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DOI: 10.1002/qua.24085

## Special Issue: In honor of Professor Ilya Kaplan

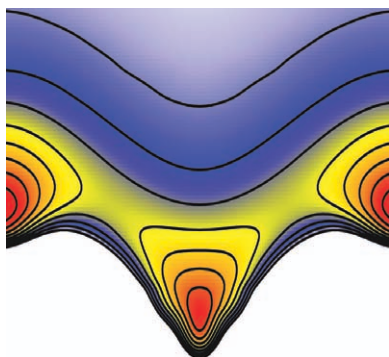


### Jahn-Teller Effects

Large scale Jahn-Teller systems, such as  
the biologically important iron-sulfur  
proteins, polynuclear metal-oxide clusters,  
and metal ions in crystals, present a  
complicated dynamic problem that, in  
general, cannot be solved analytically. In  
fact, the vibronic properties of these  
systems have remained unknown due to  
the lack of efficient computational tools.  
On page 2957, Boris Tsukerblat, Andrew  
Palii, Juan M. Clemente-Juan, Alejandro  
Gaita-Ariño, and Eugenio Coronado  
present a symmetry-adapted approach  
aimed at the accurate solution of this  
problem. The image on the cover and left  
illustrates an ideal system for the  
application of this method, the reduced  
mixed-valence dodecanuclear Keggin  
anion, in which the electronic pair is  
delocalized over 12 sites.

### Potential Energy Surface Generation

The generation procedure of the potential  
energy surface (PES) can, in some systems,  
influence the relative stability of  
conformers. In the case of the triatomic  
van der Waals molecule  $\text{He}_2$ , presented  
on page 2971 by Gerardo Delgado-Barrio  
and coworkers, it is concluded that  
different procedures provide PESs of  
similar quality, determined by the accuracy  
of the available ab initio data. Confirming  
the results of previous experimental  
studies, the surface depicted on the cover  
shows two potential minima  
corresponding at the linear and T-shaped  
configurations with very similar well-  
depths.





# A Symmetry Adapted Approach to the Dynamic Jahn-Teller Problem: Application to Mixed-Valence Polyoxometalate Clusters with Keggin Structure<sup>†</sup>

Boris Tsukerblat,<sup>\*,[a]</sup> Andrew Palii,<sup>[b]</sup> Juan M. Clemente-Juan,<sup>[c]</sup> Alejandro Gaita-Ariño,<sup>[c]</sup> and Eugenio Coronado<sup>[c]</sup>

In this article, we present a symmetry-adapted approach aimed to the accurate solution of the dynamic vibronic problem in large scale Jahn-Teller (JT) systems. The algorithm for the solution of the eigen-problem takes full advantage of the point symmetry arguments. The system under consideration is supposed to consist of a set of electronic levels mixed by the active JT and pseudo JT vibrational modes. Applying the successive coupling of the bosonic creation operators, we introduce the irreducible tensors that are called multivibronic operators. Action of the irreducible multivibronic operators on the vacuum state creates the vibrational symmetry adapted basis that is subjected to the Gram-Schmidt orthogonalization at each step of evaluation. Finally, the generated vibrational basis is coupled to the electronic one to get the symmetry adapted electron-

vibrational (vibronic) basis within which the full matrix of the JT Hamiltonian is blocked according to the irreducible representations (irreps) of the point group. The proposed approach is a part of our study of the nanosized mixed valence (MV) clusters with large number of delocalized electrons that are at the border line between quantum and classical objects. Here, we illustrate in detail the developed technique by the application to the 2e-reduced MV dodecanuclear Keggin anion in which the electronic pair is delocalized over 12 sites (overall symmetry  $T_d$ ) giving rise to the  $({}^1T_2+{}^1E+{}^1A_1)\otimes(e+t_2)$   $({}^3T_1+{}^3T_2)\otimes(e+t_2)$  combined JT/pseudo JT problems for the spin-singlet and spin-triplet states. © 2012 Wiley Periodicals, Inc.

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## Introduction

Jahn-Teller (JT) and pseudo JT effects lead to a complicated dynamic problem that, in general, cannot be solved in an analytical way.<sup>[1–3]</sup> The difficulties are progressively aggravated for the multimode systems or/and when the energy pattern contains several low-lying levels mixed by the active JT and pseudo JT vibrations. This especially refers to the large scale mixed valence (MV) systems, like biologically important systems such as iron-sulfur proteins,<sup>[4–6]</sup> polynuclear metal-oxide clusters in which several electrons are delocalized over metal network (e.g., reduced polyoxometalates [POMs], with Keggin and Wells-Dawson structures),<sup>[7,8]</sup> impurity metal ions in crystals,<sup>[9–11]</sup> etc. In these cases, the dimension of the truncated vibronic matrices to be diagonalized becomes very high due to sizeable electronic basis and multiple degeneracy of the excited vibrational levels. Convergence of the results is always questionable, so that the truncation of the vibronic matrices can result in a dramatic lack of precision not only when the vibronic coupling is strong but also providing moderate or even relatively weak coupling.

For this reason, many efforts have been applied toward elaboration of the approximate approaches among which the adiabatic approximation plays a key role. In some cases, the adiabatic approximation provides a general insight on the important features of the JT systems, for example, for a qualitative discussion of the broad electron-vibrational light absorption bands, asymmetric electronic distribution of the electronic

density in complex MV systems,<sup>[8c]</sup> structural peculiarities of polyatomic molecules,<sup>[2,3]</sup> spin-crossover complexes,<sup>[12]</sup> and crystals subjected to the structural phase transitions.<sup>[13]</sup> At the same time, the applicability of the semiclassical adiabatic approximation is greatly restricted due to the dynamic character of the vibronic coupling, resulting in a discrete energy

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pattern of the hybrid electron-vibrational levels. Even in a favorable case of strong vibronic coupling, the adiabatic approximation fails in the description of the physical characteristics of the JT systems related to the quantum structure of the levels, like spectroscopic phenomena, and in particular, wide optical bands for which transitions in the nonadiabatic anticrossing area of the potential surfaces play an important role in the adequate description of the band-shapes.<sup>[11]</sup>

Many attempts have been undertaken to get an accurate solution of the dynamic problem (for a review see Refs. [1–3,11,14]). A powerful approach is based on the symmetry combined with the Lanczos algorithm<sup>[15,9b]</sup> (see also references therein). Alternatively, a significant progress in the solution of the dynamic problem has been achieved by the exploration of the Lie symmetries of the JT Hamiltonians that not only bring a beauty but really allows to essentially simplify the solution of the dynamic problem.<sup>[16–19]</sup> Nevertheless, the vibronic Hamiltonian only exhibits high (unitary) symmetry in the model restricted by the linear vibronic coupling, in which a special interrelation between the coupling constants and vibrational frequencies exists. This significantly reduces the area of practical applicability of the extremely elegant approaches based on the unitary symmetries. If these special requirements are not fulfilled or/and the quadratic (or/and high order) vibronic terms are significant, the unitary symmetries prove to be reduced to the point symmetries. That is why the task of the full exploration of the advantages provided by the point symmetry of the JT and pseudo JT systems remains a current challenge even when the computational abilities are strongly increased.

