Ultrafast S₁ to S₀ Internal Conversion Dynamics for Dimethylnitramine through a Conical Intersection

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ABSTRACT: Electronically nonadiabatic processes such as ultrafast internal conversion (IC) from an upper electronic state (S₁) to the ground electronic state (S₀) though a conical intersection (CI), can play an essential role in the initial steps of the decomposition of energetic materials. Such nonradiative processes following electronic excitation can quench emission and store the excitation energy in the vibrational degrees of freedom of the ground electronic state. This excess vibrational energy in the ground electronic state can dissociate most of the chemical bonds of the molecule and can generate stable, small molecule products. The present study determines ultrafast IC dynamics of a model nitramine energetic material, dimethylnitramine (DMNA). Femtosecond (fs) pump–probe spectroscopy, for which a pump pulse at 271 nm and a probe pulse at 405.6 nm are used, is employed to elucidate the IC dynamics of this molecule from its S₁ excited state. A very short lifetime of the S₁ excited state (∼50 ± 16 fs) is determined for DMNA. Complete active space self-consistent field (CASSCF) calculations show that an (S₁/S₀)CI CI is responsible for this ultrafast decay from S₁ to S₀. This decay occurs through a reaction coordinate involving an out-of-plane bending mode of the DMNA NO₂ moiety. The 271 nm excitation of DMNA is not sufficient to dissociate the molecule on the S₁ potential energy surface (PES) through an adiabatic NO₂ elimination pathway.

INTRODUCTION

Decomposition of energetic materials (e.g., explosives, propellants, pyrotechniques, fuels) can be initiated by different processes, including sparks, arcs, shocks, compression waves, and light. These events induce electronic excitation in energetic molecules.1−14 In principle, a number of photochemical and photophysical processes can occur following electronic excitation of an energetic molecule: these include radiative transitions, such as fluorescence and phosphorescence, nonradiative transitions, such as internal conversion (IC) and intersystem crossing (ISC), and excited state photochemistry. IC is particularly important for the initial steps of the decomposition of energetic molecules because, by utilizing this process, energetic molecules can transfer electronic energy to the vibrational degrees of freedom of the ground electronic state potential energy surface (PES).15 This vibrational energy can eventually dissociate the covalent bonds of an energetic molecule and begin the chain reaction to release the stored chemical energy of energetic materials. Additionally, ultrafast IC is often found to occur through one or more conical intersections (CIs, minimum energy crossing points) of adiabatic PESs, thereby generating an ultra short (fs) lifetime for the excited electronic state S₁. Such ultra short lifetimes for excited electronic states can also play an important role in the energy material sensitivity to initiation events.15 CIs have been firmly established to be key features in the excited electronic state chemistry of polyatomic molecules.16−18 The concept of a CI was first introduced by von Neumann and Wigner19 and has been now recognized as essential for describing the ultrafast dynamics and mechanisms for deactivation of polyatomic molecules from their excited electronic states to their ground electronic surfaces.20−24

Manaa et al.25 explored the electronic properties of a single N−NO₂ moiety in order to explain the behavior of nitramine energetic materials. They consider the role of singlet—triplet ISC through ab initio quantum chemistry calculations, in order to model the pathway for fast nonradiative relaxation. They predicted a singlet—triplet minimum energy crossing point (T₁/S₀)CI to establish a nonradiative transition mechanism to deactivate the T₁ state of a nitramine. They further proposed that existence of such a (T₁/S₀)CI can generate fast nonradiative energy transfer from T₁ to S₀ but they did not consider the role of the S₁ excited state IC through a singlet—singlet minimum energy crossing point (S₁/S₀)CI for vibrational excitation of the nitramine S₀ state.

In the present study, the fast IC from S₁ to S₀ of dimethylnitramine (DMNA), a model energetic material, is determined, and the role played in this process by the CI of S₁ and S₀ adiabatic
Figure 1. Chemical structures of the nitramine energetic material RDX and model system DMNA.

