

Manuscript Details

Manuscript number	CHEMPHYS_2018_272_R1
Title	Comparison of Internal Conversion Dynamics of Azo and Azoxy Energetic Moieties through the (S1/S0)CI Conical Intersection: Ab Initio Multiple Spawning Study
Article type	Full length article

Abstract

To compare the ultrafast internal conversion process of azo and azoxy-based energetic molecules from the first singlet electronically excited state, we have explored the nonadiabatic chemical dynamics of trans-azomethane (abbreviated as AM) and trans-azoxymethane (abbreviated as AOM) using ab initio multiple spawning (abbreviated as AIMS) simulation and complete active space self-consistent field (abbreviated as CASSCF) theory. A trans-to-cis isomerization around the N=N bond and a pyramidalization of the N(O)=N moiety are predicted to be involved in the internal conversion process of AM and AOM molecules, respectively. AIMS-based simulation reveals that electronically excited AM and AOM molecules undergo extremely fast (approximately in 125 femtoseconds for AM and 64 femtosecond for AOM) relaxation to the ground state via the conical intersection between the S1 and the S0 States (abbreviated as (S1/S0)CI).

Keywords (1) ab initio multiple spawning; (2) trans-azomethane and trans-azoxymethane; (3) Internal conversion through (S1/S0)CI conical intersection. (4) Complete active space self-consistent field theory. (5) electronic excitation of energetic molecules.

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Suggested reviewers	Lluís Blancafort, Elena Jakubikova, Elliot Bernstein, Michael Bearpark, Todd Martinez

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From
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To
The Editor
Professor Tianquan Lian
Chemical Physics
E-mail:

Sub: *CHEMPHYS_2018_272, response to your communication dated 13th May-2018*

Dear Professor Tianquan Lian,

Thank you very much for giving us another opportunity to revise our manuscript. We thank all three reviewers for their constructive comments to improve our manuscript. We have made changes in the revised version of our manuscript according to their suggestions and comments. Detailed changes and responses to referees' concerns are listed below.

Reviewer #1 (Comments to the Author):

(1) This could be an interesting theoretical work, but unfortunately, authors are apparently not aware that photophysics of these systems (AM, in particular) were *ab initio* investigated years ago (cf. J. Chem. Phys. 1996, 105, 2333 and ChemPhysChem 2003, 4, 445, for instance). These works investigated not only isomerization of the compound which determines internal conversion rate, but also dissociation into molecular fragments which determines its explosive nature. Moreover, to latter work measures dissociation dynamics of AM upon excitation within the lowest singlet state. It has been found that the two C-N bonds break in a stepwise manner within ca. 70fs and 100fs, respectively. The paper is not recommended for publication in Chem. Phys. in the present form. Authors have to refer to previous works on these compounds and in particular they have to discuss the estimated time of 125 fs to reach the CI-S1/S0 with observation of dissociation that occurs on a shorter time-scale.

Internal conversion dynamics of the AM molecule from the $S_1(n\pi^*)$ electronically excited state to the ground electronic state has attracted immense attention for a long time because this molecule undergoes dissociation (which yields N_2 and CH_3 products) on the ground potential energy surface immediately following the internal conversion. Furthermore, dissociation mechanism of this molecule has raised several controversial questions, including involvement of concerted or step-wise process. The timescale for the internal conversion from the $S_1(n\pi^*)$ excited state to the ground S_0 state of AM was experimentally observed to be 70 ± 10 fs. The same is predicted to be 125 fs from our present AIMS simulation at the SA-CASSCF(6,4)/6-31G(d) level of theory. This is why we believe that our AIMS-predicted internal conversion time scale is in close agreement with that observed experimentally. Furthermore, our AIMS-predicted internal

conversion time scale is in better agreement with the experimental result than recent surface-hopping results which predict 200 fs for the same. In the present work, we must note that our primary motivation is not to explore the dissociation dynamics of the trans-azomethane molecule following the internal conversion to the ground electronic state; rather, we are only interested in the internal conversion dynamics of the trans-azomethane molecule and its comparison with that of structurally similar trans-azoxymethane molecule.

To clarify this point in the revised version of the manuscript, we add following paragraphs at page 8:

“Internal conversion dynamics of the AM molecule from the $S_1(n\pi^*)$ electronically excited state to the ground electronic state has attracted immense attention for a long time because this molecule undergoes dissociation (which yields N_2 and CH_3 products) on the ground potential energy surface immediately following the internal conversion.[17-30] Furthermore, dissociation mechanism of this molecule has raised several controversial questions, including involvement of concerted or step-wise process. The timescale for the internal conversion from the $S_1(n\pi^*)$ excited state to the ground S_0 state of AM was experimentally observed to be 70 ± 10 fs.[17] The same is predicted to be 125 fs from our present AIMS simulation at the SA-CASSCF(6,4)/6-31G(d) level of theory. This is why we believe that our AIMS-predicted internal conversion time scale is in close agreement with that observed experimentally. Furthermore, our AIMS-predicted internal conversion time scale is better agreement with the experimental result than recent surface-hopping results which predict 200 fs for the same.[28]

In the present work, we must note that our primary motivation is not to explore the dissociation dynamics of the trans-azomethane molecule following the internal conversion to the ground electronic state; rather, we are only interested in the internal conversion dynamics of the trans-azomethane molecule and its comparison with that of structurally similar trans-azoxymethane molecule.”

In addition, we add following references in the revised version of the manuscript:

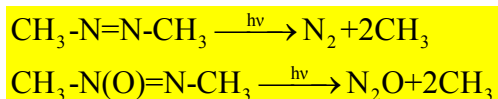
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28. B. Sellner, M. Ruckebauer, I. Stambolic, M. Barbatti, A. J. A. Aquino, and H. Lischka, “Photodynamics of Azomethane: A Nonadiabatic Surface-Hopping Study”, *J. Phys. Chem. A* **114** (2010) 8778–8785.
29. P. Cattaneo and M. Persico, “Semiclassical Simulations of Azomethane Photochemistry in the Gas Phase and in Solution” *J. Am. Chem. Soc.* **123** (2001) 7638-7645.
30. P. G. Szalay, A. J.A. Aquino, M. Barbatti and H. Lischka, “Theoretical study of the excitation spectrum of azomethane” *Chemical Physics* **380** (2011) 9–16

Furthermore, we add following paragraphs at page 6 of revised version of the manuscript:

“It is already mentioned earlier that in the present work we are only interested in a comparative study of the internal conversion dynamics of AM and AOM molecules through the respective (S₁/S₀)_{CI} conical intersection. However, to comment on the possible C-N bond cleavage of the AM and AOM molecules (and N-O bond cleavage of the AOM molecule) during the internal conversion through the respective (S₁/S₀)_{CI} conical intersection, we have monitored time-evolution of the respective bond length during simulation. Figure 7(a) shows no significant elongation of the C-N bond length during the relaxation process of the AM molecule from the S₁ excited state to the S₀ excited state. Similar observation is also evident in Figure 7(b) for the AOM molecule. In addition, Figure 7(b) also exhibits that the N-O bond does not undergo significant elongation during the internal conversion process of the AOM molecule.

Photophysics and photochemistry AM [17-30] and AOM [16] molecules have attracted interest of scientific community for a long time. Several literature reports support that both AM and AOM molecules, following photoexcitation to the low-lying electronically excited states, undergo dissociation. Following photodissociation mechanisms for the AM and AOM molecules are proposed:



Quite interestingly, we have not observed any substantial elongation of the C-N bond during the internal conversion process of the AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection. Therefore, we believe that both AM and AOM molecules do not dissociate during the internal conversion process. This leads us to conclude that dissociation of these molecules occurs only on the ground potential energy surface following the internal conversion. In fact, similar conclusion also was experimentally drawn by Zewail and co-workers for the AM molecule.[17,27] They concluded that dissociation of the AM molecule occurs only on the ground state following internal conversion through the $(S_1/S_0)_{CI}$ conical intersection. However, the appearance of the CH_3N_2 fragment in 70 fs after the photoexcitation in Zewail and co-workers' experiment is not supported by our AIMS simulation. Present AIMS simulation predicts 125 fs time scale for the internal conversion of the AM molecule. AIMS simulation further predicts that this internal conversion does not cause any C-N bond dissociation. Therefore, our AIMS simulation infers that dissociation of the AM molecule should take much longer than 125 fs. The contrast between the time scale of the dissociation obtained from Zewail and co-workers' experiment and our AIMS-predicted time scale as well as previous surface-hopping results suggest that further study is undoubtedly required to resolve existing theory-experiment disagreement."