The main goal of this article is to describe a symmetry adapted approach aimed to an accurate solution of the dynamic problem for the JT and pseudo JT systems. This goal is part of our study of the nanosized MV clusters that are at the border line between quantum and classical objects. An accurate solution for the states of the delocalized electronic pair in MV POMs based on symmetry arguments have been obtained in Ref. [8]. In our recent articles,<sup>[20]</sup> we proposed a general approach for the evaluation of the energy pattern of high nuclearity MV systems with an arbitrary number of itinerant electrons. The vibronic interaction inherent to the problem of mixed valency can not be neglected in particular for the description of the intervalence optical absorption. That is why here we attempt to extend our efforts in the study of mixed valency by the elaboration of an effective approach to the dynamic vibronic problem.

We introduce the mathematical procedure through the consideration of the MV POM with Keggin structure reduced by 2e. This dodecanuclear MV system belongs to a large class of POMs, the so-called “heteroblues,” which are attracting considerable interest in solid state chemistry, biomedical applications, catalysis, and materials science in view of its unique electronic properties.<sup>[21]</sup> In terms of mixed-valency, the Keggin anion can be viewed as a high-nuclearity cluster belonging to Class II in Robin and Day classification. Owing to its complexity, this system provides a complicated high symmetric JT system for which the dynamic problem seems to be actual for the adequate description of the nontrivial magnetic and optical

(intervalence bands) properties of these compounds. In this article, we will focus on the elaboration of the theoretical approach, while the associated computer program aimed to solve the multimode multilevel vibronic problems together with the detailed discussion of the experimental data on the Keggin anion will be published elsewhere (Clemente-Juan et al., to be submitted).

## General Statements

The Hamiltonian of a JT (or, in general, pseudo JT) system can be represented as:

$$H = H_e + \sum_i \hbar\omega_i \left( q_i^2 - \frac{\partial^2}{\partial q_i^2} \right) + \sum_i v_i \mathbf{O}_i q_i \quad (1)$$

Here,  $q_i$  are the dimensionless vibrational coordinates,  $\omega_i$  are the vibrational frequencies so that the second term in Eq. (1) is the harmonic oscillator Hamiltonian. The symbol  $i \equiv v\bar{\Gamma}\bar{\gamma}$  involves active vibrational irreps  $\bar{\Gamma}$ ,  $\bar{\gamma}$  numerates the basis functions of the irrep  $\bar{\Gamma}$  and symbol  $v$  is introduced to distinguish the repeated irreps  $\bar{\Gamma}$ . The electronic subsystem described by the Hamiltonian  $H_e$  is supposed to consist of a set of the closely spaced electronic levels  $\Gamma_1, \Gamma_2, \dots, \Gamma_t$  labeled by the irreps of the actual point group (the basis functions will be marked by the symbols  $\gamma_1, \gamma_2, \dots, \gamma_t$ ). Conventionally, this electronic Hamiltonian (and consequently the point group) is defined with respect to the high symmetric nuclear configuration (all  $q_i = 0$ ). The electronic levels  $\Gamma_1, \Gamma_2, \dots, \Gamma_t$  are mixed by the active JT and pseudo JT vibrational modes  $\bar{\Gamma}_1, \bar{\Gamma}_2, \dots, \bar{\Gamma}_f$ . The third term in Eq. (1) represents the linear (with respect to  $q_i$ ) term of the vibronic interaction in which  $\mathbf{O}_i$  are the so-called vibronic matrices defined in the electronic basis restricted to the levels  $\Gamma_1, \Gamma_2, \dots, \Gamma_n$  and  $v_i$  are the dimensionless (in  $\hbar\omega$  units) vibronic coupling parameters. In general, the approach described hereunder is not limited to the case of the linear vibronic coupling.

The full JT Hamiltonian, Eq. (1), can be diagonalized in the basis composed as the direct product of the electronic functions  $|\Gamma_f \gamma_f\rangle$  ( $f = 1, 2, \dots, t$ ) and the harmonic oscillators states  $|n_i\rangle$  ( $n_i = 0, 1, 2, \dots$ ):

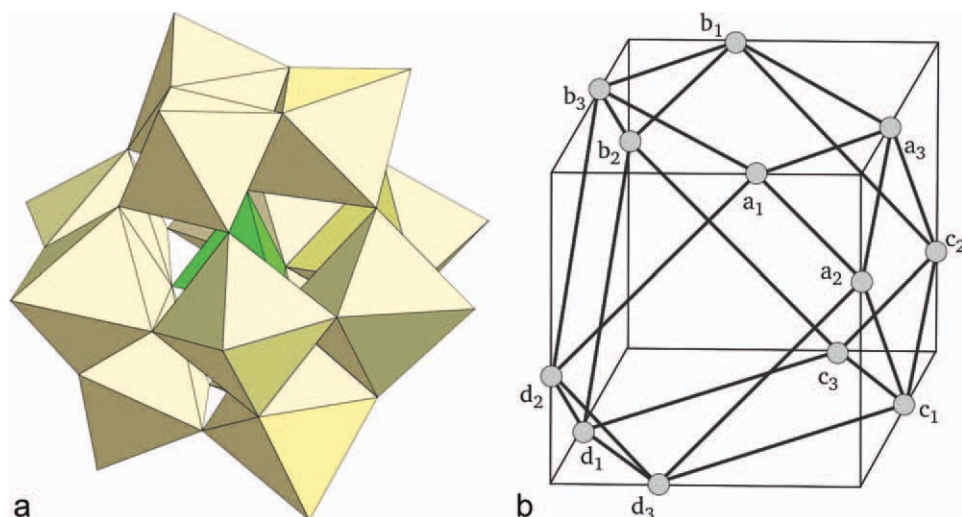
$$|\Gamma_f \gamma_f\rangle |n_1\rangle |n_2\rangle \dots |n_k\rangle \equiv |\Gamma_f \gamma_f\rangle |n_1, n_2, \dots, n_k\rangle \quad (2)$$

Due to multiple degeneracy of the excited vibrational levels in multimode JT systems the size of the matrices of the full Hamiltonian proves to be rather large even if the basis is restricted to a relatively small number of vibrational levels. On the other hand, the truncation of the basis leads to a significant lack of precision providing moderate or even relatively weak JT coupling.

