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Abstract

To gain insight into the ultrafast internal conversion process of azo and azoxy-based energetic molecules from the first signet 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 (S1/S0)CI conical intersection.

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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To
The Editor
Chemical Physics

Dear Sir/Madam,

Attached is a manuscript, "Ab Initio Multiple Spawning Study of Internal Conversion of Azo and Azoxy Energetic Moieties through the $(S_1/S_0)_{CI}$ Conical Intersection" by Jayanta Ghosh, Suman Bhaumik, and Atanu Bhattacharya. We submit this paper as an article for publication in Chemical Physics. We affirm that all authors have seen and approved the submission of the manuscript. The correspondence should be sent to Dr. Atanu Bhattacharya.

To the best of our knowledge, we believe that our work is significant because nonadiabatic chemical dynamics of azo and azoxy energetic groups has never been compared before. In this work, we have employed *ab initio* multiple spawning dynamics to address our present state-of-the-art understanding of ultrafast internal conversion of these two energetic moieties.

Our work is summarized below:

"To gain insight into 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 $(S_1/S_0)_{CI}$ conical intersection."

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If any information is required, please let us know.

Regards,

Atanu Bhattacharya

Ab Initio Multiple Spawning Study of Internal Conversion of Azo and Azoxy Energetic Moieties through the (S₁/S₀)_{CI} Conical Intersection

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Abstract:

To gain insight into 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 (S₁/S₀)_{CI} conical intersection.

Introduction:

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.

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 excited electronic states. Details of this argument with recent literature support are given elsewhere by us.[1] Therefore, the specific topography of the excited electronic potential energy surfaces (PESs) will determine and control the relaxation steps for 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 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 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 through the $(S_1/S_0)_{CI}$ conical intersection for azo and azoxy energetic moieties.

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. Details are given elsewhere.[10,11]

Each AIMS simulation starts with a single initial 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 $CSThresh < 3.0a.u.$) 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 geometry of AM and AOM (referred to as $S_{0,opt}$), optimized at the CASSCF(6,4)/6-31G(d) level of theory, is illustrated in Figure 3. For both molecules, C-N=N-C and C-N(O)=N-C moieties exhibit planar structure (note the C1N2N2C2 dihedral angle). 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] The excitation energy is also in good agreement with the computed excitation energy 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. Furthermore, Figure 4 depicts the

orbitals involved during this electronic excitation of AM and AOM. 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 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 AM, the non-nonbonding orbital in AOM is not localized in $N=N$ moiety. It is found to be localized at O-end of azoxy moiety. We argue that this causes slightly higher vertical S_1 excitation energy for the AOM molecule than the AM molecule.

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 $(S_1/S_0)_{CI}$ for both 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 exhibit any trans-to-cis isomerization. Instead, the $-N(O)=N-$ moiety is found to lose the 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 when we shall discuss AIMS results.

All AIMS simulations, we have run, begin with entire population on the S_1 excited state. Total 28 and 36 initial conditions are selected for 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. Top and bottom panels in Figure 5 depict the average population of AOM and AM, 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). Figure 5 also depicts snapshots of geometries sampled at two different simulation times: at zero femtosecond and at the simulation time when 50% excited state population is quenched. Geometries sampled at the 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 AM molecule; however, a pyramidalization of the $-N(O)=N-$ azoxy moiety is involved in the internal conversion process of AOM. These different structural evolutions become more evident when we inspect the variation of the average C1N1N2C2 dihedral angle of MA molecule and the average C1N1N2O1 dihedral angle of AOM molecule as a function of simulation time (see Figure 6).

General Discussion and Conclusions:

Our primitive thinking of internal conversion between different electronic states was primarily dominated by the application of Jablonski diagram and 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]

In general, the internal conversion processes are mediated by conical intersections (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:

$$\left\langle \psi_f \left| \frac{\partial}{\partial R} \psi_i \right. \right\rangle = \frac{\left\langle \psi_f \left| \frac{\partial H}{\partial R} \right| \psi_i \right\rangle}{(E_i(R) - E_f(R))} \quad (2)$$

The equation (2) highlights the singular behaviour of the nonadiabatic coupling term near a conical intersection, at which the adiabatic electronic energies E_i and E_f are equal. 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. In the search of MECI, the energy of the excited state is minimized. At the same time, the energy difference between the excited state and the closest lower energy state is also minimized.

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 AZ and AOZ are shown in Figure 7. 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 7 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 MA.

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 -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.[16] 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 internal conversion process of azo and azoxy energetic groups.

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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) 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 S_0 minimum				
		CASSCF(6,4)/ 6-31G(d)	CASSCF(6,4)/ 6-31+G(d,p)	CASSCF(6,4)/ -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).