Minor points:

1. What is the reason of lengthy discussion of explosives in the Introduction if only the photophysical process of internal conversion of an electronic excitation is investigated?

Following reviewer's suggestions, we have removed following paragraph from the Introduction section:

"Energetic materials (explosives) are controllable storage systems of usable chemical energy. In order to maximize release of the stored chemical energy in the most efficient and useful manner, and to design new energetic materials, very initial steps of the energy release mechanisms and dynamics for these systems should be understood. The process of understanding the initial steps of energy release process of energetic materials must begin with an exploration of their unimolecular behavior. Such detailed information at the microscopic level may be used directly or as input for molecular dynamics simulations to gain insight for condensed phase processes. If certain key unimolecular steps can be identified, one can, in principle, make a material less or more sensitive or "energetic" by some chemical modification that raises or lowers the activation energy barriers for these steps."

2. First few paragraphs of Discussion and Conclusions Section have to be skipped.

According the reviewer's suggestion, we have removed following two paragraphs from the Discussion and Conclusions section:

"Our primitive thinking of internal conversion between different electronic states was primarily dominated by the application of Fermi's golden rule (equation (1)): [9] the rate of internal conversion from the S_1 to the S_0 state is expressed as

$$k_{IC}(S_1 \rightarrow S_0) = \frac{2\pi}{\hbar} \sum |V_{if}|^2 \rho(E) \quad (1)$$

Here, i and f refer to the initial and final vibrational Eigen states on the S_1 and the S_0 adiabatic Born-Oppenheimer electronic potential energy surfaces, respectively. The matrix element V_{if} represents the electronic coupling between these adiabatic Born-Oppenheimer states. Finally the density of states of S_0 at the given energy E is denoted by $\rho(E)$.

Fermi's golden rule is valid as long as the coupling between electronic states is fairly weak (because Fermi's golden rule is derived from the perturbation theory).[9] In general, however, it is found that the coupling between electronic states is weak near the Franck-Condon region (in short, the FC region, where the vertical electronic excitation occurs on the multidimensional potential energy surfaces); however, the same can be very strong near the conical intersection region (CI region, where multi-dimensional surfaces cross). When a CI is present, internal conversion process is dominated by geometry near the CI where the coupling between electronic states is strong. This is why quantitative application of the Fermi's golden rule approach to the internal conversion (IC) dynamics becomes questionable when the internal conversion (IC) involves a CI.[16] Furthermore, the form of the nuclear wavefunction and electronic coupling in the CI region can only be poorly approximated by low order expansions around the FC point. This low order expansion of a PES around its FC point is often used to evaluate $|V_{if}|$ in Fermi's golden rule and this is why quantitative application of the Fermi's golden rule approach to the internal conversion dynamics becomes also difficult. In this regard, detailed electronically nonadiabatic theory (which includes nonadiabatic coupling terms) is more appropriate to describe the internal conversion processes. This is well-argued in recent literature by Martinez.[16]"

3. Why discussing the Fermi's Golden Rule which is not applicable here. This also concerns eq.(2) and properties of CI. This is a research paper, not a text-book. By the way, Eigen is the name of German scientist, not the "eigenstate".

According to the reviewer's suggestion, we have removed following paragraphs:

"Our primitive thinking of internal conversion between different electronic states was primarily dominated by the application of Fermi's golden rule (equation (1));[9] the rate of internal conversion from the S_1 to the S_0 state is expressed as

$$k_{IC}(S_1 \rightarrow S_0) = \frac{2\pi}{\hbar} \sum |V_{if}|^2 \rho(E) \quad (1)$$

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4. "Explosive" references have to be replaced by photophysical and photochemical ones.

We want to take the liberty of retaining explosive references here. Our motivation of working on azo and azoxy molecules comes from our interest in finding molecule basis of explosive property. To clarify this point, however, we have included all photophysical and photochemical references pertaining to azo and azoxy molecules. Please see above.

Reviewer #2 (Comments to the Author):

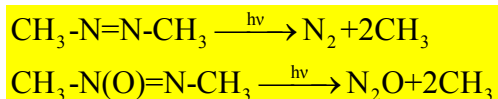
The multiple spawning nonadiabatic dynamics has been performed for studying ultrafast internal conversion process of trans-azomethane (AM) and trans-azoxymethane (AOM) molecules at SA-CASSCF level of theory. However, little information for the photochemical mechanisms of AM and AOM are properly discussed. The manuscript more or less looks like data collection. Even some conventional discussion for static electronic structure and dynamic simulation are missing. I would say that results are interest, but the writing is terrible. It is not acceptable to be published in Chemical Physics in the present form.

We have carefully rewritten our manuscript to make it suitable for Chemical Physics. In the revised version of the manuscript, we have compared and contrasted our results with previous studies. In order to improve the quality of the discussion we have included following paragraphs at page 6 of the revised version of the manuscript:

"It is already mentioned earlier that in the present work we are only interested in a comparative study of the internal conversion dynamics of AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection. However, to comment on the possible C-N bond cleavage of the AM and AOM molecules (and N-O bond cleavage of the AOM molecule) during

the internal conversion through the respective $(S_1/S_0)_{CI}$ conical intersection, we have monitored time-evolution of the respective bond length during simulation. Figure 7(a) shows no significant elongation of the C-N bond length during the relaxation process of the AM molecule from the S_1 excited state to the S_0 excited state. Similar observation is also evident in Figure 7(b) for the AOM molecule. In addition, Figure 7(b) also exhibits that the N-O bond does not undergo significant elongation during the internal conversion process of the AOM molecule.

Photophysics and photochemistry AM [17-30] and AOM [16] molecules have attracted interest of scientific community for a long time. Several literature reports support that both AM and AOM molecules, following photoexcitation to the low-lying electronically excited states, undergo dissociation. Following photodissociation mechanisms for the AM and AOM molecules are proposed:



Quite interestingly, we have not observed any substantial elongation of the C-N bond during the internal conversion process of the AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection. Therefore, we believe that both AM and AOM molecules do not dissociate during the internal conversion process. This leads us to conclude that dissociation of these molecules occurs only on the ground potential energy surface following the internal conversion. In fact, similar conclusion also was experimentally drawn by Zewail and co-workers for the AM molecule.[17,27] They concluded that dissociation of the AM molecule occurs only on the ground state following internal conversion through the $(S_1/S_0)_{CI}$ conical intersection. However, the appearance of the CH_3N_2 fragment in 70 fs after the photoexcitation in Zewail and co-workers' experiment is not supported by our AIMS simulation. Present AIMS simulation predicts 125 fs time scale for the internal conversion of the AM molecule. AIMS simulation further predicts that this internal conversion does not cause any C-N bond dissociation. Therefore, our AIMS simulation infers that dissociation of the AM molecule should take much longer than 125 fs. The contrast between the time scale of the dissociation obtained from Zewail and co-workers' experiment and our AIMS-predicted time scale as well as previous surface-hopping results suggest that further study is undoubtedly required to resolve existing theory-experiment disagreement.”

In addition, we have included following paragraphs at page 8 of the revised version of the manuscript:

“Internal conversion dynamics of the AM molecule from the $S_1(n\pi^*)$ electronically excited state to the ground electronic state has attracted immense attention for a long time because this molecule undergoes dissociation (which yields N_2 and CH_3 products) on the ground potential energy surface immediately following the internal conversion.[17-30] Furthermore, dissociation mechanism of this molecule has raised several controversial questions, including involvement of concerted or step-wise process. The timescale for the internal conversion from the $S_1(n\pi^*)$ excited state to the ground S_0 state of AM was experimentally observed to be 70 ± 10 fs.[17] The same is predicted to be 125 fs from our present AIMS simulation at the SA-CASSCF(6,4)/6-31G(d) level of theory. This is why we believe that our AIMS-predicted internal conversion time scale is in close agreement with that observed experimentally. Furthermore, our

AIMS-predicted internal conversion time scale is better agreement with the experimental result than recent surface-hopping results which predict 200 fs for the same.[28]

In the present work, we must note that our primary motivation is not to explore the dissociation dynamics of the trans-azomethane molecule following the internal conversion to the ground electronic state; rather, we are only interested in the internal conversion dynamics of the trans-azomethane molecule and its comparison with that of structurally similar trans-azoxymethane molecule.”