Let us introduce the creation and annihilation bosonic operators  $b_{v\bar{\Gamma}\bar{\gamma}}^+$  and  $b_{v\bar{\Gamma}\bar{\gamma}}$  for the vibrational modes  $v\bar{\Gamma}\bar{\gamma}$ . The creation operator has the following property:

$$\hat{b}^+ |n\rangle = \sqrt{n+1} |n+1\rangle \quad (3)$$

Therefore by applying the creation operators to the vacuum state in a successive way



**Figure 1.** Two-electron reduced polyoxoanion with Keggin structure: network of the octahedral units (a) and scheme of the metal sites (b) [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$$(\hat{b}^+)^n |0\rangle = \sqrt{n!} |n\rangle \quad (4)$$

one can build the excited states  $|n\rangle$ . For the sake of brevity we will use the notation  $\hat{b}^+ = \hat{c}$ .

### Electronic States and Vibrations of the 2e-Reduced Keggin Polyanion

POMs are molecular metal-oxides containing networks of octahedral  $MO_6$  units which share edges or corners.<sup>[7,8]</sup> The Keggin structure consists of the four edge-sharing triads of  $MO_6$  units arranged around the heteroatom X (= B, Si, P, Co, Cu,...) by sharing corners in such a way that the system consisting of the twelve sites possesses overall tetrahedral symmetry  $T_d$  (Fig. 1a). Figure 1b shows the idealized scheme of the metal sites of the Keggin system that consists of the four metal triangles ( $a_1a_2a_3$ ,  $b_1b_2b_3$ , etc.) perpendicular to the  $C_3$  axes of the tetrahedron. The Keggin anion can be reversibly reduced by adding one or more electrons, which are delocalized over the metal network. The resulting MV systems usually belongs to Class II in the Robin and Day classification<sup>[22]</sup> (see also review article Ref. [23]) exhibiting thus an intermediate vibronic coupling. In this respect, the Keggin anion with the delocalized electronic pair is of a special interest due to its unusual magnetic properties. In fact, as it was suggested in Refs. [8,24] the delocalization results in the effective stabilization of the antiferromagnetic spin state of the electronic pair in the Keggin anion. This physical conclusion is rather general and valid also for other 2e-reduced POMs, for example, for the Wells-Dawson systems.<sup>[8]</sup>

Due to the complexity of the vibronic problem in its general form, it is conventional to use the model formulated by Piepho, Krausz, and Schatz<sup>[22]</sup> (referred to as PKS model) to treat this problem. This model deals with the independent "breathing" displacements (that are assumed to be the normal coordinates) of the ions around the sites of the electron localization. Being very efficient and at the same time relatively simple, this

model is able to describe the most important features of the phenomena related to mixed valency.

The interpretation of the spin pairing in the Keggin anion proposed in Ref. [8a] is based on the model including delocalization (single and double electron transfer processes) of the two electrons over 12 sites (Fig. 1b) as well as the Coulomb repulsion. The energy levels can be divided into five groups corresponding to the different distances between delocalized electrons in the 66 dispositions.

The Coulomb repulsion tends to keep the electrons as far as possible in the ground configuration that is shown to consist of the three spin-singlets  $^1A_1$ ,  $^1E$ ,  $^1T_2$  and two spin triplets  $^3T_1$  and  $^3T_2$  and the energy levels are given in Ref. [8a]. The conditions were elucidated under which spin pairing can occur as a result of competition between the single- and double electron transfer processes and depends also on the interelectronic interaction. It was emphasized that these conditions are strongly affected by the vibronic interactions that tends to localize the electrons and thus effectively reduce the transfer parameters. The degrees of localization prove to be different for the spin-triplet and spin-singlet states that essentially influence the magnetic properties of the reduced Keggin anion. That is why in our article,<sup>[8c]</sup> we presented a study of the electronic localization based on the vibronic PKS model. It was shown that the doubly degenerate ( $e$ ) and triply degenerate vibrations ( $t_2$ ) are active and hence, the potential surfaces are determined by the JT/pseudo JT interactions of the types of ( $^1T_2 + ^1E + ^1A_1$ )  $\otimes$  ( $e + t_2$ ) for the spin singlets and ( $^3T_1 + ^3T_2$ )  $\otimes$  ( $e + t_2$ ) for the spin triplets. The adiabatic approximation used in Ref. [8c] provides an important qualitative information about the symmetry of the localized configurations of the electronic pair (broken symmetry states) but strongly restricts the accuracy of calculations of the magnetic characteristics and especially, the profiles of the intervalence optical bands for which the quantum structure of the excited vibronic levels is crucially important. It is important also to note that within the PKS model both types of vibrations essentially contribute to the vibronic coupling (the parameters are interrelated) and therefore, the problem can not be simplified by neglecting, for example, one type ( $E$  or  $T_2$ ) of the active vibrations.

Within the PKS model, the frequencies of  $T_2$  and  $E$  vibrations are equal as they both simply represent the frequencies of the local "breathing" mode and therefore, the electronic system is effectively coupled to a five-dimensional oscillator. Therefore, the dimension of the vibrational space  $G(N)$  including five modes ( $E$  and  $T_2$ ) can be estimated as:

$$G(N) = \sum_{n=0}^N \frac{1}{24} (n+1)(n+2)(n+3)(n+4) \\ = \frac{1}{120} (N+1)(N+2)(N+3)(N+4)(N+5), \quad (5)$$

where,  $n = n_1 + n_2 + n_3 + n_4 + n_5$  is the total number of excitation of the five-dimensional harmonic oscillator (label of the energy level), the expression under summation is the total degeneracy of the level with a given  $n$  and  $N$  is the number of the levels included in the basis. The total degeneracy of the electron-vibrational space for spin-singlets and spin-triplets is  $6G(N)$ , which leads to a very high dimension of the vibronic matrices. For example, in the cases under consideration the size  $6G(N)$  of the truncated matrix (without symmetry based simplifications) for  $N = 40$  as large as 7330554. This choice of the basis can probably ensure a reasonable (but not high) accuracy in the description of several low lying vibronic levels required for an adequate evaluation of the profiles of the intervalence optical bands in the Keggin anion. At the same time, one can see that even a relatively small number of the vibronic levels involved in the evaluation lead to the huge size of the matrices in the multimode systems and demonstrate a necessity of the efficient use of the symmetry. To design the symmetry adapted basis we will first consider  $E$  and  $T_2$  vibrations separately and then the results will be combined taking into account the electronic states.

