# Mechanism of Excited State Double Proton Transfer in 2-Amino-3-Methoxypyridine and Acetic Acid Complex

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*The excited-state double-proton transfer (ESDPT) mechanism of 2-amino-3-methoxypyridine and acetic acid complex is studied by the density functional theory (DFT) and time-dependent DFT with CAM-B3LYP functional. The complex is connected through two different types of inter-molecular hydrogen bonds. After photo-excitation, both hydrogen bonds get strengthened, which can facilitate the ESDPT reaction. The scanned potential energy curve along the proton transfer coordinate indicates that the ESDPT reaction proceeds in a stepwise pattern.*

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Hydrogen bonding interactions and proton transfer (PT) reactions related to nitrogen containing heterocyclic systems are fundamental issues in biological systems.[1] As is known, the double helix of DNA are constrained by inter-molecular hydrogen bonding interactions. Revealing the proton transfer processes in these systems can provide us with more of a clear vision about the mechanism of DNA mutation.[1] Since the first observation by Weller *et al.*,[2] excited state proton transfer has attracted tremendous attention in experiment and theory for the past several decades.[3] To achieve proton transfer, a pre-formed hydrogen bond is usually requested. Recently, Zhao and Han proposed that the hydrogen bond may get strengthened or weakened after photo-excitation owing to the redistributed electron density,[4] which is also the driving force of excited state proton transfer. There has long been a dispute about the pattern of double proton transfer. The 7-azaindole dimer is a model system to study this issue. Steady state, time-resolved spectroscopic techniques as well as first principle calculations were employed to reveal the underlying mechanisms of this fast process.[5] In addition, an excited state double proton transfer (ESDPT) process was observed experimentally in 2-amino-3-methoxypyridine (2A3MOP) and acetic acid (AcOH) complex.[6] After photo-excitation, 2A3MOP shows a normal emission in pure $n$-hexane solvent. When adding acetic acid to the solution, the normal emission band gets decreased accompanied by an increased new emission band with larger Stokes shift. It was proposed that the new emission band came from an excited tautomer of 2A3MOP-AcOH complex with 1:1 molar ratio, which was originated from the ESDPT process.[6] However, steady-state spectra can only provide indirect evidence about the ultrafast proton transfer mechanism. Thus we carried out a theoretical investigation of the ESDPT mechanism of the 2A3MOP-AcOH complex.

All calculations were performed using the Gaussian 16 program suite.[7] Density functional theory (DFT)[8] and time-dependent DFT (TD-DFT)[9] were used for ground-state and excited-state geometry optimizations as well as energy calculations. The TD-DFT method has been proved to be very powerful to describe hydrogen bonding and PT reactions in the excited state. The Becke three-parameter hybrid exchange functional with the Lee–Yang–Parr gradient-corrected correlation functional in the long-range corrected version of Yanai *et al.*, the CAM-B3LYP[10] functional was used. To better describe the hydrogen bonding interaction, we used the $6-311++G(d,p)$ basis set for the hydrogen bonds related atoms (i.e., O1, H2, N3, N4, H5, and O6 labeled in Fig. 1.) and the $6-31+G(d,p)$ basis set for the rest atoms. The integral equation formalism variant polarizable continuum model (IEFPCM) was employed. The solvent was chosen as $n$-hexane, in agreement with the experimental work.[6] The potential energy curve (PEC) was relaxedly scanned along the generalized internal coordinates defined as $PT = PT1 + PT2$ where $PT1 = R(\mathrm{O1,H2}) - R(\mathrm{H2,N3})$ and $PT2 = R(\mathrm{N4,H5}) - R(\mathrm{H5,O6})$. The integral accuracy was $10^{-12}$ and the DFT grid was ultrafine, as the default settings in Gaussian 16.

The structures of 2A3MOP-AcOH complexes in normal (N) and excited normal (N*) forms were optimized. The scheme of the complex is shown in Fig. 1, where two different types of inter-molecular hydrogen bonds, i.e., O1-H2$\cdots$N3 and N4-H5$\cdots$O6, were formed. Key inter-molecular hydrogen bond parameters of the N form structure in both the ground state and the excited state were also labeled. After photo-

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excitation, the hydrogen bonds H2···N3 and H5···O6 are shortened from 1.643 and 1.909 Å to 1.568 and 1.776 Å, respectively. Meanwhile, the O1–H2 and N4–H5 bond are elongated from 1.023 and 1.017 Å to 1.041 and 1.030 Å, respectively. These geometric changes indicate that both inter-molecular hydrogen bonds O1-H2···N3 and N4-H5···O6 get strengthened in the excited state. This strengthening is originated from the excited state charge redistribution, which is also the driving force of excited state proton transfer reaction.