We hope that the reviewer will like the presentation after incorporating all the changes mentioned above.

Reviewer #3 (Comments to the Author):

This manuscript presents a theoretical study of the photophysics of azomethane and azoxymethane. These molecules are of interest as explosives. In the simulations, both decay in an ultrafast fashion to the ground state, and the main point of interest is that while azomethane shows a tendency to carry out cis-trans isomerization, azoxymethane does not. The photophysics of azomethane has been studied previously with very similar approaches as here and the current results do not provide any new insight on this molecule, but the comparison with azoxymethane is actually quite interesting and, overall, the results are potentially of interest for Chem. Phys. However, the manuscript in its present form is not ready for publication. In particular, points 1 and 2 below should be carefully considered in order to clarify the main point(s) of interest of this contribution. The experimental and theoretical literature should also be referenced properly. Therefore, a thorough revision and further review is required. See points below.

We thank the reviewer for the suggestions. We have thoroughly revised the manuscript. Details are given below.

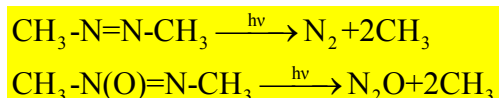
Main points:

(1) Azomethane photodynamics has been studied previously with AIMS (Ref. 15) and with trajectory surface hopping (see 10.1021/jp101745t), see also the optimized CI structure described in JCP1996, vol. 105, p. 2333. However, this is not acknowledged properly. The results of Ref. 15 are only mentioned in the results section, and the other studies are not mentioned at all. My recommendation is to follow common practice and dedicate a few paragraphs in the introduction to comment on the results of the literature, and then compare them with the current ones in the results and discussions sections. This will provide the right perspective on the value of the present contribution.

We have carefully included the all other studies on trans-azomethane (AM) in the revised version of the manuscript. In order to address the issues raised by the reviewer, following paragraphs are included at page 6 of the revised versions of the manuscript:

“It is already mentioned earlier that in the present work we are only interested in a comparative study of the internal conversion dynamics of AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection. However, to comment on the possible C-N bond cleavage of the AM and AOM molecules (and N-O bond cleavage of the AOM molecule) during the internal conversion through the respective $(S_1/S_0)_{CI}$ conical intersection, we have monitored time-evolution of the respective bond length during simulation. Figure 7(a) shows no significant elongation of the C-N bond length during the relaxation process of the AM molecule from the S_1 excited state to the S_0 excited state. Similar observation is also evident in Figure 7(b) for the AOM molecule. In addition, Figure 7(b) also exhibits that the N-O bond does not undergo significant elongation during the internal conversion process of the AOM molecule.

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In addition, following references are added to the revised version of the manuscript:

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30. P. G. Szalay, A. J.A. Aquino, M. Barbatti and H. Lischka, "Theoretical study of the excitation spectrum of azomethane" *Chemical Physics* **380** (2011) 9–16

(2) In this context, the authors should be aware that the main point of interest of their manuscript is the comparison between azomethane and azoxymethane, since the results for azomethane are very similar to the previously published ones.

We thank the review for giving emphasis on an important point of our present contribution. In order to do the same in the revised version of the manuscript we add following at page 8:

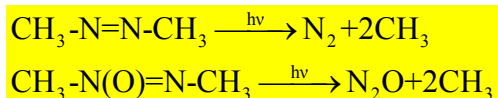
"In the present work, we must note that our primary motivation is not to explore the dissociation dynamics of the trans-azomethane molecule following the internal conversion to the ground electronic state; rather, we are only interested in the internal conversion dynamics of the trans-azomethane molecule and its comparison with that of structurally similar trans-azoxymethane molecule.."

(2a) The author start the introduction discussing energetic materials, but it is not clear why the current results should be relevant for the 'energetic' character of these molecules. For instance, azoalkanes seem to decompose photochemically but for both molecules no decomposition is seen in the simulations, can the authors discuss this point?

According to the first reviewer we have removed rigorous discussion on energetic material from Introduction. In addition, we add following paragraph at page 6 of the revised version of the manuscript:

"It is already mentioned earlier that in the present work we are only interested in a comparative study of the internal conversion dynamics of AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection. However, to comment on the possible C-N bond cleavage of the AM and AOM molecules (and N-O bond cleavage of the AOM molecule) during the internal conversion through the respective $(S_1/S_0)_{CI}$ conical intersection, we have monitored time-evolution of the respective bond length during simulation. Figure 7(a) shows no significant elongation of the C-N bond length during the relaxation process of the AM molecule from the S_1 excited state to the S_0 excited state. Similar observation is also evident in Figure 7(b) for the AOM molecule. In addition, Figure 7(b) also exhibits that the N-O bond does not undergo significant elongation during the internal conversion process of the AOM molecule.

Photophysics and photochemistry AM [17-30] and AOM [16] molecules have attracted interest of scientific community for a long time. Several literature reports support that both AM and AOM molecules, following photoexcitation to the low-lying electronically excited states, undergo dissociation. Following photodissociation mechanisms for the AM and AOM molecules are proposed:



Quite interestingly, we have not observed any substantial elongation of the C-N bond during the internal conversion process of the AM and AOM molecules through the respective (S_1/S_0)_{CI} conical intersection. Therefore, we believe that both AM and AOM molecules do not dissociate during the internal conversion process. This leads us to conclude that dissociation of these molecules occurs only on the ground potential energy surface following the internal conversion. In fact, similar conclusion also was experimentally drawn by Zewail and co-workers for the AM molecule.[17,27] They concluded that dissociation of the AM molecule occurs only on the ground state following internal conversion through the (S_1/S_0)_{CI} conical intersection. However, the appearance of the CH_3N_2 fragment in 70 fs after the photoexcitation in Zewail and co-workers' experiment is not supported by our AIMS simulation. Present AIMS simulation predicts 125 fs time scale for the internal conversion of the AM molecule. AIMS simulation further predicts that this internal conversion does not cause any C-N bond dissociation. Therefore, our AIMS simulation infers that dissociation of the AM molecule should take much longer than 125 fs. The contrast between the time scale of the dissociation obtained from Zewail and co-workers' experiment and our AIMS-predicted time scale as well as previous surface-hopping results suggest that further study is undoubtedly required to resolve existing theory-experiment disagreement..”

(2b) The authors should also discuss what experimental results are explained by their simulations. They only mention a review on the photochemistry of azoalkanes, but they should provide more details.

In order to clarify this point we add following paragraph at page 8:

“Internal conversion dynamics of the AM molecule from the $S_1(n\pi^*)$ electronically excited state to the ground electronic state has attracted immense attention for a long time because this molecule undergoes dissociation (which yields N_2 and CH_3 products) on the ground potential energy surface immediately following the internal conversion.[17-30] Furthermore, dissociation mechanism of this molecule has raised several controversial questions, including involvement of concerted or step-wise process. The timescale for the internal conversion from the $S_1(n\pi^*)$ excited state to the ground S_0 state of AM was experimentally observed to be 70 ± 10 fs.[17] The same is predicted to be 125 fs from our present AIMS simulation at the SA-CASSCF(6,4)/6-31G(d) level of theory. This is why we believe that our AIMS-predicted internal conversion time scale is in close agreement with that observed experimentally. Furthermore, our AIMS-predicted internal conversion time scale is better agreement with the experimental result than recent surface-hopping results which predict 200 fs for the same.[28]”

(2c) Related with this, the authors compare the calculated vertical excitation for AM with a literature value. Here the specific reference (and not a review) should be given. A similar comparison with AOM should be given to assess the quality of the level of theory for this molecule (look up Gowenlock, Can. J. Chem. 1964, vol. 42, p. 1936).

According to the reviewer's suggestions, we have include correct references to the vertical excitation energies for AM molecules. [Please see page 10:](#)

"14. (a) S. S. Collier, D. H. Slater, and J. G. Calvert, "THE PHOTOCHEMISTRY OF THE AZOALKANES", Photochem. Photobiol. 7 (1968) 737; (b) M. B. Robin, B. R. Hart, and N. A. Kuebler, "Electronic States of the Azoalkanes", J. Am. Chem. Soc. 89 (1967) 1564; (c) P. S. Engel, *Mechanism of the Thermal and Photochemical Decomposition of Azoalkanes*. Chem. Rev. 80 (1980) 99–150.."