## Group-Theoretical Classification for a Two-Dimensional Oscillator

The vibrational functions in the full electron-vibrational basis in Eq. (2) do not possess definite symmetry properties with respect to the operations of the point group. To adapt them to the definite irreps let us first consider the case of the two-dimensional ( $E$ ) harmonic oscillator. The basis of the irrep  $E$  in  $T_d$  will be chosen in a standard way:  $u \propto 3z^2 - r^2$ ,  $v \propto \sqrt{3}(x^2 - y^2)$ .<sup>[25]</sup> The functions  $|n_u n_v\rangle$  can be built by applying the creation operators as follows:

$$|n_u n_v\rangle = \frac{1}{\sqrt{n_u! n_v!}} \hat{c}_u^{n_u} \hat{c}_v^{n_v} |00\rangle. \quad (6)$$

Each level with a certain  $n = n_u + n_v$

$$E_n = \hbar\omega(n_u + n_v + 1) \quad (7)$$

is  $g = (n + 1)$ -fold degenerate. For example, the first excited level  $n = 1$  is double degenerate ( $n_u = 1, n_v = 0$  and  $n_u = 0, n_v = 1$ ), etc. The dimension of the vibrational space including levels  $n = 0, 1, \dots, N_e$  is  $p_{eN} = \sum_{n=0}^N (n+1) = \frac{1}{2}(N_e + 1)(N_e + 2)$  where,  $N_e$  is the number of the vibrational levels included in the basis for the solution of the dynamic vibronic problem.

Before evaluation of the symmetry adapted basis, it is worthwhile to classify the resulting irreps. Such kind of the group-theoretical classifications of the electronic and spin states of the molecules<sup>[26]</sup> and spin systems<sup>[27]</sup> prove to be useful for their qualitative discussion and evaluations of the

energy levels. In the case under consideration, this can be done using the correlation between the angular momentum representation for a two-dimensional oscillator<sup>[28]</sup> and point group irreps. The results for several vibrational levels are collected in Table 1.

**Table 1.** Group-theoretical classification of the vibrational states for  $E$  vibrations in  $T_d$  symmetry.

| $n$ | $g(n)$ | Vib. irreps     |
|-----|--------|-----------------|
| 1   | 2      | $E$             |
| 2   | 3      | $A_1 + E$       |
| 3   | 4      | $A_1 + A_2 + E$ |
| 4   | 5      | $A_1 + 2E$      |

## Symmetry Adapted Basis for a Two-Dimensional Harmonic Oscillator

Creation operators  $\hat{c}_u$  and  $\hat{c}_v$  can be related to the irrep  $E$  and therefore, the basis functions for each  $n$  belonging to the definite irreps ( $A_1, A_2, E$  for  $E$  vibrations in  $T_d$ ) can be obtained by the application of the symmetry adapted polynomials constructed from operators  $\hat{c}_u^{n_u} \hat{c}_v^{n_v}$  to the ground (vacuum) state  $|00\rangle$  (full symmetric,  $A_1$ ). Action of the symmetry adapted operator polynomials (let say, of  $\Gamma\gamma$  type) on the vacuum state  $|00\rangle$  creates thus the vibrational function  $|n, \Gamma\gamma\rangle$  with a given  $n$ .

Let us introduce the symmetry adapted operators  $T_{\Gamma\gamma}^{(n)}$  constructed from operators  $\hat{c}_u^{n_u} \hat{c}_v^{n_v}$  with definite  $n = n_u + n_v$ , where,  $\Gamma$  is one the irreps ( $\Gamma = A_1, A_2, E$ ) corresponding to the set of the vibrational functions belonging the energy level  $n$ . The operators  $T_{\Gamma\gamma}^{(n)}$  realize the transformation from the basis  $|n_u n_v\rangle$  with a certain  $n$  to the symmetry adapted basis  $|n, \Gamma\gamma\rangle$ :

$$|n, \Gamma\gamma\rangle = \sum_{\substack{n_u, n_v \\ (n_u + n_v = n)}} c(n_u, n_v, v, \Gamma\gamma) |n_u, n_v\rangle, \quad (8)$$

where,  $v$  is an additional quantum number that is introduced to distinguish the states of the system in the case when the irrep  $\Gamma$  occurs several times in the set  $n$ . By definition, the operator  $T_{\Gamma\gamma}^{(n)}$  acts on the vacuum state  $|00\rangle \equiv |n_u = 0, n_v = 0\rangle$  and creates a basis function of the type of  $\Gamma\gamma$  belonging to a certain excited vibrational state  $n$ :

$$T_{\Gamma\gamma}^{(n)} |00\rangle = |n, \Gamma\gamma\rangle. \quad (9)$$

For this reason, we will refer  $T_{\Gamma\gamma}^{(n)}$  to as multivibronic symmetry adapted creation operators that can be considered as the irreducible tensor operators of the type of  $\Gamma\gamma$  in the actual point group ( $T_d$  in the case under consideration). This allows one to build the multivibronic operators with the use of the well developed technique for manipulation with the irreducible tensor operators in the point groups<sup>[28]</sup> (see for example Refs. [25,29–31]). This technique allows to construct the symmetry adapted basis  $\psi_{\Gamma\gamma} \equiv |\Gamma\gamma\rangle$  belonging to the irreps  $\Gamma$  of a point group from the direct products  $\phi_{\Gamma_1\gamma_1} \psi_{\Gamma_2\gamma_2} \equiv$



$[\Gamma_1\gamma_1\Gamma_2\gamma_2]$  of the basis functions  $u_{\Gamma_1\gamma_1}$  and  $v_{\Gamma_2\gamma_2}$  which are the bases of the irreps  $\Gamma_1$  and  $\Gamma_2$ , correspondingly:

$$|\Gamma\gamma\rangle = \sum_{\gamma_1\gamma_2} |\Gamma_1\gamma_1\Gamma_2\gamma_2\rangle \langle \Gamma_1\gamma_1\Gamma_2\gamma_2 | \Gamma\gamma \rangle, \quad \Gamma \in \Gamma_1 \times \Gamma_2 \quad (10)$$

The coupling coefficients (Clebsch-Gordan coefficients) for all point groups are given by Koster et al.<sup>[29]</sup> We will use the Malliken notations for the irreps of  $T_d$  and the notations for the basis functions introduced in the book by Sugano, Tanabe, and Kamimura.<sup>[25]</sup>

