

A molecular symmetry analysis of the electronic states and transition dipole moments for molecules with two torsional degrees of freedom

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We present a molecular symmetry analysis of electronic states and transition dipole moments for molecules which undergo large amplitude intramolecular torsions. The method is based on the correlation between the point group of the molecule at highly symmetric configurations and the molecular symmetry group. As an example, we determine the global irreducible representations of the electronic states and transition dipole moments for the quinodimethane derivative 2-[4-(cyclopenta-2,4-dien-1-ylidene)cyclohexa-2,5-dien-1-ylidene]-2H-1,3-dioxole for which two torsional degrees of freedom can be activated upon photo-excitation and construct the resulting symmetry adapted transition dipole functions. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4907405>]

I. INTRODUCTION

Symmetry is a powerful concept in modern physics and chemistry. Symmetry operations are defined as operations which leave the Hamiltonian of a system invariant. For molecules in their equilibrium structure, the elements of the molecular point groups, i.e., geometric operations like reflections and rotations, are such operations. They have been used to describe vibrational and electronic properties of molecules since the 1930s.^{1,2} The concept of point groups is based on the picture of a molecule as a rigid skeleton of nuclei which is surrounded by electrons. It is very powerful in dealing with processes where only small perturbations from the equilibrium configuration of the nuclei are considered. The concept fails, however, when large amplitude motions are considered which do not conserve the (point group) symmetry of the molecule. A more general concept of symmetry for non-rigid molecules, the concept of molecular symmetry³ has been introduced by Longuet-Higgins⁴ (see also Ref. 5), influenced by the work of Hougen.⁶ Here, the symmetry operations are feasible permutations of identical nuclei, the inversion of all nuclear and electronic coordinates as well as combinations thereof. Developments in high-resolution spectroscopy of non-rigid molecules brought many applications for Longuet-Higgins approach to molecular symmetry (see Ref. 3 and references therein). Molecular symmetry allows a symmetry analysis of molecular properties independent of the specific nuclear configuration. It is thus the concept of choice for describing the global symmetry in processes involving large amplitude intramolecular motions. Thus, another application of molecular symmetry is the characterization of electronic states and construction of multidimensional potential energy surfaces for chemical reactions where the motion of the nuclei destroys the point group symmetry of the equilibrium structure.^{7,8} An

important class of large amplitude nuclear motion in molecules are photoisomerization processes: activated by light, intramolecular torsion leads to a change of conformation. Photoisomerization reactions proceed on at least two potential energy surfaces, often connected by conical intersections.^{9,10} A famous example is the photo-induced torsion of ethylene. Molecular symmetry has been applied to construct its coupled (diabatic) electronic states.^{11,12} In the presence of conical intersections, non-adiabatic coupling terms¹³ lead to fast radiation-less decay. A molecular symmetry analysis of the conical intersection and the resulting non-adiabatic coupling terms for intramolecular torsion has been carried out in Ref. 14. Recently, symmetry adapted non-adiabatic coupling terms have also been investigated for Na₃ and K₃ clusters.^{15,16}

Photo-induced torsion and the underlying molecular symmetry becomes particularly interesting in systems with more than one torsional degree of freedom, as it has been shown recently for 2-[4-(cyclopenta-2,4-dien-1-ylidene)cyclohexa-2,5-dien-1-ylidene]-2H-1,3-dioxole, abbreviated as CCD.¹⁷ The light induced torsional dynamics of the nuclear spin isomers of CCD has been simulated in Ref. 18. Photo-excitation implies the interaction of the molecule with light, usually with a femtosecond laser pulse via the electronic transition dipole moments of the molecule. As the non-adiabatic coupling terms,¹⁴ the transition dipole moments transform according to the irreducible representations of the molecular symmetry group. Using the symmetry adapted transition dipole functions is important for a reliable description of large amplitude nuclear dynamics.¹⁹ In the following, we present a method to analyze the molecular symmetry properties of (diabatic) electronic states, construct symmetry adapted transition dipole moments, and apply it to photo-excited CCD. The method is based on the correlation between the molecular point group of CCD at highly symmetric configurations and the molecular symmetry group.³

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