In addition, we have carefully checked the reference Gowenlock, Can. J. Chem. 1964, vol. 42, p. 1936; however, we could not find any vertical excitation information in this article. After even an exhaustive literature search, we could not find any reference related to the experimental vertical excitation energy of the AOM molecule.

[To clarify this point we add following lines at page 5 in the revised version of the manuscript:](#)

"To the best of our knowledge, thus far, no literature is reported on the experimental vertical excitation energy for the $S_1(n,\pi^*)$ excited state of the AOM molecule. This is why it is impossible to validate the (6,4) active space for the AOM molecule by comparing theoretical results with the experimental ones. For the AOM molecule, however, we argue that observation of very similar vertical excitation energies computed at all levels of theory (CASSCF and CASPT2 with different basis sets) with the (6,4) active space validates appropriateness of this active space for the present CASSCF-computation of the AOM molecules.."

(3) In the General Discussion and Conclusions section, the authors discuss the differences between Fermi's golden rule for internal conversion and conical intersections. This discussion can be found in a large number of reviews and books and is therefore unnecessary here. A brief mention in the introduction should be enough. The same can be said about the description of the g and h vectors.

According to the reviewer's suggestion, we have removed long discussion on Fermi's golden rule and g-h vectors in the revised version of the manuscript.

(4) The authors state that the CI for AM is of peaked type, whereas simple visual inspection does not allow them to determine the local topography of the CI for AOM. However, the local topography can be easily determined mathematically by calculating the projection of the state

gradients along the g and h coordinates, see eg: Yarkony, "Conical intersections: their description and consequences" in: Conical Intersections. Adv. Series in Physical Chemistry Vol. 15, edited by Domcke, Yarkony, Köppel, World Scientific 2004; Atchity et al, JCP 1991, vol. 95, p. 1862; Sicilia et al, TCA 2007, vol 118, p. 241. I recommend to carry out this type of characterization.

We thank the reviewer to point this out to us. We shall definitely write computer code to perform the suggested analysis in future. However, in the present work, we have only presented g - h planes for AM and AOM molecules without mathematical analysis.

To clarify this point we add following at page 7 of the revised version of the manuscript:

“Here we note that the nature of the local topography (whether peak or slope type) can be determined mathematically by calculating the projection of the state gradients along the \vec{g} and \vec{h} coordinates, as proposed by Yarkoni, Bearpark, Atchity and Others.[31] In the present work, we have not performed such mathematical analysis..”

(5) The authors state at the beginning of the Computational Methods section that in their approach, the time evolution of the nuclei is modelled classically. However they are using AIMS, where the nuclei are not treated classically, but the nuclear wave packet is described with frozen Gaussians (as stated correctly in the following paragraph). Please correct this inconsistency.

The centre of each Gaussian follows classical equation of motion.

We have clarified this point at page 3 of revised version of the manuscript.

We hope that we have addressed all the issues raised by the reviewers. If any other information is required, please let us know.

Regards,

Atanu Bhattacharya

Comparison of Internal Conversion Dynamics of Azo and Azoxy Energetic Moieties through the (S_1/S_0)_{CI} Conical Intersection: Ab Initio Multiple Spawning Study

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Abstract:

To compare the ultrafast internal conversion process of azo and azoxy-based energetic molecules from the first singlet electronically excited state, we have explored the nonadiabatic chemical dynamics of trans-azomethane (abbreviated as AM) and trans-azoxymethane (abbreviated as AOM) using *ab initio* multiple spawning (abbreviated as AIMS) simulation and complete active space self-consistent field (abbreviated as CASSCF) theory. A trans-to-cis isomerization around the N=N bond and a pyramidalization of the N(O)=N moiety are predicted to be involved in the internal conversion process of AM and AOM molecules, respectively. AIMS-based simulation reveals that electronically excited AM and AOM molecules undergo extremely fast (approximately in 125 femtoseconds for AM and 64 femtosecond for AOM) relaxation to the ground state via the conical intersection between the S_1 and the S_0 States (abbreviated as (S_1/S_0)_{CI}).

Introduction:

The energy release process of energetic materials can be initiated with a shock/compression wave, spark, or laser ignition. About a decade ago, Bernstein argued that such events generate molecules in the excited electronic states. Details of this argument with recent literature support are given elsewhere by us.[1] Therefore, it is speculative that specific topography of the excited electronic potential energy surfaces (PESs) will determine and control the relaxation steps for the electronically excited energetic molecules. In particular, conical intersections, which arise due to the crossing of multidimensional electronic potential energy surfaces (PESs) and due to breakdown of the Born-Oppenheimer approximation, may play an important role in the initial relaxation step of energetic molecules following electronic excitation.[1-6] One of the most important consequences of the presence of conical intersections is to allow extremely fast and efficient relaxation of the electronically excited molecules from upper to the lower electronic state. This includes internal conversion (a physicochemical process by which electronically excited molecules are relaxed back to the lower electronic state of the same spin, converting electronic excitation energy to the vibrational energy on the lower potential energy surface). Therefore, understanding internal conversion process of energetic moieties through the conical intersections between the first electronically excited singlet state S_1 and the ground singlet state S_0 (this conical intersection is referred to as $(S_1/S_0)_{CI}$) is an important pursuit if we want to understand the initial step of energy release mechanisms and dynamics of energetic molecules fundamentally.[1]

The performance of high energy density materials is often judged based on detonation pressure and velocity. Synthetic organic chemists often introduce certain (energetic) functional groups as substituents into candidate compounds to improve detonation properties of energetic molecules by monitoring their detonation pressure and velocities. For a long time, this idea has been a very effective and widely-used method for the synthesis of better energetic materials. Two very frequently-used energetic functional groups include azo and azoxy.[7-8] It has been irrevocably observed that these functional groups efficiently enhance detonation performance of the candidate molecules. Hence, one obvious question arises: what is the mechanisms and dynamics of the internal conversion process of azo and azoxy energetic functional groups? The present article is focused on this question.

In our Chemical Dynamics Lab at the Indian Institute of Science, for last few years, we have been using multi-configuration-based methodologies coupled with *ab initio* multiple spawning (AIMS) method to explore the internal conversion of electronically excited energetic molecules through the conical intersections. Our primary motivation in this effort is to explore the correlation between the nature of the internal conversion of energetic molecules (which is the initial step of the relaxation process of energetic molecules following electronic excitation) and functional group-based superior performance of energetic moieties. Continuing with this theme of research, in the present contribution, we have explored compared and contrasted internal conversion process of trans-azomethane (AM) and trans-azoxymethane (AOM). These two molecules contain azo ($-N=N-$) and azoxy ($-N(O)=N-$) energetic groups, respectively (see Figure 1 for chemical structure). We have selected these two model systems with an expectation that these two molecules would unravel salient features of the internal conversion process for azo and azoxy energetic moieties through the $(S_1/S_0)_{CI}$ conical intersection.

Computational Methods

We have used complete active space self-consistent field (abbreviated as CASSCF) wavefunction to perform mixed quantum-classical *ab initio* molecular dynamics (abbreviated as AIMD). In this method, the time evolution of an electronically excited system (nuclei) is modeled classically, while the energies of the relevant electronic states are computed “on the fly” using *ab initio* quantum mechanical (QM) method. In CASSCF theory, the time-independent electronic states (ground or electronically excited) are described using linear combination of Configuration State Functions (abbreviated as CSFs).[9] Each CSF features an antisymmetrized product (Slater determinant) of one electron molecular orbitals (MO). Therefore, in the CASSCF theory, both the configuration mixing coefficients and the MO expansion coefficients are variationally optimized. For the present work, we have used state-average CASSCF (abbreviated as SA-CASSCF) electronic wavefunction to explore the nonadiabatic chemical dynamics of energetic molecules through the (S_1/S_0)_{CI} conical intersection. A SA-CASSCF wavefunction gives equal weights to several roots (several electronic states which are chemically important or nonadiabatically coupled).