Let us first illustrate the approach by the evaluation of the multivibronic operators for several low lying vibrational levels (in the case of  $E$  vibrations) and corresponding symmetry adapted basis functions. Operators  $\hat{c}_u$  and  $\hat{c}_v$  and belong to the irrep  $E$ , the ground state  $|00\rangle$  is full symmetric ( $A_1$ ) that means that in the case under consideration  $\mathbf{T}_{\Gamma\gamma}^{(1)} = b_{\Gamma\gamma}^+$ . Then for  $n = 1$  one obtains:

$$\mathbf{T}_{\Gamma\gamma}^{(1)}|00\rangle = |1, \Gamma\gamma\rangle. \quad (11)$$

This leads to the following obvious result:

$$\begin{aligned} \hat{c}_u|n_u = 0, n_v = 0\rangle &= |n_u = 1, n_v = 0\rangle \equiv |1, Eu\rangle \\ \hat{c}_v|n_u = 0, n_v = 0\rangle &= |n_u = 0, n_v = 1\rangle \equiv |1, Ev\rangle \end{aligned} \quad (12)$$

In general, according to the coupling scheme the operator  $\mathbf{T}_{\Gamma\gamma}^{(2)}$  can be represented as a tensor product:

$$\hat{\mathbf{T}}_{\Gamma\gamma}^{(2)} = \{ \hat{c}_{\Gamma_1} \otimes \hat{c}_{\Gamma_2} \}_{\Gamma\gamma}, \quad \Gamma \in \Gamma_1 \times \Gamma_2, \quad (13)$$

The reducible representation  $\Gamma_1 \times \Gamma_2$  can be decomposed into irreps (in our case  $E \times E = A_1 + A_2 + E$ ) by the use of the coupling scheme, Eq. (10) that gives the following result:

$$\begin{aligned} \hat{\mathbf{T}}_{A_1}^{(2)} &= \frac{1}{\sqrt{2}} (\hat{c}_u^2 + \hat{c}_v^2), \\ \hat{\mathbf{T}}_{Eu}^{(2)} &= -\frac{1}{\sqrt{2}} (\hat{c}_u^2 - \hat{c}_v^2), \\ \hat{\mathbf{T}}_{Ev}^{(2)} &= \sqrt{2} \hat{c}_u \hat{c}_v, \\ \hat{\mathbf{T}}_{A_2}^{(2)} &= 0. \end{aligned} \quad \left. \vphantom{\begin{aligned} \hat{\mathbf{T}}_{A_1}^{(2)} \\ \hat{\mathbf{T}}_{Eu}^{(2)} \\ \hat{\mathbf{T}}_{Ev}^{(2)} \\ \hat{\mathbf{T}}_{A_2}^{(2)} \end{aligned}} \right\} E \quad (14)$$

One can see that the operator  $\mathbf{T}_{A_2}^{(2)}$  corresponding to the antisymmetric part  $\{E \times E\}$  of the direct product  $E \times E$  vanishes in the case of  $n = 1$  so that the full dimension of the obtained basis is  $g(n) = n + 1 = 3$ . Applying operators  $\mathbf{T}_{\Gamma\gamma}^{(2)}$  to the vacuum state  $\mathbf{T}_{\Gamma\gamma}^{(2)}|00\rangle = |2, \Gamma\gamma\rangle$  one obtains the three-dimensional vibrational basis for  $n = 2$  with  $\Gamma = A_1, E$  (Table 1). The final results for the normalized states (that are also orthogonal) are the following:

$$\begin{aligned} |2, A_1\rangle &= \frac{1}{\sqrt{2}} (|20\rangle + |02\rangle), \\ |2, Eu\rangle &= -\frac{1}{\sqrt{2}} (|20\rangle - |02\rangle), \\ |2, Ev\rangle &= |11\rangle \end{aligned} \quad \left. \vphantom{\begin{aligned} |2, A_1\rangle \\ |2, Eu\rangle \\ |2, Ev\rangle \end{aligned}} \right\} E. \quad (15)$$

Then one has to build the operators  $\mathbf{T}_{\Gamma\gamma}^{(3)}$  applying the subsequent step of the coupling procedure:

$$\begin{aligned} \hat{\mathbf{T}}_{\Gamma\gamma}^{(3)} &= \left\{ \{ \hat{c}_{\Gamma_1} \otimes \hat{c}_{\Gamma_2} \}_{\Gamma_{12}} \otimes \hat{c}_{\Gamma_3} \right\}_{\Gamma\gamma} \\ &\equiv \sum_{\gamma_{12}\gamma_3} \{ \hat{c}_{\Gamma_1} \otimes \hat{c}_{\Gamma_2} \}_{\Gamma_{12}\gamma_{12}} \hat{c}_{\Gamma_3\gamma_3} \langle \Gamma_{12}\gamma_{12}\Gamma_3\gamma_3 | \Gamma\gamma \rangle, \\ &\Gamma_{12} \in \Gamma_1 \times \Gamma_2, \quad \Gamma \in \Gamma_{12} \times \Gamma_3. \end{aligned} \quad (16)$$

The four-dimensional space for  $n = 3$  ( $g(n) = 4$ ) is split according to the irreps  $A_1, A_2$ , and  $E$ . Evaluation of the operators  $\mathbf{T}_{\Gamma\gamma}^{(3)}$  gives the following results:

$$\begin{aligned} \hat{\mathbf{T}}_{A_1}^{(3)} &= -\frac{1}{2} (\hat{c}_u^2 - 3\hat{c}_v^2) \hat{c}_u, \\ \hat{\mathbf{T}}_{A_2}^{(3)} &= -\frac{1}{2} (\hat{c}_u^2 - 3\hat{c}_v^2) \hat{c}_v, \\ \left. \begin{aligned} \hat{\mathbf{T}}_{Eu}^{(3)} &= \frac{1}{\sqrt{2}} (\hat{c}_u^2 + \hat{c}_v^2) \hat{c}_u, \\ \hat{\mathbf{T}}_{Ev}^{(3)} &= \frac{1}{\sqrt{2}} (\hat{c}_u^2 + \hat{c}_v^2) \hat{c}_v. \end{aligned} \right\} E \quad (17)$$

