Available online at www.sciencedirect.com

ScienceDirect

Journal of Molecular Structure 838 (2007) 66–73

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

# The Jahn–Teller effect in $(h_u^+)^2 \otimes h_g$ systems

Ian D. Hands, Wajood A. Diery [1], Janette L. Dunn *, Colin A. Bates

School of Physics and Astronomy, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Received 14 December 2006; accepted 24 December 2006
Available online 20 January 2007

**Abstract**

A general consideration is made of the vibronic coupling in a $(h_u^+)^2 \otimes h_g$ Jahn–Teller system, that is to say, a system in which two holes of $H_u$ symmetry are coupled to vibrations of $h_g$ symmetry. We find that the resulting high-spin states may undergo spontaneous distortion into species exhibiting one of the following four possible symmetries: $D_{5d}$, $D_{3d}$, $D_{2h}$ or $C_{2h}$.

The system may be viewed as a first approximation to a $C_{60}^{2+}$ ion, but our intention here is to make a general consideration of the model without application to any specific molecular system. Coulombic interactions between holes, which must be important in real systems, are therefore ignored throughout. However, they could be included in the model, if required, using the method described in an earlier work [I.D. Hands, J.L. Dunn, W.A. Diery, C.A. Bates, Phys. Rev. B 73 (2006) 115435].

For each of the different symmetry types, projection operators are used to create symmetry-adapted states (SASs) that give a good account of the states of the system over a wide range of coupling strengths. These SASs are used, in turn, to derive energies for the vibronic states.

*PACS:* 31.30.Gs; 61.48.+c; 78.30.Na

*Keywords:* Jahn–Teller effect; Vibronic coupling; Hole-doping; $C_{60}^{2+}$

## 1. Introduction

The high degeneracy of the electronic and vibrational modes in the fullerenes, as exemplified by $C_{60}$, makes them a rich field for the study of Jahn–Teller (JT) and other vibronic effects. When electrons are removed from the highest occupied molecular orbital (HOMO) of the $C_{60}$ molecule, for example, a partially filled set of degenerate orbitals is produced. This makes the resulting cation liable to distortion in order to split the degenerate levels and lower the total energy. This is the essential ingredient required in the occurrence of the Jahn–Teller effect. Removal of two electrons, or equivalently addition of two positive 'holes', produces the $C_{60}^{2+}$ dication. As the HOMO of $C_{60}$ has $H_u$ symmetry, this means that we have a set of 5-fold degenerate molecular orbitals (MOs) which have been doped with two holes.

In the present study, we consider a system in which the important coupling is between these two holes and vibrational modes of $h_g$ symmetry. The holes can, in general, also couple to two $a_g$ modes and six $g_g$ modes. However, it has been shown that for the particular case of $C_{60}^{2+}$ ions these modes do not result in any significant distortions [1]. Therefore, in order to simplify matters and to make our results immediately applicable to this dication, these additional modes will not be considered any further here. Thus, the system of interest is the $(h_u^+)^2 \otimes h_g$ coupling problem (in the notation of Nikolaev and Michel [2]).

In the hole-doped fullerenes, the resistivity and the superconducting transition temperature are expected to be higher than in the corresponding negatively doped fullerenes [1]. A strong JT effect in the isolated ion is expected to be important for both properties, but the actual coupling strengths are so far unknown.

Coupling to the $h_g$ mode is complicated as the $H$ irreducible representation (irrep) appears twice in the symmetric square of the Kronecker product $H \otimes H$. This means

---

* Corresponding author.
*E-mail address:* janette.dunn@nottingham.ac.uk (J.L. Dunn).
*URL:* http://www.nottingham.ac.uk/~ppzjld (J.L. Dunn).

[1] Present address: Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia.

0022-2860/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2006.12.060

that there are two different ways in which each $h_g$ vibration may be coupled to the $H_u$ electronic state. Therefore, two different linear coupling constants are required to describe the system. In general, both of these coupling constants must be taken into account simultaneously.

Another complication arises in doubly doped systems due to interaction between the added charges. Even simple Coulombic interactions can have significant effects on the energies of the allowed multiplet terms [2], which lowers the degeneracy of the system, even in the absence of JT interactions. Clearly, this complication is one which is system specific. Therefore, in order to make a first approximation to the general $(h_u^+)^2 \otimes h_g$ system, we ignore interelectronic interactions from the outset. A qualitative discussion of the inclusion of such effects is given in Section 6.

In this paper, we follow the notation introduced by Fowler and Ceulemans [3] and label the two different sets of Clebsch–Gordan (CG) coefficients inherent in the $H \otimes H$ problem as $H_a$ and $H_b$. $H_a$ is associated with the first column within the table of CG coefficients for $H \otimes H$ appearing in Ref. [3]. Similarly, $H_b$ is associated with the second column of the same table. From a symmetry point of view, the two sets of CG coefficients corresponding to $H_a$ and $H_b$ are totally equivalent and indistinguishable. Therefore, it is possible to take a linear combination of the two sets and deal with them as a single set. A full description of the coupling problem subsequently involves consideration of all the possible combinations of these two basic sets of CG coefficients. This is conveniently done by expressing the coupling constants in polar form and treating the polar angle as a 'mixing' parameter, as we show more explicitly in the next section.