We have already stated that electronic part of the total wavefunction is represented by SA-CASSCF wavefunction (which is considered to be time-independent in the present work). For the AIMD simulations, *ab initio* Multiple Spawning (abbreviated as AIMS) method,[10] which was developed by the Martinez group, is used to represent time-dependent nuclear wavefunction. The travelling frozen (with fixed width) Gaussian basis (under frozen Gaussian approximation) is used to expand the nuclear wavefunction. **The centre of each Gaussian follows classical equation of motion.** Details are given elsewhere.[10,11]

Each AIMS simulation starts with a single initial trajectory basis function (TBF). Typically different initial TBFs are created on the excited state surface with the help of different initial conditions. These different initial TBFs are then run independently. In all AIMS simulations, initial positions and momenta are sampled from the Wigner distribution for the ground vibrational state (under harmonic oscillator approximation) on the ground electronic state surface. Although AIMS simulation may start with a single TBF on the upper electronic state (assuming all the population on the upper excited state), unique spawning mechanism of AIMS methodology allows to spawn (generate) new TBF on the lower electronic state surface, if the strength of nonadiabatic coupling (which depends inversely on the energy difference between the coupled electronic states) increases beyond a certain threshold value (CSThresh which is taken as 3.0 a.u. in the present work). This, in turn, transfers population from upper state to the lower state stochastically. It is quite implicit that the nonadiabatic coupling is stronger near conical intersection (where potential energy surfaces cross each other, creating, in principle, degenerate point on the potential energy landscape) than that near the Franck-Condon region (where upper and lower potential energy surfaces energetically stay well-separated). Therefore, spawning occurs primarily near conical intersection region in AIMS simulation. More details of the spawning mechanisms are given in Martinez’s publications.[10,11]

In the present work, the ultrafast nonadiabatic relaxation dynamics of different energetic molecules from the first singlet (S_1) electronically excited state to the S_0 ground states is studied using AIMS module with the SA-CASSCF wavefunction and the 6-31G(d) basis set, as

implemented in Molpro.[12] The simulation time step is set to be 20 atomic unit (or 0.48 femtosecond) for regions far away from conical intersection (regions with $CSThresh < 3.0$ a.u.) and the same changes to 5 atomic unit (or 0.12 femtosecond) for regions near the conical intersection (regions with $CSThresh > 3.0$ a.u., indicating strong nonadiabatic coupling). Furthermore, the active space (which decides the number of the configuration state function involved) used to construct the SA-CASSCF wavefunction for the AM and AOM molecules is shown in Figure 2(a) and (b), respectively. Appropriateness of the selected active space is discussed in the Results and Discussion section.

In addition to the AIMS simulations, the $(S_1/S_0)_{CI}$ minimum energy conical intersection (which is abbreviated as MECI), geometries for the AM and AOM molecules are also optimized with SA-CASSCF wavefunction and 6-31G(d) basis set using the algorithm implemented in Gaussian 09.[13] We shall note that this MECI geometry quite resembles spawned geometries (at these geometries 50% of the upper state population is transferred to the lower state) sampled from the AIMS simulations.

Results and Discussion:

The most stable geometries of AM and AOM (referred to as $S_{0,opt}$), optimized at the CASSCF(6,4)/6-31G(d) level of theory, are illustrated in Figure 3. For both molecules, C-N=N-C and C-N(O)=N-C moieties exhibit planar structure (note the C1N1N2C2 and C1N1O1N2 dihedral angles given in Figure 3). Furthermore, the N=N bond distance does not change significantly upon N-oxide formation.

We have computed the vertical excitation energies of the AM and AOM molecules using the SA-CASSCF theory with different basis sets (6-31G(d), 6-31+G(d,p), 6-311++G(d,p) and aug-cc-pVDZ) as well as including dynamical correlation (CASPT2). Different results are summarized in Table I. This table directly evidences that basis set and dynamical correlation do not play significant role in the present computation. The S_1 state of AM exhibits the vertical excitation energy of 3.95 eV at the SA-CASSCF(6,4)/6-31G(d) level of theory. Furthermore, a good agreement is found between this computed vertical excitation energy for the $S_1(n,\pi^*)$ excited state of AM and the experimental value of 3.6 eV.[14] This excitation energy is also in good agreement with the computed excitation energy of the same molecule which is recently reported by Gordon and co-workers.[15] This comparison of the vertical excitation energies validates appropriateness of the (6,4) active space for the present CASSCF-computations of the AM molecules. Finally, Figure 4 depicts the orbitals involved during the electronic excitation of both the AM molecule. The CSF associated with the highest coefficient shows that the S_1 excited state of AM is of (n,π^*) character. Both nonbonding and π^* orbitals are localized in azo (N=N) group only.

Similar to the AM results, Table I also suggests that both basis set and dynamical correlation do not play important role for the AOM molecule. The vertical excitation energy associated with the S_1 excited state of AOM is computed to be 4.71 eV at the SA-CASSCF(6,4)/6-31G(d) level of theory. At all levels of theory (with different basis sets and including dynamical correlation), we find that AOM exhibits higher (more than 0.5 eV) vertical

excitation energy for the S_1 excited state as compared to that of the AM molecule. In addition, as shown in Figure 4, the S_1 excited state of AOM exhibits an (n,π^*) electronic excitation character; however, in contrary to the AM molecule, the non-bonding orbital in AOM is not localized on the N=N moiety. Rather, it is found to be localized at the O-end of the azoxy moiety. We argue that this causes slightly higher vertical S_1 excitation energy for the AOM molecule than the AM molecule.

To the best of our knowledge, thus far, no literature is reported on the experimental vertical excitation energy for the $S_1(n,\pi^*)$ excited state of the AOM molecule. This is why it is impossible to validate the (6,4) active space for the AOM molecule by comparing theoretical results with the experimental ones. For the AOM molecule, however, we argue that observation of very similar vertical excitation energies computed at all levels of theory (CASSCF and CASPT2 with different basis sets) with the (6,4) active space validates appropriateness of this active space for the present CASSCF-computation of the AOM molecules.

As in the present work, we are only interested in internal conversion of AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection, we directly now turn our attention to the optimized geometry of the respective $(S_1/S_0)_{CI}$ MECI. The optimized geometries of the $(S_1/S_0)_{CI}$ both for the AM and AOM molecules are depicted in Figure 3. The $(S_1/S_0)_{CI}$ geometry of AM exhibits significantly different C1N1N2C2 dihedral angle as compared to its $S_{0,Opt}$ geometry: the C1N1N2C2 dihedral angle is found to be $\sim 94^\circ$ at the optimized conical intersection geometry; whereas the same is found to be $\sim 180^\circ$ at the FC-point (ground state equilibrium geometry) of the S_1 surface. Geometrical transformation from the $S_{0,Opt}$ to the $(S_1/S_0)_{CI}$ suggests that the AM molecule attempts to undergo trans-to-cis isomerization while evolving from the FC point of the S_1 surface to the $(S_1/S_0)_{CI}$. Similar trans-to-cis isomerization has also been predicted for the same molecule recently by Gordon and co-workers.[15]

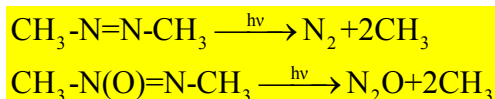
On the contrary, the $(S_1/S_0)_{CI}$ geometry of AOM does not predict any trans-to-cis isomerization. Instead, the -N(O)=N- moiety is found to lose planarity of the moiety at the $(S_1/S_0)_{CI}$ conical intersection (see Figure 3). The C1N1O1N2 dihedral angle is found to be $\sim 119^\circ$ at the optimized conical intersection geometry; whereas, the same is found to be $\sim 180^\circ$ at the FC-point (ground state equilibrium geometry) of the S_1 surface. More details of this geometrical transformation will be evident soon when we shall discuss AIMS results.