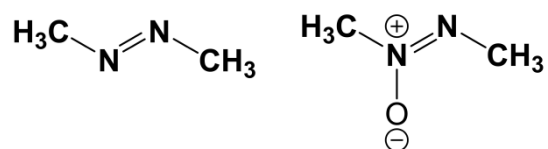
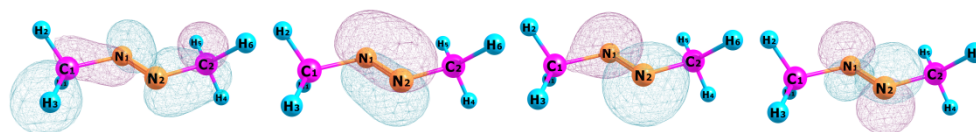


Figure 2: Orbitals used in the (6,4) active space of (a) AM and (b) AOM for the SA-CASSCF/6-31G(d) computations. These orbitals were obtained after optimizing the ground state geometry at the same SA-CASSCF/6-31G(d) level of theory.

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



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

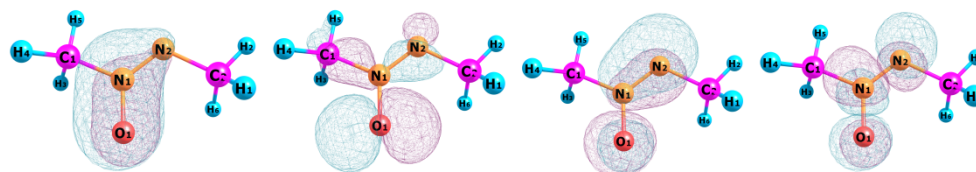


Figure 3: Optimized geometries of AM and AOM at different critical points (ground state equilibrium geometry ($S_{0,Opt}$) and the $(S_1/S_0)_{CI}$ conical intersection geometry), obtained at the CASSCF(6,4)/6-31G(d) level of theory. Bond distances are given in Å. Bond angles and dihedral angles are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

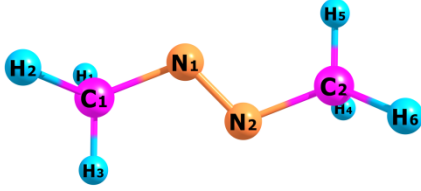
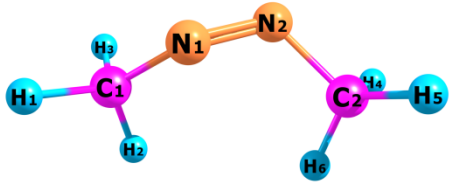
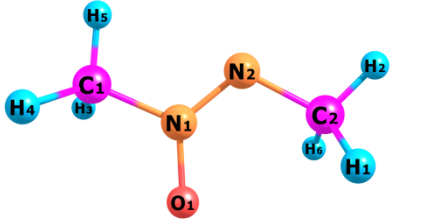
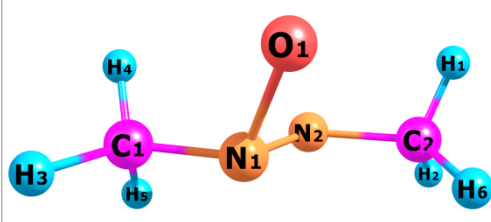
Molecules	$S_{0,Opt}$	$(S_1/S_0)_{CI}$
Trans-Azomethane	 <p> C1-N1= 1.455, N1-N2= 1.237 N2-C2= 1.456, C1-N1-N2= 113.13, N1-N2-C2= 113.10, C1-N1-N2-C2= 179.93 </p>	 <p> C1-N1= 1.433, N1-N2= 1.278 N2-C2= 1.462, C1-N1-N2= 130.922, N1-N2-C2= 114.79, C1-N1-N2-C2= 94.172 </p>
Trans-Azoxymethane	 <p> C1-N1= 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 electronic excitation from the $S_{0,FC}$ to the $S_{1,FC}$ of AM and AOM, 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 coefficient is also given).

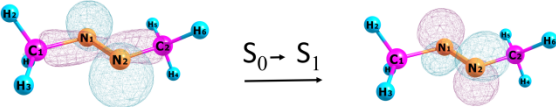
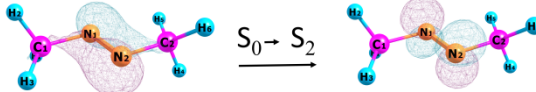
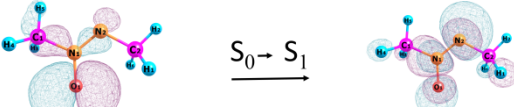
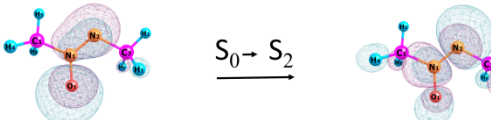
Molecule	CSF Contribution	Excitation
trans-Azomethane	0.967	
	0.808	
trans-Azoxymethane	0.963	
	0.877	

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 AM and 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.