## 2. The $(h_u^+)^2 \otimes h_g$ interaction Hamiltonian

In order to derive a matrix representation for the interaction Hamiltonian $\mathcal{H}_{\text{int}}$, the electronic states for the system, which will be used as the basis for the description, must first be derived. The electronic terms pertinent to the two-hole system can be predicted from the Kronecker product of the $H$ irrep with itself. Both low- and high-spin terms arise, and those of high-spin are calculated to have the lowest energies [2]. The high-spins terms, which have symmetries $^3T_{1g}$, $^3T_{2g}$, and $^3G_g$, may therefore be used as the electronic basis for our calculation. In real molecular systems, these basis states are of different energies due to Coulombic interactions. The actual energies will be specific to the particular system in question. However, to make our analysis generally applicable we will treat the terms as degenerate and leave the non-degeneracy as a refinement to be considered when making specific applications.

The bases states themselves are written as products of the single-electron states using the CG coefficients in Ref. [3]. For example, the $x$-component of the $^3T_{1g}$ state, $|^3T_{1g\ x}\rangle$, is given by

$$\begin{aligned}|^3T_{1g}x\rangle = \frac{1}{2\sqrt{5}}(&\phi^2|H\theta\rangle_1^-|Hx\rangle_2^- - \phi^2|Hx\rangle_1^-|H\theta\rangle_2^- \\ &- \sqrt{3}\phi^{-1}|H\epsilon\rangle_1^-|Hx\rangle_2^- + \sqrt{3}\phi^{-1}|Hx\rangle_1^-|H\epsilon\rangle_2^- \\ &+ \sqrt{2}|Hy\rangle_1^-|Hz\rangle_2^- - \sqrt{2}|Hz\rangle_1^-|Hy\rangle_2^-),\end{aligned} \tag{1}$$

where $|H\theta\rangle_1^-|Hx\rangle_2^-$ represents a product state, where hole 1 is in the $|H\theta\rangle$ orbital with spin component $-\frac{1}{2}$, and hole 2 is in the $|Hx\rangle$ orbital also with spin component $-\frac{1}{2}$. Also $\phi = (1+\sqrt{5})/2$. is the golden mean.

This $\{^3T_{1g}, {}^3T_{2g}, {}^3G_g\}$ basis can now be used to derive the matrix representation of the interaction Hamiltonian between and within the terms of the same spin; there is no coupling between terms of different spin.

The total Hamiltonian is

$$\mathcal{H} = \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{int}}, \tag{2}$$

where

$$\mathcal{H}_{\text{vib}} = \frac{1}{2}\sum_i \left[\frac{1}{\mu}P_i^2 + \mu\omega^2 Q_i^2\right] \tag{3}$$

is the Hamiltonian for the five uncoupled oscillators and $\mathcal{H}_{\text{int}}$ is the JT interaction Hamiltonian. In Eq. (3), $\mu$ is the reduced mass of each oscillator of frequency $\omega$, $P_i$ is the momentum operator conjugate to $Q_i$ and the sum is taken over all components of the $H$ irrep $(\theta, \epsilon, x, y, z)$.

The interaction Hamiltonian takes the form of a 10 × 10 matrix, which for display purposes may be split into smaller sub-matrices such that each sub-matrix represents a coupling between certain terms,

$$\mathcal{H}_{\text{int}} = \begin{bmatrix} C_{T_1T_1}M_{T_1T_1} \vdots & C_{T_1T_2}M_{T_1T_2} \vdots & C_{T_1G}M_{T_1G} \\ \cdots & \cdots & \cdots \\ C_{T_1T_2}M_{T_1T_2}^{\mathsf{T}} \vdots & C_{T_2T_2}M_{T_2T_2} \vdots & C_{T_2G}M_{T_2G} \\ \cdots & \cdots & \cdots \\ C_{T_1G}M_{T_1G}^{\mathsf{T}} \vdots & C_{T_2G}M_{T_2G}^{\mathsf{T}} \vdots & C_{GG}M_{GG} \end{bmatrix}. \tag{4}$$

Here, for example, $M_{T_1T_2}$ is the interaction matrix between the $^3T_{1g}$ and $^3T_{2g}$ terms,

$$M_{T_1T_2} = \frac{1}{\sqrt{6}}\begin{bmatrix} Q_\theta - \sqrt{3}Q_\epsilon & \sqrt{2}\phi Q_z & -\sqrt{2}\phi^{-1}Q_y \\ -\sqrt{2}\phi^{-1}Q_z & Q_\theta + \sqrt{3}Q_\epsilon & \sqrt{2}\phi Q_x \\ \sqrt{2}\phi Q_y & -\sqrt{2}\phi^{-1}Q_x & -2Q_\theta \end{bmatrix}, \tag{5}$$

where $(Q_\theta, Q_\epsilon, Q_x, Q_y, Q_z)$ are the components of the oscillator representing the $h_g$ mode of vibration. Also in Eq. (4), a superscript T denotes the transpose of a matrix and $C_{T_1T_1}$, etc. are numerical constants, expressions for which are detailed below.

As discussed earlier, two sets of CG coefficients are involved, and so the interaction Hamiltonian also has the form

$$\mathcal{H}_{\text{int}} = V_{Hh_a}\mathcal{H}_a + V_{Hh_b}\mathcal{H}_b, \tag{6}$$