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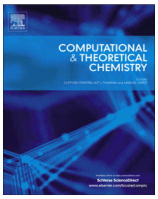

Tuning molecular excitation energy with external forces

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ABSTRACT

Mechanical forces can be coupled to chemical reactions modifying their chemical reactivity and physical properties. Among the latter, optical properties, and more specifically radiative absorption, is sensitive to external forces due to the clear dependence between structure and excitation energy. Here we develop theoretical and computational tools aimed to guide molecular design of new or modified chromophores with a mechano-responsive excitation energy. In particular, we describe a methodology for determining the optimal external force (i.e. with lower possible magnitude) modifying the excitation energy of a molecular system. This optimal external force may serve as a guide to conveniently modify chemically the system in order to make feasible the exertion of such forces. Moreover, as force pairs are the easiest and more frequent kind of external forces acting over a molecular system, a protocol to determine the more efficient force pair modulating the excitation energy is proposed. Finally, these methods are tested with a chromophore, the semibullvalene molecule, finding the more efficient way to reduce its excitation energy with the application of simple external forces.

1. Introduction

The use of mechanical force in chemical processes is well known in industry. Illustrative examples are mastication, compression or ball-milling, for polymers and solids [1]. The development of single molecule manipulation methods such as atomic force microscopy (AFM) [2,3] made possible more sophisticated experiments at a molecular level [4,5]. In this way, the study of the role of external mechanical forces has recently established emerging fields such as mechanobiology [6,7] and mechanoresponsive materials [8,9]. The application of external forces in a molecular system may change their reactivity and properties, as they can vary (increase or decrease) the activation energy of a given process or even the reaction mechanism itself [10]. In this regard, different theoretical approaches pursue to explain the variation in these properties, and several computational strategies are available, among them isometric [11,12] and isotensional approaches [13,14]. Isotensional and isometric approaches are derived from the conditions imposed in mechanochemical experiments: in isotensional experiments the external force, F_{ext}, is the fixed variable and the structural change is the measurement variable, in contrast to isometric experiments, where F_{ext} is measured as a function of fixed distances. Computationally, the isotensional approach leads to the concept of force-modified potential energy surfaces which can be studied systematically in order to predict phenomena such as force-induced reaction mechanisms; while the isometric approach is similar to constrained optimization (i.e. relaxed scan).

The use of light to induce changes of macroscopic properties of matter is well known and is also referred as photomechanical processes. Examples such as mechanochromic phenomena prove the effect of exerting mechanical forces in photophysical and photochemical properties of matter [15]. Also, single-molecule manipulation techniques such as AFM made possible measure coupling photoexcitations and mechanical exerted forces [16], as is the case of optomechanical cycle generating work in photoswitches [17]. In this regard, efficient excitation energy tuning by external forces has been proved in cis- and trans-azobenzene by means of molecular dynamics simulations, where different transitions have different response to similar external forces [18]. Moreover, the excitation energy of a chromophore can be influenced by chemical substituents, being possible to rationalized this effect in terms of the force exerted by the substituent over the chromophore,[19] as is explained by the so-called “structural substituent excitation energy effect” [20]. Even a chiral environment in a photoswitch can provide the necessary driving-force to yield unidirectional rotation, converting the photoswitch into a photoactive molecular motor, therefore changing the photochemical properties of the photoswitch [21].

Nevertheless, although the interesting properties of optomechanical systems, a systematical approach to computational prediction of photoinduced properties under external forces has not

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already been afforded. Moreover, there is also a noticeable lack of computational methods aimed to guide the molecular design of such kind of system. More specifically, the theoretical and computational tools for understanding photophysical properties as excitation spectrum, or photochemical behavior in molecular systems under external forces are essentially in a very early stage.

Here we develop theoretical and computational tools for studying the variation of the excitation energy of a given molecular system under external forces. The specific mechanism of force transmission to the mechanophore (e.g. through the polymer backbone) is a complex process that has been studied for some mechanochemical systems in recent years [22,23]. Nevertheless, it has to be emphasized that here we focus on the study of vertical excitation energy variation under the effect of a final (i.e. transmitted) force, independently on how the force is effectively transmitted to the mechanophore. In particular these tools allow to elucidate the nature of the external forces permitting the most efficient variation of the excitation energy, providing a valuable guidance in the molecular design of optomechanical devices.

2. Computational methods

All the electronic structure calculations were performed using the time-dependent extension of the density functional theory (TD-DFT) as implemented in Gaussian09 suite of programs [24]. The excitation energy variation is obtained by applying the isometric approach, which is performed by restraining a given coordinate which implicitly defines the applied force. DFT calculations were performed using the CAM-B3LYP functional [25] and the 6-31G* basis set. Energy gradients were determined analytically, while energy hessians were computed numerically for those points of interest.

3. Results

The methodology presented here permits to study the influence of external forces into the excitation energy of a given chromophore, focusing specifically on providing guidelines for the design of new absorption-responsive molecular systems. The results are organized as follows, (i) we firstly develop a method for the determination of the relevant molecular coordinates efficiently tuning the absorption spectrum of a given system under external forces. This method may permit the identification of those coordinates where the application of an external force is efficient in modulating (increasing or decreasing) the excitation energy with the minimum possible external force magnitude. Afterwards, (ii) a procedure for determining the force pairs permitting the maximum variation of the excitation energy is proposed. Contrary to considering a generic external force with multiple components in different atoms as pointed out in (i), the force pair vector is the result of applying the force in two atoms, as is the most common experimental kind of external forces in a molecular system. Finally, (iii) the developed methodology is applied to semibullvalene, an alkene presenting interesting optomechanical behavior due to a strained cyclopropane moiety.