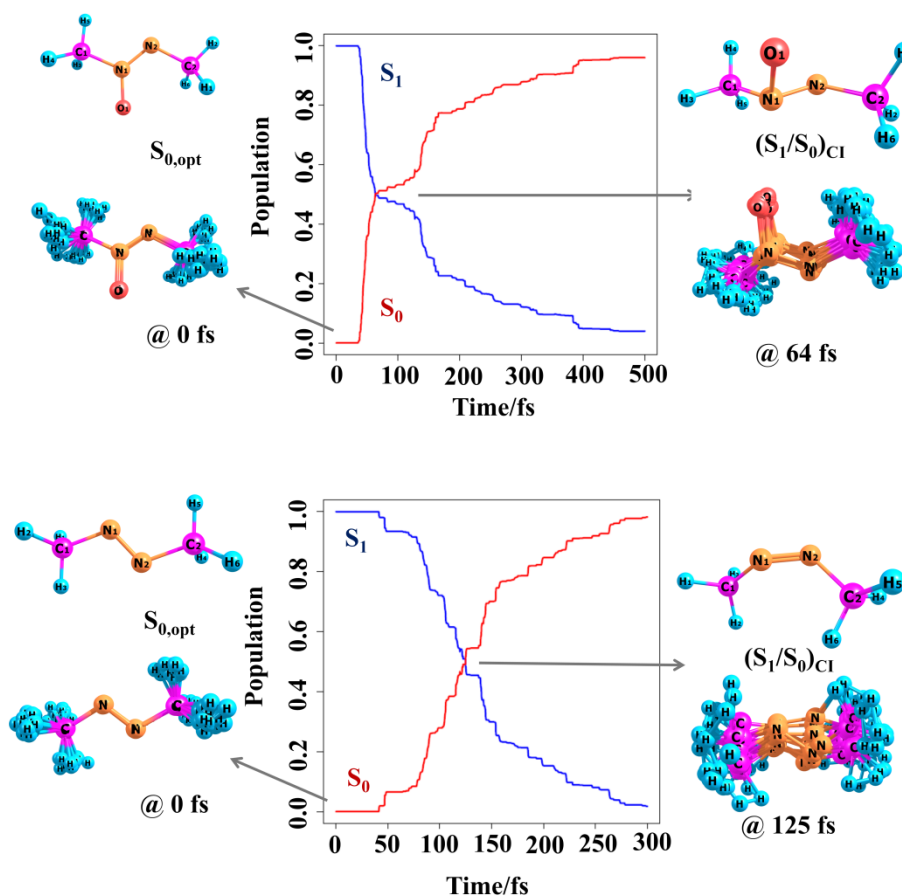


Figure 6: Plots of (top panel) average $C1N1N2C2$ dihedral angle (in degree) of MA and (bottom panel) average $C1N2N3O1$ pyramidal angle (in degree) of AOM as a function of simulation time, as revealed by AIMS simulation. Each data point in both panels represents an average of 28 and 36 independent AIMS simulations (with different initial conditions), respectively for AM and AOM. Error bar features the standard deviation of the mean. Atom numbers are given in the respective molecular structure.

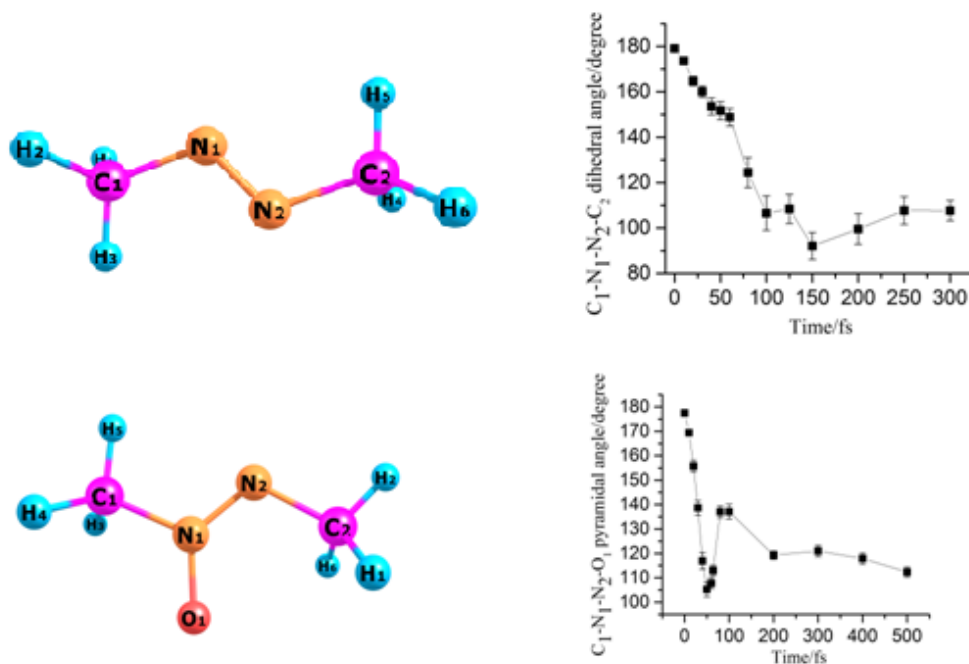


Figure 7: (a) Branching plane vectors of AM and AOM. (b) Energies of the ground state and the $S_1(n,\pi^*)$ excited state near the $(S_0/S_1)_{CI}$ conical intersection along displacements in the branching plane along the \vec{g} and \vec{h} vectors. These two vectors were calculated with the SA-CASSCF(6,4)/6-31G(d) wavefunction at the respective optimized MECI geometries which are shown in Figure 3.