We have performed all AIMS simulations which assume entire population on the S_1 excited state. Total 28 and 36 initial conditions are selected for the AM and AOM molecules, respectively. These initial conditions are randomly sampled from the ground state vibrational Wigner distribution calculated under the harmonic oscillator approximation. The scheme is already implemented in AIMS-Molpro module. Figures 5(a) and (b) depict the change of average population of the AM and AOM molecules, respectively, on the respective S_0 ground and the S_1 excited states as a function of the simulation time (expressed in femtoseconds). We find that the quenching of the S_1 excited state population to the ground electronic state for both molecules is extraordinarily fast (occurs in approximately 125 femtoseconds for AM and in approximately 64 femtoseconds for AOM). Our AIMS-predicted internal conversion time scale of AM is in very good agreement with the recent surface-hopping results which predict 200 fs for the same.[28]

Figures 5(a) and (b) also depict snapshots of geometries sampled at two different simulation times: one at zero femtosecond and another at the simulation time when 50% excited state population is quenched. Geometries sampled at zero femtosecond (from Wigner distribution) closely resemble the ground state optimized geometry of the respective molecule. On the other hand, geometries sampled at the simulation time when 50% excited state population is quenched back to the ground state closely resemble the minimum energy $(S_1/S_0)_{CI}$ conical intersection geometry (as depicted in Figure 3 for the respective molecule). Furthermore, AIMS simulation also reveals that a trans-to-cis isomerization mechanism is involved in the internal conversion process of the AM molecule; however, a pyramidalization of the $-N(O)=N-$ azoxy moiety is involved in the internal conversion process of the AOM molecule. These different structural evolutions become clearly evident when we inspect the variation of the average C1N1N2C2 dihedral angle of the AM molecule and the average C1N1N2O1 dihedral angle of the AOM molecule as a function of simulation time (see Figure 6(a) and (b), respectively).

It is already mentioned earlier that in the present work we are only interested in a comparative study of the internal conversion dynamics of AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection. However, to comment on the possible C-N bond cleavage of the AM and AOM molecules (and N-O bond cleavage of the AOM molecule) during the internal conversion through the respective $(S_1/S_0)_{CI}$ conical intersection, we have monitored time-evolution of the respective bond length during simulation. Figure 7(a) shows no significant elongation of the C-N bond length during the relaxation process of the AM molecule from the S_1 excited state to the S_0 excited state. Similar observation is also evident in Figure 7(b) for the AOM molecule. In addition, Figure 7(b) also exhibits that the N-O bond does not undergo significant elongation during the internal conversion process of the AOM molecule.

Photophysics and photochemistry AM [17-30] and AOM [16] molecules have attracted interest of scientific community for a long time. Several literature reports support that both AM and AOM molecules, following photoexcitation to the low-lying electronically excited states, undergo dissociation. Following photodissociation mechanisms for the AM and AOM molecules are proposed:



Quite interestingly, we have not observed any substantial elongation of the C-N bond during the internal conversion process of the AM and AOM molecules through the respective $(S_1/S_0)_{CI}$ conical intersection. Therefore, we believe that both AM and AOM molecules do not dissociate during the internal conversion process. This leads us to conclude that dissociation of these molecules occurs only on the ground potential energy surface following the internal conversion. In fact, similar conclusion also was experimentally drawn by Zewail and co-workers for the AM molecule.[17,27] They concluded that dissociation of the AM molecule occurs only on the ground state following internal conversion through the $(S_1/S_0)_{CI}$ conical intersection. However, the appearance of the CH_3N_2 fragment in 70 fs after the photoexcitation in Zewail and co-workers' experiment is not supported by our AIMS simulation. Present AIMS simulation predicts 125 fs time scale for the internal conversion of the AM molecule. AIMS simulation further predicts that this internal conversion does not cause any C-N bond dissociation. Therefore, our AIMS simulation infers that dissociation of the AM molecule should take much longer than 125 fs. The contrast between the time scale of the dissociation obtained from Zewail

and co-workers' experiment and our AIMS-predicted time scale as well as previous surface-hopping results suggest that further study is undoubtedly required to resolve existing theory-experiment disagreement.

General Discussion and Conclusions:

In general, the internal conversion processes are found to mediate via the conical intersections (CI are also called photochemical funnels). Near the CI, a strong coupling between electronic states completely breaks down the Born-Oppenheimer adiabatic approximation and the dominant term that controls the internal conversion processes near the CI region is the nonadiabatic coupling term. During the internal conversion process, geometry associated with a conical intersection is often found to be related to the expected outcome. Therefore, characterization of chemically relevant minimum energy conical intersection (MECI) serves as an important component in the development of theoretical understanding of the internal conversion process of molecules following electronic excitation.

For polyatomic molecules, two adiabatic electronic states, even with the same symmetry, may intersect and form a conical intersection. Only for diatomic molecules, where there is only one degree of freedom, electronic states with same symmetry do not cross, yielding a non-crossing rule. At a conical intersection, one can distinguish two directions, \vec{g} and \vec{h} such that if one were to plot the energy in the subspace of these two geometric variables (combination of bond lengths, angles, etc.), the potential energy would have the form of a double cone in the region of the degeneracy. The $g-h$ internal coordinates lift the degeneracy linearly near conical intersection. Therefore, $g-h$ plane explores the local topography of the potential energy surface near the conical intersection.

The $g-h$ planes near the CASSCF-optimized $(S_1/S_0)_{CI}$ MECI of AM and AOM are shown in Figure 8. Respective vectors are also shown in the same figure. The \vec{g} vector represents the nuclear gradient of the difference between the energy of the $S_1(n,\pi^*)$ excited state and the energy of the ground state. The \vec{h} vector is, on the other hand, represents the nonadiabatic coupling matrix element (NACME) between the ground state and $S_1(n, \pi^*)$ excited state. Simple visual inspection reveals that the $(S_1/S_0)_{CI}$ conical intersection of AM is a peaked type conical intersection, which leads to the prediction that the internal conversion from the $S_1(n,\pi^*)$ excited state to the ground state should be very fast once a nonadiabatic dynamics simulation approaches this conical intersection geometry. Simple visual inspection, however, does not allow us to determine whether the $(S_1/S_0)_{CI}$ of AOM is peak or slope type. Nonetheless, Figure 8 shows that the branching plane gets affected by N-oxide formation of the azo group and the consequence is evident in faster internal conversion dynamics predicted for AOM as compared to AM. Here we note that the nature of the local topography (whether peak or slope type) can be determined mathematically by calculating the projection of the state gradients along

the \vec{g} and \vec{h} coordinates, as proposed by Yarkoni, Bearpark, Atchity and Others.[31] In the present work, we have not performed such mathematical analysis.

Internal conversion dynamics of the AM molecule from the $S_1(n\pi^*)$ electronically excited state to the ground electronic state has attracted immense attention for a long time because this molecule undergoes dissociation (which yields N_2 and CH_3 products) on the ground potential energy surface immediately following the internal conversion.[17-30] Furthermore, dissociation mechanism of this molecule has raised several controversial questions, including involvement of concerted or step-wise process. The timescale for the internal conversion from the $S_1(n\pi^*)$ excited state to the ground S_0 state of AM was experimentally observed to be 70 ± 10 fs.[17] The same is predicted to be 125 fs from our present AIMS simulation at the SA-CASSCF(6,4)/6-31G(d) level of theory. This is why we believe that our AIMS-predicted internal conversion time scale is in close agreement with that observed experimentally. Furthermore, our AIMS-predicted internal conversion time scale is better agreement with the experimental result than recent surface-hopping results which predict 200 fs for the same.[28]

In the present work, we must note that our primary motivation is not to explore the dissociation dynamics of the trans-azomethane molecule following the internal conversion to the ground electronic state; rather, we are only interested in the internal conversion dynamics of the trans-azomethane molecule and its comparison with that of structurally similar trans-azoxymethane molecule.

The AIMS-simulated lifetime of the $S_1(n,\pi^*)$ excited state of AM and AOM was found to be ~ 125 and 64 femtoseconds, respectively. No evidence was found for elimination of CH_3 (for both molecules or O elimination for azoxy molecule) on the excited state surface at the CASSCF(6,4)/6-31G(d) level of theory. A trans-to-cis isomerization is observed for the azo group and an out-of-plane bending of the $-N(O)=N-$ group (leading to pyramidalization of this moiety) is observed for the azoxy group during the internal conversion process.

Photoinduced trans-to-cis isomerization about $C=C$ bond represents one of the well-studied mechanisms for converting light energy into mechanical motion on a molecular scale.[32] Similar trans-to-cis photoinduced isomerization is exhibited by $N=N$ bond; however, upon N-oxide formation, this photophysical mechanism is changed to pyramidalization of the $N(O)=N$ moiety. Thus, in this present work, for the first time, we used *ab initio* multiple spawning (AIMS) methodology with complete active space self-consistent field theory to compare and contrast similarities and differences of the internal conversion process of azo and azoxy energetic groups.