It should be noted that the application of the coupling scheme, Eq. (16), leads to the two identical operators of the  $E$  type one of which is eliminated. Action of the operators  $\mathbf{T}_{\Gamma\gamma}^{(3)}$  to the vacuum state leads to the following symmetry adapted functions belonging to the  $n = 3$  manifold:

$$\begin{aligned} |3, A_1\rangle &= \frac{1}{2} (-|30\rangle + \sqrt{3}|12\rangle), \\ |3, A_2\rangle &= \frac{1}{2} (-\sqrt{3}|21\rangle + |03\rangle), \\ \left. \begin{aligned} |3, Eu\rangle &= \frac{1}{2} (\sqrt{3}|30\rangle + |12\rangle) \\ |3, Ev\rangle &= \frac{1}{2} (|21\rangle + \sqrt{3}|03\rangle) \end{aligned} \right\} E \end{aligned} \quad (18)$$

The basis set for  $n = 4$  can be decomposed into three irreps of  $T_d$ :  $A_1 + 2E$ . Direct evaluation of the symmetry adapted basis functions by means of the procedure so far described gives the following expressions:

$$\begin{aligned} |4, A_1\rangle &= \frac{1}{2\sqrt{2}} (\sqrt{3}|40\rangle + \sqrt{2}|22\rangle + \sqrt{3}|04\rangle) \\ |4, A_2\rangle &= 0 \\ \left. \begin{aligned} |4, Eu\rangle &= \frac{1}{\sqrt{2}} (|04\rangle - |40\rangle) \\ |4, Ev\rangle &= \frac{1}{\sqrt{2}} (|13\rangle - |31\rangle) \end{aligned} \right\} E \\ \left. \begin{aligned} |4, Eu\rangle &= \frac{1}{\sqrt{10}} (-2|40\rangle + \sqrt{6}|22\rangle) \\ |4, Ev\rangle &= \frac{1}{\sqrt{10}} (-|31\rangle + 3|13\rangle) \end{aligned} \right\} E \quad (19) \\ \left. \begin{aligned} |4, Ey\rangle &= \frac{1}{\sqrt{10}} (2|04\rangle - \sqrt{6}|22\rangle) \\ |4, Ev\rangle &= \frac{1}{\sqrt{10}} (|13\rangle - 3|31\rangle) \end{aligned} \right\} E \end{aligned}$$

One can see that the dimension  $g = 7$  of the full vector space in Eq. (19) exceeds the dimension  $g(n = 4) = 5$  and thus this set contains linearly dependent functions. By comparing the basis in Eq. (19) with the result of the group-theoretical classification one can see that an excessive pair  $E$  type functions is present.

The case of  $n = 4$  illustrates what one can expect at the subsequent steps of the so far described approach, namely, the presence of several identical irreps resulting in an excessive dimension of the space. Therefore each step of the

procedure should be supplemented by the Gram-Schmidt orthogonalization within the repeated irreps that takes an arbitrary basis and generates a new orthogonal one excluding thus excessive functions. It does this by sequentially processing the list of vectors and generating a vector perpendicular to the previous vectors in the list. As a result, the obtained vectors are linearly independent. This should be taken into account in the design of the computer program. It should be noted that  $u$ -components of all  $E$  bases are automatically orthogonal to the  $v$ -components, and, of course, the orthogonality remains between different irreps and between the functions from the sets arising from different  $n$ . Due to this fact, the Gram-Schmidt procedure of orthogonalization is to be applied only to the corresponding basis functions of the same irreps (let's say, to the  $u$  type functions belonging to the  $E$  bases) with the same  $n$ . For example, this procedure applied to three  $Eu$  functions for  $n = 4$  can be demonstrated by the Wolfram's *Mathematica 7* notebook:

$$\text{In}[2] = \text{Orthogonalize} \left[ \left\{ \left\{ -\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right\}, \left\{ -\frac{2}{\sqrt{10}}, \frac{\sqrt{6}}{\sqrt{10}}, 0 \right\}, \left\{ 0, \frac{\sqrt{6}}{\sqrt{10}}, -\frac{2}{\sqrt{10}} \right\} \right\} \right] // \text{FullSimplify}$$

$$\text{Out}[2] = \left\{ \left\{ -\frac{1}{\sqrt{2}}, 0, \frac{1}{\sqrt{2}} \right\}, \left\{ -\frac{1}{2\sqrt{2}}, \frac{\sqrt{3}}{3}, -\frac{1}{2\sqrt{2}} \right\}, \left\{ 0, 0, 0 \right\} \right\}$$

This shows that instead of three linearly dependent vectors one obtains two orthogonal sets while the third vector vanishes. Therefore, in the case of  $n = 4$  the application of the Gram-Schmidt procedure gives the following set of the orthogonal and normalized symmetry adapted functions:

$$\left. \begin{aligned} |4, A_1\rangle &= \frac{1}{2\sqrt{2}} (\sqrt{3}|40\rangle + \sqrt{2}|22\rangle + \sqrt{3}|04\rangle) \\ |4, Eu\rangle &= \frac{1}{\sqrt{2}} (|04\rangle - |40\rangle) \\ |4, Ev\rangle &= \frac{1}{\sqrt{2}} (|13\rangle + |31\rangle) \\ |4, Ev\rangle &= \frac{1}{\sqrt{2}} (|13\rangle - |31\rangle) \\ |4, Eu\rangle &= \frac{1}{2\sqrt{2}} (-|04\rangle + \sqrt{6}|22\rangle - |40\rangle) \end{aligned} \right\} E \quad (20)$$

The procedure can be continued to reach a required number  $n$ .

### Group-Theoretical Classification for the Vibrations $T_2$ in $T_d$ Symmetry

The standard  $T_2$  basis  $\xi \propto yz$ ,  $\eta \propto xz$ ,  $\zeta \propto xy$  for  $T_d$  will be used.<sup>[25]</sup> The functions  $|n_\xi n_\eta n_\zeta\rangle$  can be built by applying the creation operators as follows:

$$|n_\xi n_\eta n_\zeta\rangle = \frac{1}{\sqrt{n_\xi! n_\eta! n_\zeta!}} \hat{c}_\xi^{n_\xi} \hat{c}_\eta^{n_\eta} \hat{c}_\zeta^{n_\zeta} |0 0 0\rangle. \quad (21)$$

Each level with a given  $n = n_\xi + n_\eta + n_\zeta$

$$E_n = \hbar\omega \left( n_\xi + n_\eta + n_\zeta + \frac{3}{2} \right) \quad (22)$$

is  $g(n) = \frac{1}{2}(n+1)(n+2)$ -fold degenerate while the dimension of the vibrational space is