PESs ((S₁/S₀)CI CI) is addressed and evaluated. DMNA is considered to be a simple analogue molecule of a nitramine energetic material, such as RDX (see Figure 1 for the structure of DMNA and RDX). DMNA has only one nitramine (N–NO₂) moiety, whereas RDX has three (see Figure 1). Determination of the S₁ excited electronic state lifetime of DMNA and exploration of its nonadiabatic relaxation pathways involved in the fast IC from S₁ to S₀ can provide many details of the electronic proper-
tions. Determination of the S₁ excited state lifetime related to 271 nm excitation can be extracted from the pump–probe transient spectrum (TOFMS spectral intensity vs pump–probe time delay) employing a single exponential decay function to fit the data.

The decomposition of DMNA from excited electronic states has been recently investigated in our laboratory. Experimentally, we determined that DMNA decomposes through a nitro-nitrite isomerization mechanism at 226 nm excitation, and generates an NO molecule as an initial product. Theoretical calculations show that the DMNA molecule is excited to the S₁ electronic state following 226 nm excitation, and the (S₂/S₁)CI CI between the S₂ and S₁ electronic states along the nitro-nitrite isomerization reaction coordinate plays an important role in the overall decomposition of DMNA.

III. THEORETICAL PROCEDURES

All geometry optimizations relevant to excited electronic state decomposition of DMNA are executed at the CASSCF(14,11)/6-31G(d) level of theory employing the Gaussian 03 program. No symmetry restrictions are applied to the calculations. To explore the excited state PESs of DMNA, an active space comprising 14 electrons distributed in 11 orbitals, denoted as CASSCF(14,11), is employed. A large active space, (14, 11), is employed for these CASSCF calculations, not necessarily to include dynamic correlation energy, which has been included in CASMP2 calculations, but for the CI calculations. Here CASMP2 calculation is not performed because energies calculated at the CASSCF level of theory show good agreement with the gas phase absorption maximum of DMNA, which indicates that the dynamic correlation is not important for the present system. Orbitals used in the active space are one N nonbonding 2S orbital, two NO bonding orbitals σNO, two NO antibonding orbitals σNO**, one delocalized ONO π-bonding orbital ξONO, one delocalized ONO π-antibonding orbital ξONO**, one bonding NN orbital σNN, one NN antibonding σNN*, one π-nonbonding orbital nπCI, and one σ nonbonding nσN. Vertical excitation energies are calculated by state averaging over the ground and various excited states with equal weight for each state. Critical point structures (minima and transition states) are characterized by analytical frequency calculations, and minimum energy paths are calculated using an intrinsic reaction coordinate.
pulses. To probe relaxation dynamics of DMNA from the $S_1$ state, and a probe pulse (two photons) at 406.5 nm is used to ionize the molecule from the $S_1$ state. The CASSCF(14,11)/6-31G(d) calculated vertical excitation energy (4.57 eV at 271 nm) used in the present experimental work with the calculated vertical excitation energies (5.13 and 5.5 eV for $S_1$ and $S_2$ states, respectively) reveals that DMNA is excited below the Franck-Condon (FC) point of the $S_1$ state by electronic excitation of the molecule at 271 nm.

In order to determine the relaxation path involved in fast IC of DMNA from the $S_1$ state, the minimum energy, steepest decent path connecting the FC points of $S_1$ and $S_0$ surfaces of DMNA to the minimum energy ($S_1/S_0$)$_{CI}$ CI is determined (see Figure 4). This path is computed at the CASSCF(14,11)/6-31G(d) level of theory. The reaction pathways from the FC point on $S_1$ to the $S_1/S_0$ CI, and from the $S_1/S_0$ CI back to the ground state minimum are different in Figure 4, and the plot is sketched for energy with respect to number of steps, which is computed through the IRC algorithm based on the phase that is associated with the bending mode of the $N^−−NO_2$ moiety. Figure 4 shows that vertical excitation of DMNA to even below the FC point of the $S_1$ PES can potentially lead to a nonadiabatic IC of electronically excited DMNA from the $S_1$ PES to the $S_0$ PES through the ($S_1/S_0$)$_{CI}$ CI. This CI is energetically accessible even below the FC point of the $S_1$ PES because no energy barrier exists in this reaction pathway. Molecular structure of DMNA at ($S_1/S_0$)$_{CI}$ shows a bent $N^−−NO_2$ moiety.

