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RAPID COMMUNICATION

Spin polarization and dispersion effects in emergence of roaming transition state for nitrobenzene isomerization*

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Since roaming was found as a new but common reaction path of isomerization, many of its properties, especially those of roaming transition state (TS_R), have been studied on many systems. However, the mechanism of roaming is still not clear at an atomic level. In this work, we use first-principles calculations to illustrate the detailed structure of TS_R in an internal isomerization process of nitrobenzene. The calculations distinctively show its nature of antiferromagnetic coupling between two roaming fragments. Moreover, the effect of dispersion is also revealed as an important issue for the stability of the TS_R. Our work provides a new insight into the TS_R from the view of electronic structure and contributes to the basic understanding of the roaming systems.

Keywords: spin polarization, dispersion, first-principles

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1. Introduction

Roaming, as a newly discovered chemical reaction path, different from the conventional ones,[1] plays an important role in the isomerization process in many systems,[2–10] which has broadened our sight of view towards the reaction path. As a transition state (TS) in the roaming reaction path, roaming transition state (TS_R) takes a critical place in the process,[11] for which its configuration and electronic structural properties have received a lot of attention. However, for experimental approaches, only indirect information could be observed from TS_R and even normal TS. Besides, the differences between TS_R and other conventional TS[12,13] are not clearly revealed at an atomic level, for which we hope to understand the mechanism in this work.

Nitrobenzene is one of the typical energetic materials whose geometries and spectrum properties, isomerizations and even dissociation channels have been studied theoretically and experimentally.[14–19] Recently, a new reaction channel in the photodissociation process of nitrobenzene was reported, suggesting a unimolecular isomerization process through a typical TS_R.[20] So far, most of the previous researches have focused on the dynamic properties of the roaming systems, with certain atoms or functional groups roaming around the rest part and then dissociated or isomerized. However, more detailed mechanism of electronic structure in this roaming system still needs further investigating. Here in our work, we carry out a theoretical investigation, with density functional theory (DFT), about the properties of roaming process of nitrobenzene, and particularly discover the critical role that spin polarization interaction plays in the TS_R, proving it to be the spin polarized roaming state (SPRS). Meanwhile, dispersion is also found to have a significant effect on stabilizing the SPRS, obviously reducing the distance between the functional groups. We hope that this result can be a valuable reference for a more regular recognition of the roaming mechanism.

In this work, based on the density function theory (DFT), the calculations are performed using B3LYP-D3 level[21] and 6-311+g(2df,2pd) basis set by means of Gaussian 09 package.[22] Two d and one f polarization functions are added to the C, N, and O atoms, while two p and one d polarization functions are added to the H atom.[23] Diffuse functions are also introduced into the calculation.[24] The single point energy corrections are calculated under CCSD(T)/6-311++(2df,2pd). Owing to the fact that the distance between the roaming separations is commonly larger than most of the bonding distances, dispersion, as an important issue in the intermolecular interaction, which was seldom discussed previously for the roaming systems, is more effective to describe such systems. Therefore, the 3rd generation dispersion correction is introduced into B3LYP,[25] namely B3LYP-D3, from which most of the conclusions are drawn. This result is also checked using M06-2X level.[26] The energies decomposition

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are calculated using ADF package.[27]

2. Results and discussion

Firstly, we obtain the roaming reaction path and especially the optimized TS_R by means of the TS optimization and the intrinsic reaction coordinate (IRC) analysis at a B3LYP level. The result shows that both NO_2 and C_6H_5 fragments are neutral with nearly one single spin election on each of them in the initial structure, showing a spin polarized singlet state structure. The distance between the ipso C atom in C_6H_5 fragment and the N atom in NO_2 ($D_{C–N}$) is 3.30 Å, corresponding to the 3.29 Å distance in the previous work.[20]

Since dispersion is an important issue for describing intermolecular interactions, the calculations with dispersion corrections at the same level (B3LYP-D3) are also performed. In the vibration calculation, one imaginary frequency is found in the spectrum for each of the two cases, indicating that the stabilizations are qualitatively consistent no matter whether dispersion is introduced. However, after the dispersion correction is introduced into the calculation, the results show that $D_{C–N}$ decreases by nearly 0.30 to 3.01 Å (2.96 Å for the M06-2X level), which has not been found in the conventional TS structure of the unimolecular isomerization. From this side, the special properties could also be seen.