3.1. Prediction of optimal excitation tuning external forces

Here we establish a general procedure applicable to any chromophore to determine the optimal variation (increase or decrease) of the excitation energy as the effect of an applied external force. More specifically, a second-order expansion of the potential energy surfaces (PES) is made for both, ground (E_0) and excited (E_1) bright electronic states taking the origin of the expansion on the ground state equilibrium structure. Based on this approximated PES, for each point of the configuration space ($\boldsymbol{q}$) the energy of each state is a function of the first and second energy derivatives:

$$E_0(\mathbf{q}) = E_0(\mathbf{0}) + \frac{1}{2}\mathbf{q}^T\mathbf{H}_0\mathbf{q} \quad (1)$$

$$E_1(\mathbf{q}) = E_1(\mathbf{0}) + \mathbf{q}^T\mathbf{g}_1 + \frac{1}{2}\mathbf{q}^T\mathbf{H}_1\mathbf{q} \quad (2)$$

where $E_0(\mathbf{q})$ and $E_1(\mathbf{q})$ are the energies of the ground and excited states for a given nuclear configuration $\mathbf{q}$, being $E_0(\mathbf{0})$ and $E_1(\mathbf{0})$ the corresponding energies of both states for the ground state equilibrium structure, $\mathbf{H}_0$ and $\mathbf{H}_1$ are the hessian matrices for ground and excited states computed at the equilibrium structure, and $\mathbf{g}_1$ is the energy gradient vector for the excited state for the same structure.

Thus, the excitation energy variation of a given configuration is calculated as follows:

$$\Delta E(\mathbf{q}) - \Delta E(0) = \mathbf{q}^T g_1 + \frac{1}{2}\mathbf{q}^T(\mathbf{H}_1 - \mathbf{H}_0)\mathbf{q} \quad (3)$$

where $\Delta E(\mathbf{0})$ is the vertical excitation energy for the ground-state equilibrium geometry ($\mathbf{0}$).The energy gradient vector (opposite to the internal force vector, $\mathbf{F}_{int}$) on the ground-state for any given nuclear configuration $\mathbf{q}$ is therefore:

$$\nabla E_0(\mathbf{q}) = \mathbf{H}_0\mathbf{q} = -\mathbf{F}_{int} \quad (4)$$

Let us consider the effect of an external force ($\mathbf{F}_{ext}$) applied over the molecular system in its ground state. On one hand, the equilibrium geometry in the ground-state under these external forces (denoted as $\mathbf{q}_{eq}^{\mathbf{F}}$) changes in order to be the net force acting on each nuclei equal to zero (i.e. $\mathbf{F}_{int} + \mathbf{F}_{ext} = 0$). Therefore, the new equilibrium geometry under external forces is given by:

$$\mathbf{q}_{eq}^{\mathbf{F}_{ext}} = \mathbf{H}_0^{-1}\mathbf{F}_{ext} \quad (5)$$

On the other hand, the excitation energy of the system changes as a result of the new ground-state structure. The new excitation energy can be easily determined from (3) by evaluating the energy difference function in $\mathbf{q} = \mathbf{q}_{eq}^{\mathbf{F}_{ext}}$. It is therefore clear that an external force might produce a shift in the excitation energy. Among all possible external force vectors, we are interested in finding that one able to shift more efficiently (i.e. yielding the largest variation) the excitation energy with the lowest possible magnitude (i.e. the lowest possible force vector norm). In order to determine such a vector, the force magnitude has to be minimized subject to the constraint of a given shift of the excitation energy. For convenience the function to be minimized is chosen to be the square of the magnitude of the force vector:

$$(\nabla E_0(\mathbf{q}))^T(\nabla E_0(\mathbf{q})) = \mathbf{q}^T\mathbf{H}_0^2\mathbf{q} \quad (6)$$

By applying the Lagrange multipliers' method to find the lowest force providing a given energy gap (i.e. $\Delta E(\mathbf{q}) - \Delta E(\mathbf{0}) = S$, being S the energy gap variation), the following Lagrangian function (L) has to be optimized:

$$L(\mathbf{q}) = \mathbf{q}^\mathbf{T}\mathbf{H}_0^2\mathbf{q} + \lambda(\Delta E(\mathbf{q}) - \Delta E(0) - S) \quad (7)$$

So its gradient must vanish at the optimal configuration ($\mathbf{q}_{opt}$):

$$\nabla L(\mathbf{q}_{opt}) = 2\mathbf{H}_0^2\mathbf{q}_{opt} + \lambda(\mathbf{g}_1 + (\mathbf{H}_1 - \mathbf{H}_0)\mathbf{q}_{opt}) = 0 \quad (8)$$

By rearrangement of (8):

$$\mathbf{q}_{opt} = -\left(\frac{2}{\lambda}\mathbf{H}_0^2 - \mathbf{H}_0 + \mathbf{H}_1\right)^{-1}\mathbf{g}_1 \quad (9)$$

where $\mathbf{q}_{opt}$ is the optimal distortion (i.e. reached with the lowest possible external force) providing a given decrease (or increase) of the excitation energy. The corresponding target force vector