Acknowledgements

We thank Prof. Todd Martinez (Stanford University) for helping us understand different aspects of AIMS theory and its interpretation in Molpro. We thank Dr. Sai G. Ramesh for selflessly maintaining departmental computational cluster facility. All computations were performed in this computational cluster facility.

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Table I: Vertical excitation energies and energies associated with the minimum energy $(S_1/S_0)_{CI}$ conical intersection (MECI) of trans-azomethane (AM) and trans-azoxymethane (AOM), as computed at the CASSCF(6,4)/6-31G(d), CASSCF(6,4)/6-31+G(d,p), CASSCF(6,4)/6-311++G(d,p), CASSCF(6,4)/aug-cc-pVDZ, and CASPT2(6,4)/6-31G(d) levels of theory. Relative energies (in eV) are calculated with respect to the S_0 FC point of the respective molecule.

Molecule	FC point or $(S_1/S_0)_{CI}$ MECI	Relative Energy (eV) with respect to the S_0 minimum				
		CASSCF(6,4)/ 6-31G(d)	CASSCF(6,4)/ 6-31+G(d,p)	CASSCF(6,4)/ 6-311++G(d,p)	CASSCF(6,4)/ aug-cc-pVDZ	CASPT2(6,4)/ 6-31G(d)
AM	$S_{1,FC}$	3.95	3.99	3.98	4.02	3.39
	$(S_1/S_0)_{CI}$	3.10	3.15	3.13	3.16	2.90
AOM	$S_{1,FC}$	4.71	4.74	4.74	4.78	4.82
	$(S_1/S_0)_{CI}$	3.38	3.39	3.46	3.74	3.72

Figure 1: Chemical Structure of *trans*-azomethane (AM, left figure) and *trans*-azoxymethane (AOM, right figure).

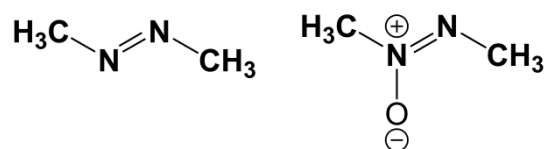
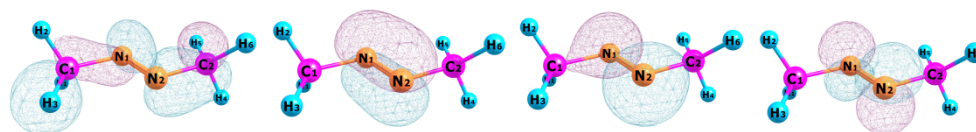


Figure 2: Orbitals used in the (6,4) active space of (a) AM and (b) AOM for the SA-CASSCF/6-31G(d) computations. These orbitals were obtained after optimizing the ground state geometry at the same SA-CASSCF/6-31G(d) level of theory.

(a) Active space of trans-Azomethane: @ CASSCF(6,4)/6-31G(d)



(b) Active space of trans-Azoxymethane : @ CASSCF(6,4)/6-31G(d)

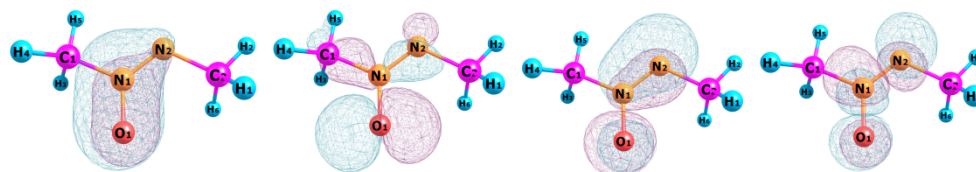


Figure 3: Optimized geometries of AM and AOM at different critical points (ground state equilibrium geometry ($S_{0,Opt}$) and the $(S_1/S_0)_{CI}$ conical intersection geometry), obtained at the CASSCF(6,4)/6-31G(d) level of theory. Bond distances are given in Å. Bond angles and dihedral angles are given in degree.

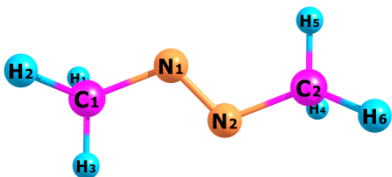
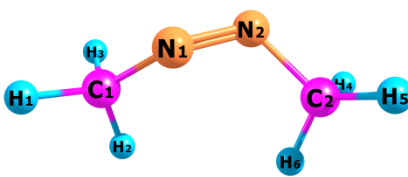
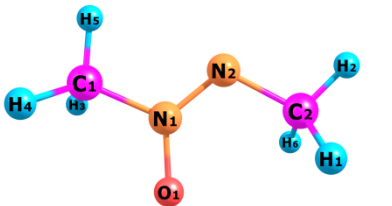
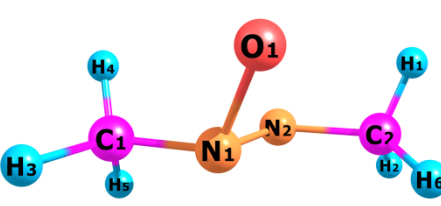
Molecules	$S_{0,Opt}$	$(S_1/S_0)_{CI}$
trans-Azomethane (AM)	 <p>C1-N1= 1.455, N1-N2= 1.237 N2-C2= 1.456, C1-N1-N2= 113.13, N1-N2-C2= 113.10, C1-N1-N2-C2= 179.93</p>	 <p>C1-N1= 1.433, N1-N2= 1.278 N2-C2= 1.462, C1-N1-N2=130.922, N1-N2-C2= 114.79, C1-N1-N2-C2= 94.172</p>
trans-Azoxymethane (AOM)	 <p>C1-N1= 1.465, N1-N2= 1.256, N1-O1= 1.231, N2-C2= 1.449, C1-N1-N2= 117.02, N1-N2-C2= 112.90, C1-N1-O1= 116.42, C1-N1-N2-C2= 180.00, C1-N1-O1-N2= 179.99</p>	 <p>C1-N1= 1.452, N1-N2= 1.335, N1-O1= 1.419, N2-C2= 1.456, C1-N1-N2= 114.16, N1-N2-C2= 114.35, C1-N1-O1= 112.57, C1-N1-N2-C2= 178.63, C1-N1-O1-N2= 118.68</p>

Figure 4: Orbitals involved during the electronic excitation from the $S_{0,FC}$ to the $S_{1,FC}$ of AM and AOM, as computed at the SA-CASSCF(6,4)/6-31G(d) level of theory. These orbitals are identified from the configuration state function (CSF) with highest coefficient (value of the respective coefficient is also given).

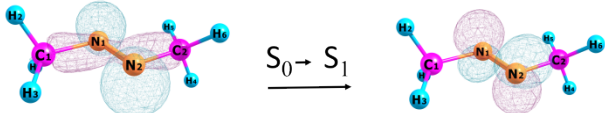
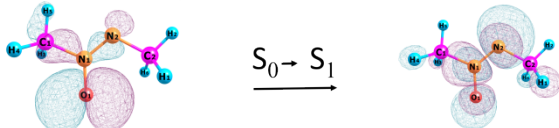
Molecule	CSF Contribution	Excitation
trans-Azomethane (AM)	0.967	
trans-Azoxymethane (AOM)	0.963	

Figure 5: Plots of average population of the S_1 excited state (S_1 , blue) and the S_0 ground state (S_0 , red) as a function of simulation time for (a) AM and (b) AOM, as revealed by the AIMS simulation using the SA-CASSCF(6,4)/6-31G(d) wave function. Minimum energy $(S_1/S_0)_{CI}$ conical intersection (optimized at the same level of theory) is also shown to compare with the superimposed spawning geometries. All plots represent an average of 28 independent AIMS simulations (with different initial conditions) for AM and 36 independent AIMS simulations (with different initial conditions) for AOM.

