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The electronic excited states of ethylene with large-amplitude deformations: A dynamical symmetry group investigation

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ABSTRACT

We show that the lowest manifold of electronic states of ethylene (ethene, C_2H_4) can be described correctly with a complete active space of 17 quasidiabatic configurations built on state-averaged orbitals. This space is stable upon large-amplitude deformations, such as torsion, pyramidalization, CC stretching and HCH bending. The properties of the nuclear coordinates and valence and Rydberg electronic states are investigated within the framework of nuclear-permutation-inversion group theory. This systematic analysis is compared to a previous model of the valence states of ethylene (R.P. Krawczyk, A. Viel, U. Manthe, W. Domcke, J. Chem. Phys. 119 (2003) 1397). Our approach is intended to be generalized to the non-adiabatic photochemistry of organic molecules where large-amplitude deformations require global vibronic Hamiltonian models to be expressed in terms of simple functions of polyspherical valence coordinates.

1. Introduction

Excited-state dynamics concerns molecular processes induced upon UV–visible light absorption. Simulations of photochemical reactions and calculations of electronic spectra involve nuclear dynamics methods to determine the time evolution of the molecular geometry used in concert with electronic structure methods capable of computing electronic excited state potential energy surfaces. Radiationless decay processes are governed by non-adiabatic transitions that are intense around conical intersections where potential energy surfaces are degenerate [1]. The Born–Oppenheimer approximation cannot be used, and the molecular Hamiltonian must account for non-adiabatic coupling terms. Quasidiabatic representations [2–4] allow the singular kinetic non-adiabatic couplings to be replaced by potential non-adiabatic couplings that are smooth-varying functions of the nuclear coordinates. In addition, the diabatic potential energy surfaces (diagonal elements) also are simple functions that can cross with no restriction, as opposed to the two-dimensional cusp at the conical intersection between two adiabatic surfaces. Quasidiabatic functions are thus easier to fit to regular mathematical expressions.

Adiabatic-to-diabatic transformations, also called diabatizations, are based on a smoothness condition of either the electronic wavefunctions or the expectation values of some physical properties. They often relate to the dominant electronic configurations underlying the adiabatic electronic wavefunctions in the spirit of correlation diagrams or valence-bond theory [5]. A large number of approaches have been developed over the years (see, e.g., Refs. [3,4,6] and references therein).

The approach we are interested in is called diabatization by *ansatz*, where the eigenvalues of a quasidiabatic Hamiltonian model are fitted to the adiabatic energies calculated with an electronic structure method over a range of geometries. The diabatization criterion is not explicit in terms of the electronic states, but is somewhat related to the compactness of the mathematical expressions assumed for the quasidiabatic functions. Simple expressions mean that the electronic states vary as smoothly as possible with the nuclear coordinates. In particular, the vibronic coupling Hamiltonian model developed by Köppel and co-workers [7] is based on a low-order local expansion of the quasidiabatic potential energy surfaces and coupling functions around the Franck–Condon point in terms of normal coordinates. In concert with the

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multiconfiguration time-dependent Hartree (MCTDH) quantum dynamics method [8], the vibronic coupling Hamiltonian approach has been used with great success to the calculation of many photoabsorption and photoelectron spectra [9].

Calculating electronic spectra mostly relies on short-term dynamics, especially when the conical intersection is close to the Franck–Condon point. However, describing photochemical events implies to deal with longer processes, large-amplitude nuclear motions, and complicated reaction pathways connecting several potential energy wells through transition barriers and crossings between different electronic states. There is thus a need for generalizing the vibronic coupling Hamiltonian model by making it a global description capable of dealing with large-amplitude deformations of the molecular geometry. This implies using internal coordinates that are curvilinear rather than rectilinear to get simple expressions for the potential energy functions. However, curvilinear coordinates lead to complicated expressions for kinetic energy operators. Polyspherical coordinates, as described in Ref. [10], are a good compromise, well-adapted to run MCTDH quantum dynamics calculations.

As first shown by Keating and Mead [11] and recently pointed out in Ref. [12], building a truly global representation of the electronic Hamiltonian for a flexible molecule [13] should be achieved within the framework of dynamical symmetry, also called molecular symmetry [14], when there are identical nuclei in the molecular system. This implies using the complete nuclear-permutation-inversion (CNPI) group, which is the symmetry group relevant for the vibronic Hamiltonian of the flexible molecule (as opposed to the point group of any given geometry), or a subgroup of it if some deformations are considered unfeasible. In this, the operations correspond to identical nuclei permutations and inversion of the whole molecule. See also Refs. [12,15,16] for related approaches based on CNPI projectors.