**Table 2.** Group-theoretical classification of the vibrational states for  $T_2$  vibrations in  $T_d$  symmetry.

| $n$ | $g(n)$ | $l$ (vibrational irreps)   | Vibrational irreps                          |
|-----|--------|--|---|
| 0   | 1      | 0 ( $A_1$ )  | $A_1$                                       |
| 1   | 3      | 1 ( $T_2$ )  | $T_2$                                       |
| 2   | 6      | 0 ( $A_1$ ); 2 ( $E$ , $T_2$ )   | $A_1$ , $E$ , $T_2$                         |
| 3   | 10     | 1 ( $T_2$ ); 3 ( $A_1$ , $T_1$ , $T_2$ )   | $A_1$ , $T_1$ , 2 $T_2$                     |
| 4   | 15     | 0 ( $A_1$ ); 2 ( $E$ , $T_2$ ); 4 ( $A_1$ , $E$ , $T_1$ , $T_2$ )  | 2 $A_1$ ; 2 $E$ , $T_1$ , 2 $T_2$           |
| 5   | 21     | 1 ( $T_2$ ); 3 ( $A_1$ , $T_1$ , $T_2$ ); 5 ( $E$ , $T_1$ , 2 $T_2$ )  | $A_1$ , $E$ , 2 $T_1$ , 4 $T_2$             |
| 6   | 28     | 0 ( $A_1$ ); 2 ( $E$ , $T_2$ ); 4 ( $A_1$ , $E$ , $T_1$ , $T_2$ ); 6 ( $A_1$ , $A_2$ , $E$ , $T_1$ , 2 $T_2$ ) | 3 $A_1$ , $A_2$ , 3 $E$ , 2 $T_1$ , 4 $T_2$ |

$$p_{tN} = \frac{1}{2} \sum_{n=0}^N (n+1)(n+2) = \frac{1}{6} (N+1)(N+2)(N+3). \quad (23)$$

The set of the vibrational states with a given  $n$  can be correlated with a certain value of the angular orbital momentum  $l$  and parity  $(-1)^l$  where,  $l = 0, 2, \dots, n$  for even  $n$  and  $l = 1, 3, \dots, n$  for odd  $n$ .<sup>[32]</sup> Then classifying these states accordingly to the irreps of  $T_d$  one obtains the results listed in Table 2.

### Symmetry Adapted Basis for a Three-Dimensional Harmonic Oscillator

The multivibronic operators  $\mathbf{T}_{\Gamma\gamma}^{(n)}$  are constructed from the products  $\hat{c}_\xi^{n_\xi} \hat{c}_\eta^{n_\eta} \hat{c}_\zeta^{n_\zeta}$  with a definite  $n = n_\xi + n_\eta + n_\zeta$  and with  $\Gamma$  being one the irreps of  $T_d$  ( $A_1, A_2, E, T_1, T_2$ ) corresponding to the set of the vibrational function belonging the energy level  $n$ . The operators  $\mathbf{T}_{\Gamma\gamma}^{(n)}$  realize the transformation from the basis  $|n_\xi n_\eta n_\zeta\rangle$  with a certain  $n$  (a definite vibrational level) to the symmetry adapted basis  $|n, \Gamma\gamma\rangle$ :

$$|n, \Gamma\gamma\rangle = \sum_{\substack{n_\xi n_\eta n_\zeta \\ (n_\xi + n_\eta + n_\zeta = n)}} c(n_\xi n_\eta n_\zeta, \nu \Gamma\gamma) |n_\xi n_\eta n_\zeta\rangle, \quad (24)$$

Creation operators  $\hat{c}_\xi$ ,  $\hat{c}_\eta$ , and  $\hat{c}_\zeta$  belong to the irrep  $T_2$  that means that in the case under consideration  $\mathbf{T}_{\Gamma\gamma}^{(1)} = \hat{c}_{\Gamma\gamma}$ . Then for  $n = 1$  one obtains:

$$\mathbf{T}_{T_2\gamma}^{(1)} |000\rangle = |1, T_2\gamma\rangle. \quad (25)$$

This leads to the following obvious result:

$$\left. \begin{aligned} \hat{c}_\xi |n_\xi = 0, n_\eta = 0, n_\zeta = 0\rangle &= |n_\xi = 1, n_\eta = 0, n_\zeta = 0\rangle \equiv |1, T_2\xi\rangle, \\ \hat{c}_\eta |n_\xi = 0, n_\eta = 0, n_\zeta = 0\rangle &= |n_\xi = 0, n_\eta = 1, n_\zeta = 0\rangle \equiv |1, T_2\eta\rangle, \\ \hat{c}_\zeta |n_\xi = 0, n_\eta = 0, n_\zeta = 0\rangle &= |n_\xi = 0, n_\eta = 0, n_\zeta = 1\rangle \equiv |1, T_2\zeta\rangle. \end{aligned} \right\} E \quad (26)$$

Then general expressions for  $\mathbf{T}_{\Gamma\gamma}^{(2)}$ ,  $\mathbf{T}_{\Gamma\gamma}^{(3)}$ , etc. can be used. In this way, one obtains the following result for the  $\mathbf{T}_{\Gamma\gamma}^{(2)}$  operators:

$$\left. \begin{aligned} \hat{T}_{A_1}^{(2)} &= \frac{1}{\sqrt{3}} (\hat{c}_\xi^2 + \hat{c}_\eta^2 + \hat{c}_\zeta^2), \\ \hat{T}_{Eu}^{(2)} &= \frac{1}{\sqrt{6}} (-\hat{c}_\xi^2 - \hat{c}_\eta^2 + 2\hat{c}_\zeta^2), \\ \hat{T}_{Ev}^{(2)} &= \frac{1}{\sqrt{2}} (\hat{c}_\xi^2 - \hat{c}_\eta^2), \end{aligned} \right\} E \quad (27)$$



$$\left. \begin{aligned} \hat{T}_{T_2\xi}^{(2)} &= \hat{c}_\eta \hat{c}_\xi, \\ \hat{T}_{T_2\eta}^{(2)} &= \hat{c}_\xi \hat{c}_\eta, \\ \hat{T}_{T_2\xi}^{(2)} &= \hat{c}_\xi \hat{c}_\eta. \end{aligned} \right\} T_2$$

