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Isomerization and electronic relaxation of azobenzene after being excited to higher electronic states

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ABSTRACT

In this work, some critical structures (e.g. stable structure, transition state, local minimum and conical intersection) of azobenzene photoisomerization were optimized by means of *ab initio* CASSCF calculation. The potential energy surfaces for the CNNC dihedral torsion and CNN bond angle concerted-inversion pathway were mapped to explore the relaxation process of azobenzene (AB) photoisomerization. The results indicate that the rotational mechanism favors the photoisomerization of the $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ *trans*-AB. The concerted-inversion mechanism may operate in the decay process of $S_2(\pi,\pi^*)$ or higher state *trans*-AB. By borrowing the $(n,\pi^*;\ \pi,\pi^*)$ and (n^2,π^{*2}) electronic states, *trans*-AB upon excitation to the higher states can quickly relax to the $S_1(n,\pi^*)$ or ground state via the rotation or concerted-inversion pathway. The forming ground-state species with higher vibrational energy from the higher excited states will become the stable *trans*-isomer through the concerted-inversion pathway. These relaxation processes have been confirmed by the conical intersections calculated by the high-level CASSCF method.

1. Introduction

Organic or inorganic materials based on the azobenzene (AB) unit have attracted significant attention because of their photoresponsive properties that arise from the reversible *cis–trans* photoisomerization of AB [1–10]. Accordingly, the photochemistry and photophysics of AB is again becoming a research focus in recent years [11–15]. An important subject is the photoisomerization mechanism of AB, which has been debated for a long time. It is well known that azobenzene has two important absorption bands: a weak band in the visible light region corresponding to the $n \rightarrow \pi^*$ electronic transition and an intense band in the UV spectral region corresponding to $\pi \rightarrow \pi^*$ electronic transition. An argument about photoisomerization mechanism of AB initially originated from the following experimental observation: the quantum yield (Φ) of *trans* → *cis* isomerization is 0.20–0.36 upon excitation to the $S_1(n,\pi^*)$ state and it decreases to 0.09–0.20 when excitation to the $S_2(\pi,\pi^*)$ state [16]. The dependence of Φ on the excitation wavelength obviously violates Kasha's rule. Therefore, two photoisomerization pathways (rotation around the NN double bond on the $S_2(\pi,\pi^*)$ state and inversion of CNN angle on the $S_1(n,\pi^*)$ state) were firstly proposed by Rau and Lüddecke to explain this violation [17].

Rau's photoisomerization model has been successfully applied to explain the time-resolved spectrum measurements on the excited-state decay dynamics of azobenzene and its derivatives [18–23]. However, some new experimental and high-level theoretical results challenge this original model. The picosecond time-resolved Raman and femtosecond time-resolved fluorescence spectroscopy have been applied to investigate the photoisomerization of *trans*-AB [24,25]. The results indicate that the NN bond retains a double bond nature and the molecule keeps a planar structure in the $S_1(n,\pi^*)$ state. The isomerization of AB only concerns the inversion mechanism occurring on the $S_1(n,\pi^*)$ state, and the rotational isomerization pathway starting directly from the $S_2(\pi,\pi^*)$ state does not exist. Recently, *ab initio* and density-functional calculations have been used to study the isomerization mechanism of azobenzene. The results show that the $S_1(n,\pi^*)$ state decay mainly involves the rotation mechanism [26–28]. Meanwhile, another concerted-inversion relaxation channel for the $S_1(n,\pi^*)$ excited *trans*-AB was found through *ab initio* calculations [29]. Presumably this concerted-inversion channel is inclined to produce more *trans*-isomers after *trans*-AB is excited to the $S_2(\pi,\pi^*)$ state or higher vibration energy level of the $S_1(n,\pi^*)$ state. The concerted-inversion channel has also been supported by the femtosecond fluorescence anisotropy study [30].

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In contrast to the extensive discussion on the $S_1(n,\pi^*)$ state, the thorough understanding of the $S_2(\pi,\pi^*)$ state still lacks. In several previous papers [23,25,31], it has been reported that the AB molecule can quickly decay from $S_2(\pi,\pi^*)$ state to the $S_1(n,\pi^*)$ state. The $S_2(\pi,\pi^*)$ state with a lifetime of 110–170 fs was determined by the time-resolved spectroscopy measurements. A semiclassical dynamics approach has been recently applied to simulate the potential energy surfaces (PES) and the photoisomerization dynamics of AB [32]. The result shows that the torsion around the NN double bond is the preferred mechanism upon excitation on the $S_1(n,\pi^*)$ or $S_2(\pi,\pi^*)$ state. Moreover, two conical intersections (CI) between $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$ state were found with the transoid and cisoid geometries, respectively. It is easy for the $S_2(\pi,\pi^*)$ FC species to access these conical intersections because of small geometrical distortions and energy demanded. By means of *ab initio* CASSCF calculation, it has been shown that by borrowing another singlet state that gets significant contributions of doubly excited configuration (n^2,π^{*2}), $S_2(\pi,\pi^*)$ state can rapidly relax to the $S_1(n,\pi^*)$ state [27,33]. That is to say, some other excited electronic states could play an important role in the decay process of AB after excitation to $S_2(\pi,\pi^*)$ state.

At the current stage, it seems that a general conclusion has been drawn for the isomerization mechanism and decay dynamics of AB on the $S_1(n,\pi^*)$ state, but there is still an insufficiency of understanding the details of AB on the $S_2(\pi,\pi^*)$ state. In fact, the decay dynamics and isomerization mechanism of AB on the $S_2(\pi,\pi^*)$ state are of more interest for the reason that the photoresponsive properties of materials containing AB are commonly modulated by the UV light (~365 nm) that corresponds to the maximum absorption wavelength ($S_0 \rightarrow S_2(\pi,\pi^*)$ transition) of AB [34–36]. Therefore, it is necessary to further map the thorough PES of higher excited states along CNNC rotation and CNN inversion coordinates and focus on the details in the cross-region between different excited states.