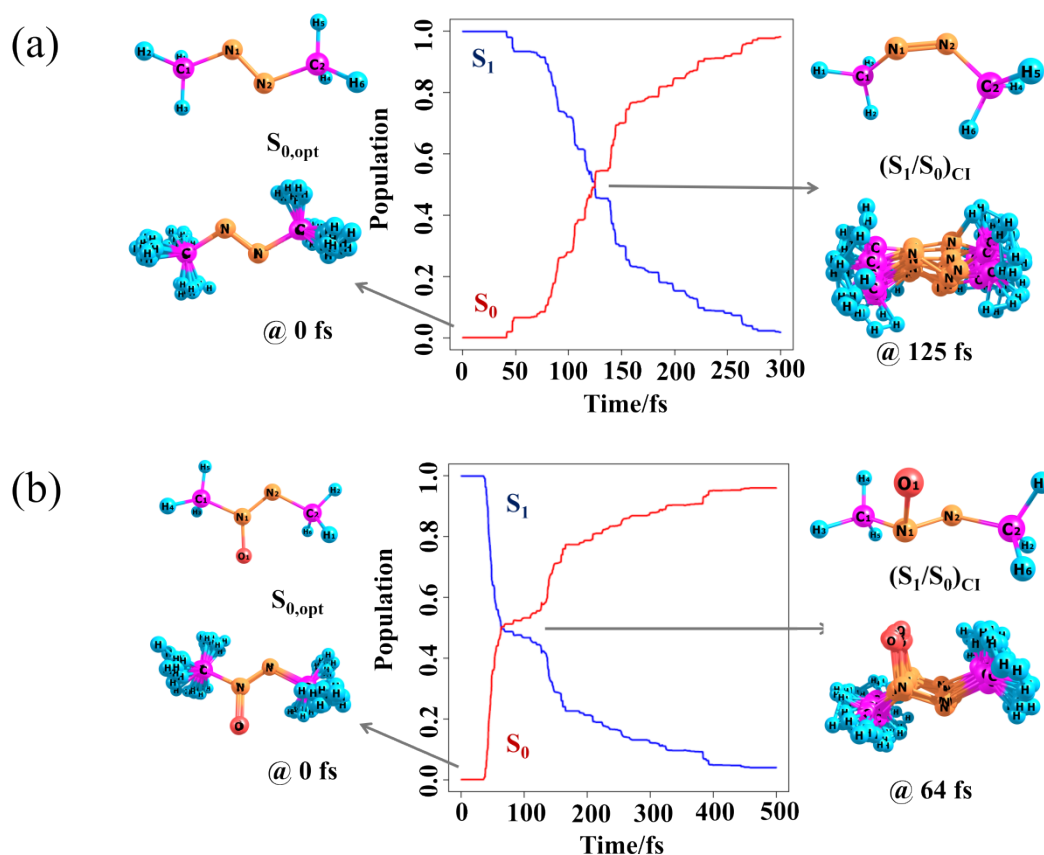


Figure 6: Plots of (a) average $C1N1N2C2$ dihedral angle (in degree) of AM and (b) of average $C1N1N2O1$ pyramidal angle (in degree) of AOM as a function of simulation time, as revealed by the AIMS simulation. Each data point in both figures represents an average of 28 and 36 independent AIMS simulations (with different initial conditions), respectively for AM and AOM. Error bar features the standard deviation of the mean value. Atom numbers are given in the respective molecular structure.

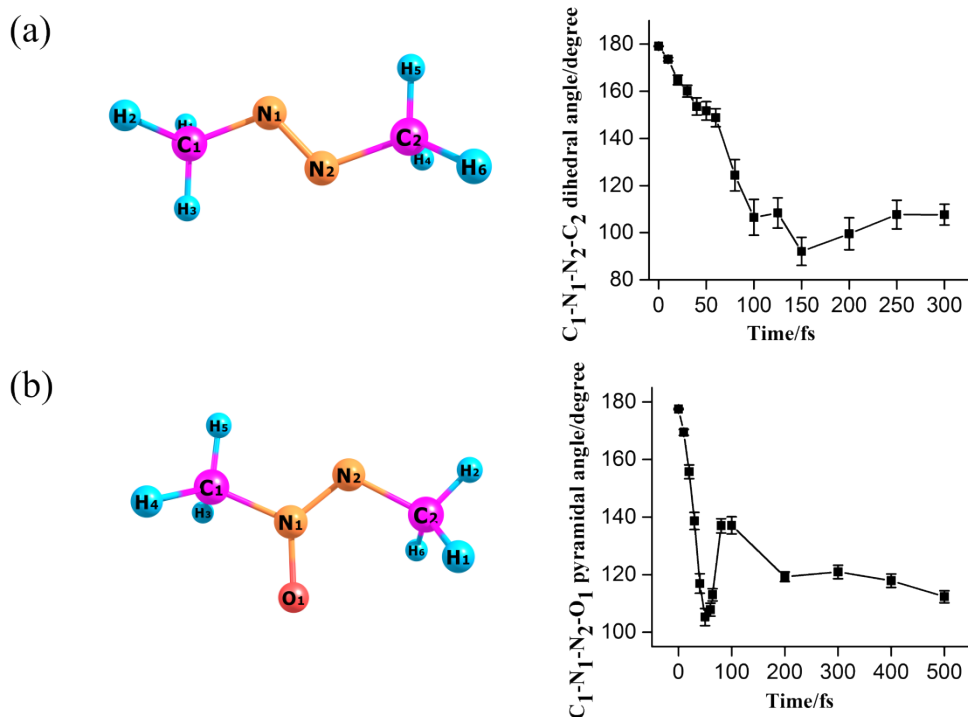


Figure 7: Plots of (a) average C-N bond distance (in Å) of AM and (b) of average C-N and N-O bond distances (in Å) of AOM as a function of the AIMS simulation time. Each data point in both figures represents an average of 28 and 36 independent AIMS simulations (with different initial conditions), respectively for AM and AOM.

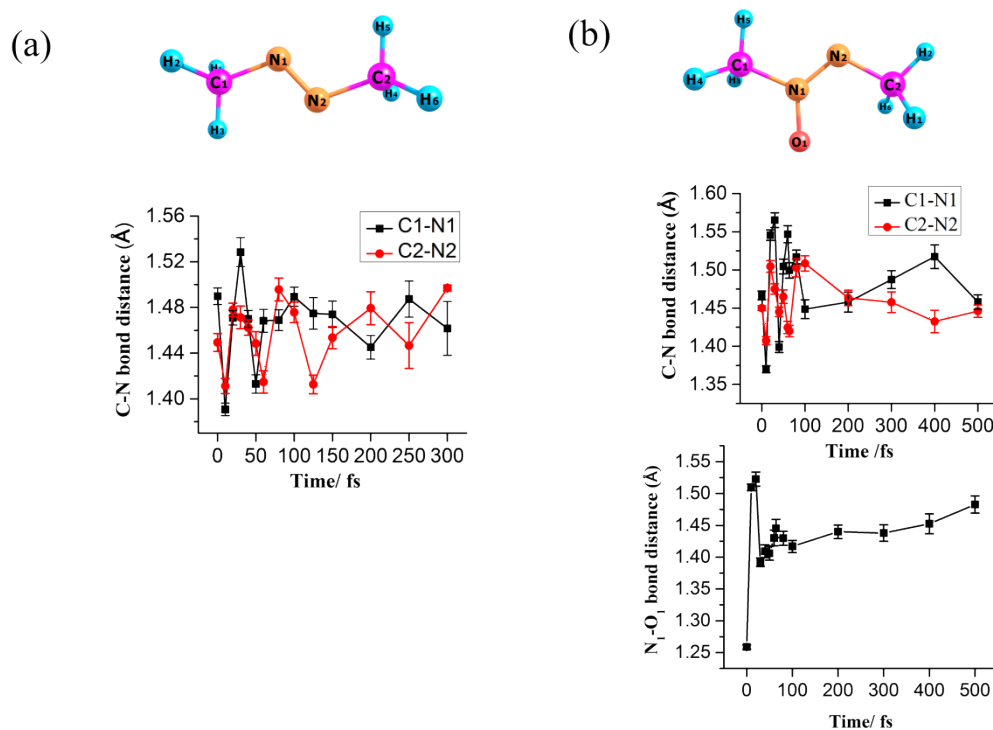


Figure 8: (a) Branching plane vectors of AM and AOM. (b) Energies of the ground state and the $S_1(n,\pi^*)$ excited state near the $(S_0/S_1)_{CI}$ conical intersection following displacements in the branching plane along the \vec{g} and \vec{h} vectors. These two vectors were calculated with the SA-CASSCF(6,4)/6-31G(d) wavefunction at the respective optimized MECI geometries which are shown in Figure 3.

