

Multi-Electronic-State Approach of Tetranitrogen

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Abstract: There is a rising interest nowadays in employing nanoscale materials as new possible types of fuels. To be considered an efficient fuel, the candidate material must be sufficiently unstable in order to react with another system and then release a considerable amount of energy. On the other hand, it must be stable enough to be synthesized and stored without spontaneously decomposing itself [1]. To accomplish the goal of being considered “green” these materials must not only generate reasonably less toxic products than the current widely spread fuels do, but also demonstrate higher performances while being technically as well as economically attractive [2]. In this context, polinitrogen systems have been studied due to their potential use as high-energy density materials (HEDM), since their dissociation into inert N₂ molecules may release huge amounts of energy [1,3]. Therefore, studies of the photochemistry of polinitrogen systems can be considered important theoretical prototypes. It is relevant either for supporting the detection of their existence through spectroscopic analysis and/or understanding their chemical behavior in Earth’s atmosphere, other astronomical environments or yet as possible fuels [4]. This subject has already been intensively studied for the nitrogen gas [5,6], while quantum chemical calculations are responsible for most of the information on larger polinitrogen systems [7,8]. The formation of linear N₃ from the reaction between two N₂ molecules, for instance, is expected to occur upon photoexcitation and to present a linear N₄ species as transition state [4]. While several calculations involving various polinitrogen isomers indicate high potential energies when compared to molecular nitrogen, only some of them exhibit an essential HEDM feature: high dissociation barrier [3]. Within this perspective, the scientific community has been giving great attention to isomers of tetranitrogen (N₄), in particular to the tetrahedral form (N₄ – T_d) [8,9]. In fact, the good understanding of atomic aggregates or clusters in general relies, foremost, on the capacity of generation of plausible structures for those compositions whose available information is scarce. At the same time, approaching systems with typical cluster dimensions requires taking into consideration the effects arising from the quantum behavior of matter, and the applicability of analytical or empirical potentials becomes questionable [10]. In this context, we have employed and upgraded a previously developed genetic algorithm coupled with electronic structure methods [11], namely QGA, tested to survey the potential energy surface of the tetranitrogen system. The QGA approach presented good cost-effectiveness ratio when it comes to the computational effort associated with electronic structure calculations. It is well-suited to assess the potential energy surface of atomic



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clusters, mainly in cases where no previous information about the structural arrangement of the system is available. The QGA provided structures in good agreement with coupled cluster results, even though it started from structures generated completely randomly. Theoretical investigations of the electronic potential energy curves associated with the dissociation of the N_4 (T_d) into two N_2 molecules were also performed for the electronic ground state and the first excited states using CASSCF(12,12) level of theory implemented in MOLPRO package [12]. The graphs containing the dissociation paths studied involved singlet and triplet states, where it was possible to observe both conical intersections and intersystem crossings. Possible alternative dissociation channels for the N_4 (T_d) were then inferred from these crossings and photoexcitation of this species. Coupled cluster (CCSD(T)-F12) calculations were also performed on specific structures to generate benchmark results, which were then compared to results provided by density functional theory (DFT) calculations with several different exchange-correlation functionals in order to find the best match. The tetrazete T_d and planar D_{2h} isomers were approached by higher level of theory (CCSD(T)-F12/cc-pCVTZ-F12) than already reported until the present date. The N_4 (T_d) was predicted to be $182 \text{ kcal.mol}^{-1}$ above $2N_2$ in energy, and 1 kcal.mol^{-1} above the D_{2h} isomer. The unraveling of a possible reaction mechanism involving the abstraction of a nitrogen atom from a N_2 molecule in an excited electronic state, by another excited N_2 molecule, to produce linear N_3 is also currently in progress.

Key-words: polinitrogen, aggregates, cluster, photochemistry

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