**Table 1.** Comparison between calculated and experimental absorption and emission parameters. The units are in $cm^{-1}$.

| Geometry | Cal. Result | | Exp. Result | |
|---|---|---|---|---|
| | EVEE | Stokes shift | Band peak | Stokes shift |
| Abs.-N | 37283 | | 34130 | |
| Em.-N* | 32244 | 5039 | 29412 | 4718 |
| Em.-DT* | 27390 | 9893 | 24272 | 9858 |

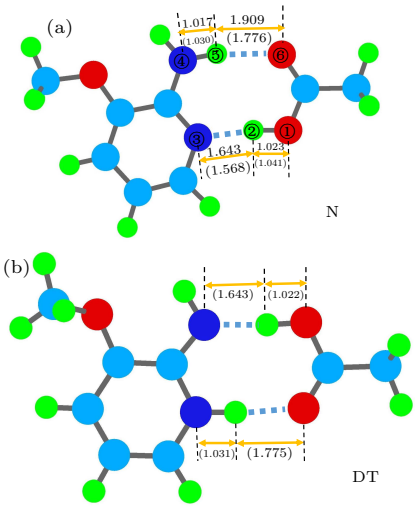


**Fig. 1.** Structures of 2A3MOP-AcOH complex in N and DT forms. The hydrogen bond parameters in the ground state (above the yellow arrows) and in the excited state (below the yellow arrows and in parentheses) as well as atomic numberings are labeled. The hydrogen bonding interactions are depicted by blue dashed lines.

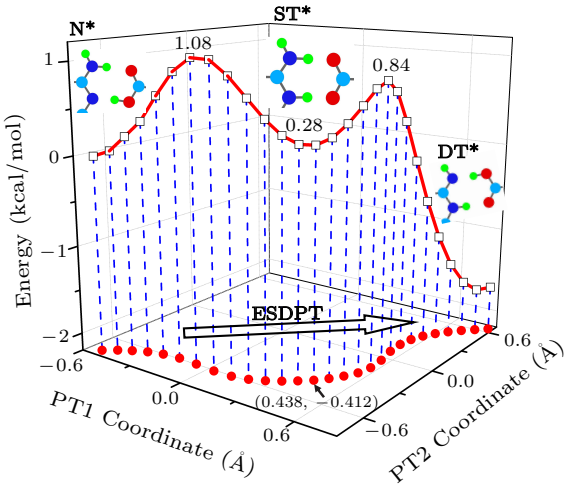


**Fig. 2.** PEC of 2A3MOP-AcOH complex. The curve was relaxedly scanned along the generalized internal coordinates defined as $PT = PT1 + PT2$, where $PT1 = R(\mathrm{O1,H2}) - R(\mathrm{H2,N3})$ and $PT2 = R(\mathrm{N4,H5}) - R(\mathrm{H5,O6})$. The PEC indicates that the ESDPT reaction is in the stepwise pattern.

The calculated electronic vertical excitation energies (EVEEs) of N, N*, and DT* forms were listed in Table 1. Even though the CAM-B3LYP functional tends to overestimate the EVEEs, the calculated Stokes shifts of the N* and DT* emission bands are in good agreement with the experimental results. The calculated Stokes shifts of the N* and DT* bands are 5039 and 9893 $cm^{-1}$, nearly identical with the experimentally detected 4718 and 9858 $cm^{-1}$. This indicates that the method is reliable to calculate the relative energy of the proton transfer energy curve in the excited state.

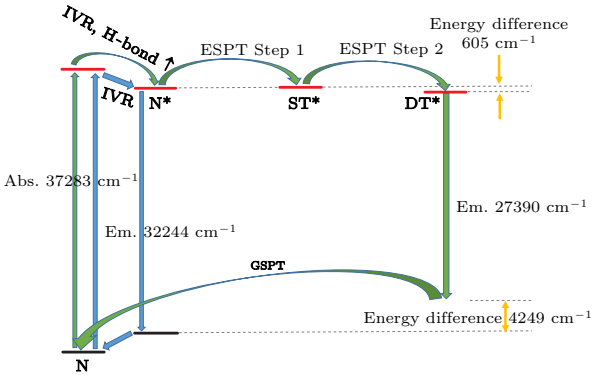


**Fig. 3.** Scheme of the photo-induced dynamical process of 2A3MOP (blue arrows) and 2A3MOP-AcOH complex (green arrows). Photo-absorption (Abs.), photo-emission (Em.), intra-molecular/intra-complex vibrational relaxation (IVR), hydrogen-bonding strengthen (H-bond ↑), excited-state proton transfer (ESPT), and ground-state proton transfer (GSPT) processes are depicted by corresponding arrows. Yellow arrows show the origin of the large Stokes shift of DT*.