The $N^−−NO_2$ bond dissociation reaction paths on the $S_1$ and $S_0$ PESs of DMNA can also be investigated by elongating the $N^−−NO_2$ bond length, as plotted in Figure 5. Note that the
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IV. DISCUSSION

An ultrafast lifetime of $\tau \sim 50 \pm 16$ fs is determined for the $S_1(n,\pi^*)$ excited electronic state of DMNA following its electronic excitation at 271 nm, using femtosecond pump–probe spectroscopy. Theoretical calculations at the CASSCF(14,11)/6-31G(d) level of theory show that the $\left(S_1/S_0\right)_{CI}$ CI in the relaxation pathway involving IC of DMNA from its $S_1$ PES to its $S_0$ PES is responsible for the ultrashort lifetime of the $S_1(n,\pi^*)$ excited electronic state. A PES scan along the $N\cdots NO_2$ bond dissociation pathway computed at the same level of theory indicates that DMNA does not have sufficient energy to surmount the adiabatic $N\cdots NO_2$ bond dissociation barrier on the $S_1$ PES following its electronic excitation at 271 nm; hence, only the nonadiabatic relaxation pathway through the $\left(S_1/S_0\right)_{CI}$ is open for DMNA following excitation at 271 nm. Geometry near the CI shows that an out of plane $NO_2$ bending mode with respect to the $N\cdots NO_2$ plane is involved in this relaxation/dissociation pathway, which is barrierless on the $S_0$ surface.

DMNA is considered to be a model system for nitramine energetic materials: this molecule is expected to evidence electronic properties of large and more complex nitramine energetic materials. Following electronic excitation of DMNA at 271 nm, the molecule can rapidly come back to the ground state, transferring electronic excitation energy to its vibrational degrees of freedom. An ultrafast lifetime of the lowest lying $S_1$ excited state of DMNA corroborates the fact that nitramine molecules are able to convert their initial electronic excitation energy to vibrational energy on their ground state PES. This behavior could be general for all nitramine systems, including large and complex energetic materials such as RDX; however, corroboration of such a consideration for true energetic systems requires further study of excited electronic states of large energetic systems.

The full mechanism for molecular explosive behavior and sensitivity is still not completely revealed. Thus far, many factors, such as chemical stability, structure, crystal density, etc. have been suggested to play a present role in the coherent description of nitramine molecular explosive behavior. In this work, we demonstrate that the ultrashort lifetime of the excited electronic state of nitramine molecules can be an important factor controlling their explosive behavior.

VII. CONCLUSION

Utilizing synergism between experiment and theory, the $S_1 \rightarrow S_0$ IC dynamics of a model nitramine energetic molecule, DMNA, is determined. Electronic excitation of DMNA to the $S_1$ excited state promotes an electron from an n to a $\pi^*$ orbital, which initially localizes the electronic excitation energy on the $NO_2$ moiety and activates a bending mode of the $NO_2$ moiety with respect to the $N\cdots NO_2$ plane. This bending mode is responsible for an ultrafast ($\sim 50 \pm 16$ fs) IC of DMNA from its $S_1$ excited state to its $S_0$ ground electronic state. This fast relaxation quenches radiative processes from the $S_1$ surface of DMNA. The present study reveals the nature of the electronic energy distribution generated in the $S_1 \rightarrow S_0$ electronic transition and the mechanism of energy transfer to the $S_0$ vibrational motion. This new insight into nitramine energy dynamics should lead to a much deeper understanding of...
molecular explosive behavior of nitramine energetic materials, in general.

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**REFERENCES**