Applying operators  $\hat{T}_{\Gamma\gamma}^{(2)}$  to the vacuum state  $\hat{T}_{\Gamma\gamma}^{(2)}|000\rangle = |2, \Gamma\gamma\rangle$  one obtains the six-dimensional vibrational basis for  $n = 2$  with  $\Gamma = A_1, E, T_2$  in full agreement with the result of the group-theoretical assignment (Table 2). The final results for the normalized states (which are also orthogonal) are the following:

$$\left. \begin{aligned} |2, A_1\rangle &= \frac{1}{\sqrt{3}}(|200\rangle + |020\rangle + |002\rangle), \\ |2, Eu\rangle &= -\frac{1}{\sqrt{6}}(-|200\rangle - |020\rangle + 2|002\rangle) \\ |2, Ev\rangle &= -\frac{1}{\sqrt{2}}(-|200\rangle - |020\rangle) \\ |2, T_2\xi\rangle &= |011\rangle \\ |2, T_2\eta\rangle &= |101\rangle \\ |2, T_2\xi\rangle &= |110\rangle \end{aligned} \right\} E \quad (28)$$

From the direct product of  $\Gamma(n = 2) \times T_2$  one finds the following irreps forming the 18-dimensional space for  $n = 3$ :  $(A_1 + E + T_2) \times T_2 = T_2 + (T_1 + T_2) + (A_1 + E + T_1 + T_2) = A_1 + E + 2T_1 + 3T_2$ . By comparing these irreps with those predicted by the group-theoretical assignment  $(A_1, T_1, 2T_2)$  one can conclude that this 18-dimensional space contains linearly dependent vectors and therefore, beginning from this step, the Gram-Schmidt procedure of orthogonalization is to be applied. The next steps are quite similar to those so far described and will not be given here.

## Symmetry Adapted Electron-Vibrational Basis

The evaluation of the vibrational basis for each type of the active modes can be extended to an arbitrary value of  $n$  by the application of the multivibronic operator of the order  $n$  to the vacuum state with the subsequent Gram-Schmidt procedure at each step  $n$ . The operator  $\hat{T}_{\Gamma\gamma}^{(n)}$  can be built by extending the consequent coupling procedure to the order  $n$ :

$$\hat{T}_{\Gamma\gamma}^{(n)} = \{ \{ \{ \hat{c}_{\Gamma_1} \otimes \hat{c}_{\Gamma_2} \}_{\Gamma_{12}} \otimes \hat{c}_{\Gamma_3} \}_{\Gamma_{123}} \dots \otimes \hat{c}_{\Gamma_n} \}_{\Gamma_\gamma},$$

$$\Gamma_{12} \in \Gamma_1 \times \Gamma_2, \Gamma_{123} \in \Gamma_1 \times \Gamma_2 \times \Gamma_3 \dots, \Gamma \in \Gamma_{n-1} \times \Gamma_n. \quad (29)$$

Then the vibrational functions for the active vibrations can be combined to get the total vibrational basis with the given symmetry. For example, for the two basis sets  $|n_1, \nu_1 \Gamma_1 \gamma_1\rangle$  and  $|n_2, \nu_2 \Gamma_2 \gamma_2\rangle$  one can directly use the coupling scheme, Eq. (12), within which one obtains the symmetry adapted vibrational functions  $|n, \nu \Gamma_v \gamma_v\rangle$  ( $n = n_1 + n_2, \Gamma_v \in \Gamma_1 \times \Gamma_2$ ).

Finally, the vibrational functions  $|n, \nu \Gamma_v \gamma_v\rangle$  are to be coupled to the electronic ones  $|\alpha \Gamma_e \gamma_e, SM\rangle$  that are eigenfunctions of the Hamiltonian  $H_e$  included in the JT/pseudo JT problem ( $SM$  are the quantum numbers of the full spin and its projection,  $\alpha$  is the additional quantum number that enumerated

the repeated irreps  $\Gamma_e$ ). To pass from the direct products of these two sets to the symmetry adapted electron-vibrational functions  $|\alpha \nu, n, \Gamma \gamma\rangle$

$$|\alpha \Gamma_e \gamma_e, SM\rangle \otimes |n, \nu \Gamma_v \gamma_v\rangle \Rightarrow |\alpha \nu, n, \Gamma \gamma\rangle \quad (30)$$

one should apply again the standard coupling scheme:

$$|\alpha \nu, n, \Gamma \gamma\rangle = \sum_{\gamma_1 \gamma_2} |\alpha \Gamma_e \gamma_e, SM\rangle |n, \nu \Gamma_v \gamma_v\rangle \langle \Gamma_e \gamma_e \Gamma_v \gamma_v | \Gamma \gamma \rangle,$$

$$\Gamma \in \Gamma_e \times \Gamma_v. \quad (31)$$

This allows to achieve the final goal of the approach, namely to evaluate the basis within which the full matrix of the JT Hamiltonian is blocked according to the irreps of the point group. Finally, the approach is realized as an efficient computer program (Clemente-Juan et al., to be submitted) that generates the blocks and evaluates required characteristics of the JT systems, like optical spectra, thermodynamic characteristics, etc. Although the classification of the active modes in the present consideration is restricted by the PKS model the approach is rather general. The procedure generates the basis assuming only point symmetry of the system without indication of the explicit form of the vibronic coupling, so it is not restricted by the linear terms of vibronic interactions and applicable also when the quadratic and high order terms are taken into account. Under this condition, the approaches based on high symmetries lose their advantages because the actual symmetry is reduced to the point one.

## Concluding Remarks

In this article, we have presented a powerful theoretical approach to obtain an accurate solution of the dynamic vibronic problem in large scale JT systems. The approach uses a symmetry adapted vibronic basis to reduce the dimension of the problem. In fact, the algorithm for the solution of the eigen-problem takes full advantage of the point symmetry arguments and thus allows to reduce the vibronic matrices to full extent. The group-theoretical assignment of the vibronic states allows to predict the symmetry labels for the vibronic levels before evaluation. This approach is applicable to an arbitrary form for the vibronic coupling, including linear and high order terms.

The possibilities provided by this approach have been illustrated by its application to the 2e-reduced MV dodecanuclear Keggin anion (overall symmetry  $T_d$ ) in which the electronic pair is delocalized over twelve metal sites giving rise (within PKS model) to the  $({}^1T_2 + {}^1E + {}^1A_1) \otimes (e + t_2)$  ( ${}^3T_1 + {}^3T_2$ )  $\otimes (e + t_2)$  combined JT/pseudo JT problems for the spin-singlet and spin-triplet states, correspondingly.

The theoretical background presented here has been used to elaborate an efficient computer program (Clemente-Juan et al., to be submitted) for the numerical analysis of the multi-mode vibronic problems. This part of the work will be published elsewhere along with the detailed discussion of the experimental data on magnetic susceptibility and intervalence optical bands of the 2e-reduced POMs possessing Keggin

structure and other complex mixed POMs containing several electrons delocalized over large metal networks.

**Keywords:** Jahn-Teller effect · dynamic problem · polyoxometalates · Keggin anion · symmetry · mixed valency

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