This treatment was used by Peyerimhoff and co-workers [17] to build a one-dimensional quasidiabatic representation for ethylene (ethene, C_2H_4) undergoing a pure torsional deformation. The aim of the present work is to extend this approach to more electronic states and more nuclear coordinates to write the elements of the effective Hamiltonian matrix in a quasidiabatic representation adapted to dynamical symmetry. Thinking further ahead, our actual purpose is to generalize the current vibronic Hamiltonian model of Köppel and co-workers by combining it to a dynamical symmetry treatment using simple basis functions of polyspherical coordinates (rather than polynomials of normal coordinates with point-group symmetry adapted to the geometry at the origin of the expansion).

The π-to-π^* photo-excitation of CC bonds and subsequent *cis–trans* photo-isomerization is one of the most fundamental processes in organic photochemistry. In particular, electronically excited ethylene experiences large-amplitude deformations that eventually lead to ground-state regeneration through a conical intersection. Despite the apparent simplicity of this system, the assignment of the photoabsorption spectrum and the radiationless decay mechanism of this prototype molecule still remain controversial. In this work, we focus on the first step that follows the photoabsorption. H migrations are not considered at this time scale, which allows a reduced-dimensionality treatment whereby six internal coordinates are frozen. We refer to Ref. [18] for a short review of experimental and theoretical investigations. See also Refs. [19–23].

In the present work, we present the first step in building such a global model. We show that the lowest manifold of adiabatic electronic states of ethylene can be described correctly with multiconfiguration self-consistent field (MCSCF) calculations restricted to 17 selected quasidiabatic configurations built on state-averaged orbitals. This space is stable upon large-amplitude deformations, such as torsion, pyramidalization, CC stretching and HCH bending. The properties of the nuclear coordinates and valence and Rydberg electronic states are investigated within the framework of dynamical symmetry. This systematic analysis is compared to a previous model of the valence states of ethylene [18]. The π-to-π^* state of ethylene is still today a computational challenge, as discussed in Ref. [23] and references therein. Although very cheap, our 17-selected-configuration approach is capable of describing the *V* state of ethylene quite remarkably.

2. Nuclear coordinates

We start with the definition of the nuclear coordinates that will be used to express the Hamiltonian matrix dependence on the molecular geometry. They are taken as symmetrized valence coordinates, directly related to the polyspherical coordinates used in Refs. [18,24,25]. The former are adapted to the expression of the potential energy functions within the framework of dynamical symmetry. The latter lead to a tractable expression for the kinetic energy operator and are suitable for further MCTDH calculations [10]. Our choice of coordinates is adapted to describing deformations that preserve the σ bonds, in particular the torsion around the CC bond involved in the *cis–trans* photo-isomerization of substituted ethylene. The dimensionality is reduced to a set of six active internal degrees of freedom.

2.1. Vector parametrization of the nuclei

The first step in building polyspherical coordinates is the definition of the vectors to be parametrized [10]. The relative motion of the six nuclei of C_2H_4 is parametrized by five independent vectors and three angular constraints. Two sets are considered here (see Fig. 1): a mixture of valence and Jacobi vectors for defining the polyspherical coordinates used in previous work [18,24,25] to which we want to compare; and valence vectors only, which will serve to define the symmetrized valence coordinates to be used here to investigate the potential energy surfaces.

The first set of valence–Jacobi vectors, $\vec{R}_i(i = 1 \text{ to } 5)$, is defined as

$$\vec{R}_1 = \overrightarrow{C_5G_R}, \tag{1a}$$

$$\vec{R}_2 = \overrightarrow{G_LC_6}, \tag{1b}$$

$$\vec{R}_3 = \overrightarrow{H_2H_1}, \tag{1c}$$

$$\vec{R}_4 = \overrightarrow{H_4H_3}, \tag{1d}$$

$$\vec{R}_5 = \overrightarrow{C_6C_5}, \tag{1e}$$

where G_R is the center of mass of H_1H_2 and G_L that of H_3H_4 [18,24,25].

The second set of valence vectors, $\vec{R}_i$ ($i = 5$ to 9), corresponds to:

$$\vec{R}_6 = \overrightarrow{C_5H_1}, \tag{2a}$$

$$\vec{R}_7 = \overrightarrow{C_5H_2}, \tag{2b}$$

$$\vec{R}_8 = \overrightarrow{C_6H_3}, \tag{2c}$$

$$\vec{R}_9 = \overrightarrow{C_6H_4}. \tag{2d}$$

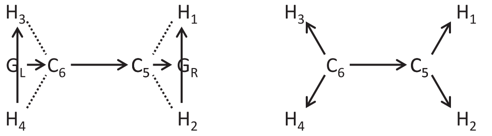

Fig. 1. The two sets of five vectors (left: Jacobi-valence; right: valence).