In the present study, through a high-level *ab initio* calculation, we scanned the PES of the first five singlet states along the CNN inversion coordinate and optimized some important points on the CNNC rotational pathway. Some CIs between two different electronic states were also optimized. The important features of the PES were described in detail in order to comprehensively understand the relaxation process of $S_2(\pi,\pi^*)$ state. The calculation strategy, the main results and discussion will be given in the following sections

2. Calculation strategy

In this work, all the computations were carried out by means of CASSCF method encapsulated in the Gaussian 03 software [37]. CASSCF calculation has been widely used to deal with the excited states relevant to photochemical and photophysical processes [38]. It can give accurate descriptions of the PESs in both the ground and excited states [39–44]. The optimization of the stable structures and transition states were performed at the state-specific CASSCF level. The state-average CASSCF calculation with equal weights was used to determine the geometries of conical intersections (CIs). The PESs of the first five singlet states along the CNN inversion coordinates were obtained at the state-average CASSCF level, in which the S_0 PES was scanned firstly and then energies of each electronic state were recomputed with single-point calculations on the basis of the geometries of the S_0 PES. The 6-31G* basis set was employed in all the CASSCF calculations.

Theoretically, the active space should contain all of the valence electrons and orbitals for the CASSCF calculation. Due to the limitation of the computational power, it is difficult to do so for azobenzene. Therefore, choosing the active space becomes a crucial step in the CASSCF calculations. According to the previous calculations on the photoisomerization reaction of azobenzene, the active space including six electrons distributed among six orbitals, referred as to CAS(6,6), can reasonably map the PES of photoisomerization on the ground state and three excited states [45]. In this study, we chose an active space of ten electrons in eight orbitals, namely CAS(10,8), in order to describe more excited states and not heavily increase the calculation workload at the same time. These orbitals included the π and π^* orbitals of –N=N– group, two non-bonding orbitals occupied by two lone-pair electrons (n_+, n_-) of –N=N– group, and two π and π^* orbitals of the aromatic ring.

3. Results and discussion

3.1. Rotational pathway

In the previous studies [26,27,29], it has been found that the rotational mechanism is most favorable in energy for the isomerization of AB on the $S_1(n,\pi^*)$ state. In this study, we also optimized the important structures involved in this rotational isomerization channel at the CAS(10,8)/6-31G* level of theory. The detailed geometries of all the structures, shown in Fig. 1, are in a good agreement with the results reported by Cembran et al. [26]. For example, the *trans*-AB with C_{2h} symmetry has the energy of 16.2 kcal/mol lower than that of the *cis*-AB with C_2 symmetry. A local S_1 minimum, $(n,\pi^*)_{min}$, with a planar configuration and a transition state, $(n,\pi^*)_{TS}$, with the CNNC dihedral of 117.5° were also found on the $S_1(n,\pi^*)$ state. The energy of $(n,\pi^*)_{min}$ is very similar to that of the $(n,\pi^*)_{TS}$. A conical intersection between the ground state and the $S_1(n,\pi^*)$ state, $(GS/n,\pi^*)_{CI\_rot}$, was found to locate on the middle of the PES along the CNNC rotational coordinate. This CI shows a twisted geometry with the CNNC dihedral of about 93°. All the above characteristics further indicate that a rotational pathway indeed plays an important role in the isomerization process of AB on the $S_1(n,\pi^*)$ state.

We attempted to optimize the key structures on the $S_2(\pi,\pi^*)$ state, such as local minimum, transition state and the conical intersection, in order to understand the energy decay pathway of AB once it is excited on the $S_2(\pi,\pi^*)$ state. However, all the attempts to optimize these structures relevant to the $S_2(\pi,\pi^*)$ state failed because of the convergence problem. It has been found that the energy of $S_2(\pi,\pi^*)$ *trans*-FC point is very close to that of the (π_P,π^*) FC point [31]. The (π_P,π^*) electronic state corresponds to the transition of π electron of phenyl ring to the π^* orbital of –N=N– group. Our calculation also showed that slight changes in the geometries of *trans*-AB could easily induce the overlap of the $S_2(\pi,\pi^*)$, (n^2,π^{*2}), (π_P,π^*) and $(n,\pi^*;\ \pi,\pi^*)$ electronic states in the vicinity of the FC region, which can be seen clearly in the following concerted-inversion PES. Therefore, the electronic states can readily flip and convergence fails during the process of optimization, which may be one of the reasons why the details of the $S_2(\pi,\pi^*)$ state are insufficient at the present stage. Because of the hop of different electronic states in the vicinity of $S_2(\pi,\pi^*)$ *trans*-FC region, *trans*-AB on the $S_2(\pi,\pi^*)$ state can rapidly decay to the other electronic state, e.g. $(n,\pi^*;\ \pi,\pi^*)$ and (n^2,π^{*2}) states, through the small bending of two CNN angles. Based on the above analysis, we examined the (n^2,π^{*2}) electronic state and found a local minimum, $(n^2,\pi^{*2})_{min}$, and a conical intersection, $(n,\pi^*/n^2,\pi^{*2})_{CI\_rot}$. Fig. 2 gives the geometrical parameters of the two structures. Apparently, these two structures belong to the key point of rotational isomerization pathway because of their twisted configuration.

The energies of all the structures shown in Figs. 1 and 2 are listed in Table 1. It should be noted that the CASSCF energies are 18–35 kcal/mol greater than experiment excitation energies because dynamic correlation energy is not included, but the energetic ordering agrees with the experiment and DFT calculation