To obtain a clearer picture of the ESDPT reaction, we scanned the PEC along the double proton transfer coordinate, as shown in Fig. 2. The final product DT* is 1.71 kcal/mol lower in energy than the N* tautomer. During the transfer reaction, there exists an intermediate species whose double protons are both covalently bonding with the 2A3MOP molecule. This intermediate species is generated by the first step proton transfer of H2. We would call it the single proton transfer tautomer (ST*). The projection of the PEC on the $PT1$–$PT2$ plane represents the geometric path of the reaction. The $PT$ coordinate for ST* is (0.438, −0.412). This indicates that the ESDPT process proceeds in the stepwise pattern and the proton in the O1-H2-N3 site has priority to transfer in comparison

with the proton in the N4-H5-O6 site. Otherwise, if the ESDPT reaction proceeds in concerted pattern, the projection of the PEC would pass nearby the (0,0) point of the $PT1$–$PT2$ plane. The energy barrier for the first step is 1.08 kcal/mol and for the second step is 0.56 kcal/mol. In view of the effect, the existence of AcOH provides a proton transfer medium for amino-imino tautomerization.

As stated above, DT* has a larger Stokes shift than the N* form. This comes from the fact that the potential energy curve of the ground state varies differently along the proton transfer coordinate than that of the excited state. The excited state energy of DT* is 605 $cm^{-1}$ lower than that of the N* form, while the ground state energy of DT* is 4249 $cm^{-1}$ higher than that of N*. More details are shown in Fig. 3.

In conclusion, we have theoretically investigated the hydrogen bonding interactions and ESDPT reaction in the 2A3MOP-AcOH complex. The geometry variations between N form complex in the ground state and in the excited state indicate that both inter-molecular hydrogen bonds get strengthened after photo-excitation. The theoretical method used perfectly reproduced the Stokes shift characters of the N* and DT* emission bands, which proves the reliability of the method used. The PEC scanned along the double proton transfer coordinate indicates that the ESDPT reaction is in a stepwise pattern and the proton in the O1-H2···N3 site has higher transfer priority than the proton in the N4-H5···O6 site. Compared with the model case of a 7-azaindole dimer, the complex studied in the present work is structurally different. The two inter-molecular hydrogen bonding sites are both N-H···N type in the 7-azaindole dimer,[5] while in the 2A3MOP-AcOH complex, the inter-molecular hydrogen bonding sites are of N-H···O and O-H···N types. This difference may result in different dynamics mechanisms. Our calculated results reveal that the hydroxyl group in AcOH has a higher proton-donating ability than the amino group in the excited 2A3MOP. We hope that this study may provide a reference for the ESDPT research in similar cases like 2A3MOP-AcOH complexes.

## References


[1] Crespo-Hernandez C E, Cohen B, Hare P M et al 2004 *Chem. Rev.* **104** 1977
[2] Beens H, Grellman K, Gurr M et al 1965 *Discuss. Faraday Soc.* **39** 183
[3] Demchenko A P, Tang K C and Chou P T 2013 *Chem. Soc. Rev.* **42** 1379
[4] Zhao G J and Han K L 2012 *Acc. Chem. Res.* **45** 404
[5] Sekiya H and Sakota K 2008 *J. Photochem. Photobiol.* C **9** 81
[6] Kitamura T, Mochida N, Okita M et al 2007 *Spectrochim. Acta Part.* A **68** 979
[7] Frisch M J, Trucks G W, Schlegel H B et al 2016 *Gaussian 16, Revision A. 03, Gaussian, Inc., Wallingford CT*
[8] Kohn W, Becke A D and Parr R G 1996 *J. Phys. Chem.* **100** 12974
[9] Marques M A L and Gross E K U 2004 *Annu. Rev. Phys. Chem.* **55** 427
[10] Yanai T, Tew D P and Handy N C 2004 *Chem. Phys. Lett.* **393** 51