In order to acquire the electronic structure of the roaming state, we carry out spin and charge density calculations, which are also important for understanding the electronic structure from wavefunction aspect. The result of spin density shows that on each of the two fragments, the spin value is 0.98, corresponding to the two single electrons mentioned above. For the C_6H_5 fragment, most of the spin densities (91.0%) are localized on the ipso C atom, while for the NO_2 fragment, the spin density shows a more delocalized feature, i.e., 46.7% on the N atom and 26.6% on each of the O atoms (see Fig. 1(a)), which can be obtained similarly from M06-2X level as 89.5% for an ipso C atom in the C_6H_5 fragment, 48.4% on an N atom and 25.8% on an O atom. Meanwhile, the analysis of electronic density difference shows a rather "intra-fragment" feature, indicating minor difference between the roaming structures of free C_6H_5 and NO_2 radicals as shown in Fig. 1(b). Moreover, a general feature for the roaming reaction path could be concluded from these results that the single electrons are still localized on each fragment, in spite of the fact that such an occupation pattern would cause unpaired electrons. This is an important property of eigenstate for a roaming system. Also, this is why only the spin unrestricted calculation could describe roaming reaction paths.[11,20]

For further verification, the potential surface is obtained theoretically at the same level. As shown in Fig. 1(c), the energy barrier is 77.13 kcal/mol (73.13 kcal/mol for B3LYP-D3, 75.20 kcal/mol for M06-2X level) corresponding to the magnitude of similar roaming process reported previously.[15] Moreover, our results also indicate that the TS_R is about 1.80 kcal/mol (2.58 kcal/mol for B3LYP-D3, 3.70 kcal/mol for M06-2X level) lower than the radical threshold, which is a similar magnitude to those of other roaming transition state systems.[28] On the other hand, for the case without dispersion correction, the TS_R turns out to be only 0.78 kcal/mol lower than the radicals. Therefore, it can be concluded that dispersion has a significant enhancement in the stability of such roaming systems.

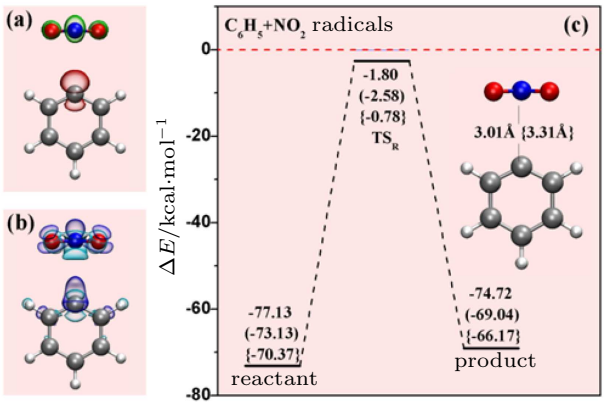


Fig. 1. (color online) Schematic potential surface (kcal/mol) of the intramolecular isomerization process through TS_R and the electron structure of roaming nitrobenzene. (a) Spin density distributions of roaming-state nitrobenzene. The green and red isosurfaces suggest two different directions of spin density. (b) The electron density difference between two radical fragments C_6H_5 and NO_2 and the roaming nitrobenzene. The purple blue isosurface indicates that the electron density increases, while the light blue isosurface means that the electron density decreases. (c) Roaming reaction path of nitrobenzene. The reactant is nitrobenzene, and the product is one of the isomers $C_6H_5NO_2$. The values of relative energy (ΔE) between these structures and free C_6H_5 and NO_2 radicals are marked. The numbers in the braces represent the results of B3LYP, those in the brackets indicate the results of B3LYP-D3, and those outside refer to the CCSD(T) results.

Furthermore, in order to understand the properties of the interaction of the IRC reaction points, especially the TS_R, the energy decomposition analyses of the configuration along the reaction path are carried out. According to the results, the bonding energy is −2.84 kcal/mol, in which the electronic absorption and Pauli repulsion are −4.80 kcal/mol and 5.70 kcal/mol respectively, indicating a 0.90 kcal/mol excluding effect for the steric case, while the orbital and dispersion are −1.71 and −2.03 kcal/mol respectively as shown in Fig. 2. Therefore, dispersion takes 23.8% of the total attraction effects, which also proves its non-negligible contribution to the stability of such an SPRS. For the other points on the IRC, which are all involved with spin polarizations, the results show that the total interaction energy of the TS_R is the lowest, corresponding to its first order saddle point state. At the same time, the trends of the electronic interaction and the Pauli repulsion are similar, especially for those close to the TS_R, causing a lesser effect from steric interaction. This also indicates that the changing of the total interaction energy is mainly contributed by the orbital interaction.

Moreover, considering that the triple state has the most similar electron structure to the spin polarized singlet state does, we also compare the energy decomposition for these two cases. The result shows that the bonding energy for the spin polarized singlet is nearly twice as large as that of the triplet, which turns out to be −1.62 kcal/mol. Among those, the electrostatic term and the dispersion term are consistent, indicating the same spatial conformation. However, it should be noticed that from the ferromagnetic triplet to the antiferromagnetic spin polarized singlet, the Pauli repulsion is reduced by 0.56 from 6.26 kcal/mol, while the orbital interaction is increased by −0.66 from −1.05 kcal/mol. These could, on the other hand, prove that a spin polarized singlet structure for TS_R involves a better stability.

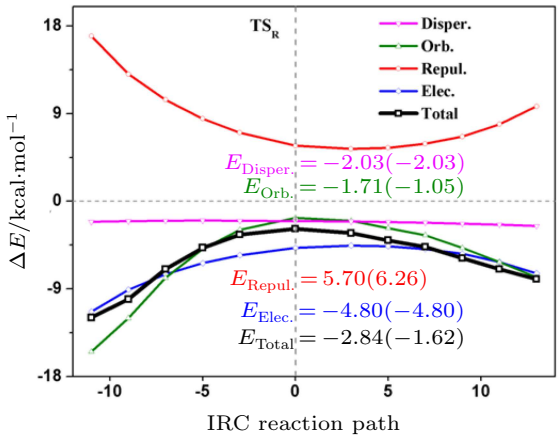


Fig. 2. (color online) Energy decompositions for part of the points along the IRC compared with those of the TS_R. The black line represents the total bonding energy. The blue curve refers to the electronic absorption, and the red curve indicates the Pauli repulsion. The green curve denotes the orbital interaction, and the violet curve indicates the dispersion results. The results of the energy decomposition for TS_R with spin polarized singlet and triplet (in the bracket) states are listed in the corresponding colors. Special technique is adapted in the calculation, introducing the restricted calculation as a "bridge", for the interactions from the restricted to the unrestricted fragments and compound can be easily obtained by specifically assigning the occupation.[29] Thus the result can be obtained with a simple subtraction: $\Delta E = \Delta E_{com} - \Delta E_{frags}$, where ΔE_{com} and ΔE_{frags} both consist of electrostatic, repulsion, orbital and dispersion terms.

Despite the fact that the value of dispersion term is merely about 2 kcal/mol, dispersion interaction is still of great importance for stabilizing the conformation of TS_R, because the interaction distance in the roaming system is far beyond the bonding area of functional groups. Moreover, the calculations above indicate that dispersion corrected DFT would bring in about 0.30 Å decrease of D_{C-N}, which is a simple but effective example of its importance, and it is also a particular property compared with other transition states. Therefore, it could be concluded that the roaming is a special kind of reaction path, which involves spin polarization, among the common reaction processes.

Since the spin–orbit coupling relativistic effects are important for open-shell systems, we further calculate the energy gaps of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with both scalar and spin–orbit coupling effects. The results show that the gap of scalar effect is 67.24 kcal/mol (2.92 eV), which is in high consistence with that without relativistic effect. As expected, the gap of spin–orbit coupling approximation is 61.87 kcal/mol, smaller than that in scalar cases. This is because the frontier orbital energy levels are sensitive to the spin–orbit coupling, resulting in the LUMO and HOMO lowering and rising in energy, respectively. Therefore, the gap between HOMO and LUMO decreases. The eigenvalue of S^2 operator $\langle S^2 \rangle$ is generally used to measure the spin contamination when compared with $s(s+1)$, where s is $1/2$ of the number of unpaired electrons, varying between systems with different spin multiplicities. For TS_R of nitrobenzene, $\langle S^2 \rangle$ turns out to be 0.99, similar to that for the O(1D) + H_2CO roaming system.[30] However, after the annihilation operation, $\langle S^2 \rangle$ decreases to 0.08, which is in a reasonable range. Therefore, we believe that the unrestricted calculations are reliable.

Meanwhile, roaming transition states have been noticed and studied for quite a long time, whose energetic properties have been discussed in depth, while the detailed electronic properties at an atomic level still need processing. Also, the DFT levels are expected to give a more unstable TS_R than ab initial ones.[11] However, our calculation proves that the dispersion could significantly improve the stability of TS_R. It is noteworthy that with dispersion correction introduced into the calculation, both the roaming distance and the energy of the TS_R obviously decline, indicating an more stable saddle point, which also suggests that dispersion does make difference and should be considered in future roaming-related calculations. Nevertheless, although such SPRS configurations are saddle points that could be found in a certain distance, they are actually not a strict transition state compared to the conventional ones, due to their large amplitude and anharmonic motions. Therefore, they are more likely to be referred to as roaming regions.

3. Conclusion

In this work, we reveal the electronic structure of the SPRS for nitrobenzene. Both spin density and electronic density difference prove that the roaming process of TS_R involves with a spin polarized singlet structure. It should be noticed that apart from the instantaneously dissociating feature, the roaming transition state belongs to a bound reaction path which leads to the recombination of radical fragments and achieving the isomerization. The spin polarized electronic structure accounts for the bounded effect when two fragments are roaming. The energy decomposition also explain the stability of such an antiferromagnetic TS_R. Dispersion correction is proved to play an important role in the roaming process by

significantly reducing the roaming distance. We hope that this work could provide a theoretical reference for the future investigations on the mechanism of roaming.

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