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Reaction Channels on Potential Energy Surface of Some Atmospherically and Astronomically Important Compounds

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Introduction:

Quantum chemical calculations are often more efficient than the corresponding experimental investigations. This is true especially in the case of astrochemical and atmospheric chemistry. In both cases it is essential to know the potential energy surface of the target materials to understand the reactions taking place in the air and in the outer space. It can also help us to detect these processes without samples using experimental tools. In this work we present the stationary points on the $[C_2NP]$ (NCCP, CNCP), $[C_2P_2]$ (PCCP), $[NO_4]$ ($O_3 + NO \leftrightarrow O_2 + NO_2$), and $[CO_4]$ ($O_3 + CO \leftrightarrow O_2 + CO_2$) potential energy surfaces.

Interest in simple and metal-free phosphalkynes has been stimulated owing to detection of phosphorous containing compounds such as PH_3 , CP and HCP in the interstellar space and planetary atmospheres. Along with the presence of polyacetylene derivatives and other hydrocarbons and nitrogen species (CN, HCN, NCCN, etc.) in extraterrestrial media, formation of mixed long-chain linear phosphalkynes appears to be plausible^{1,2}. ($[C_2NP]$, and $[C_2P_2]$ potential energy surfaces.)

The formation and decomposition of ozone is for a long while in the focus of both theoretical and experimental scientist. The ozone decomposition is damaging in the stratosphere because it protect us from the unwanted radiations. In contrast to this near to the ground level the ozone formation is unwanted because this is dangerous to human and other life forms. The origin of ozone formation and decomposition are connected to transportation. During stratospheric flights the aircraft jet engines and at the ground level transportation the internal combustion engines emit significant amount NO and CO and this affect the ozone level in the air. ($[NO_4]$, and $[CO_4]$ potential energy surfaces.)

Computational Methods:

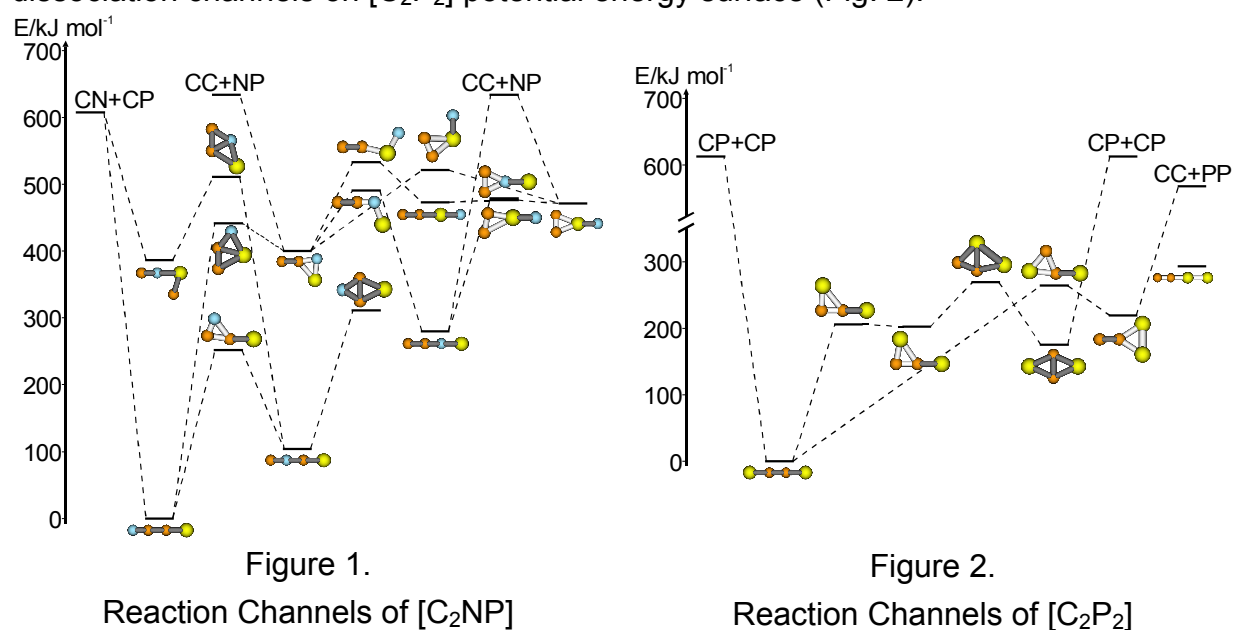
A systematic search for all reaction paths starting from an equilibrium structure is a challenging problem. The early-developed methods are usually computationally extreme demanding or not enough effective. In this present study we used the newly developed very efficient algorithm, the Scaled Hypersphere Search (SHS) Method. This algorithm search for pathways leading to transition states and dissociation channels around an arbitrary equilibrium structure, which lead to a global

search of potential energy surface for a given chemical composition to discover all transition states and all equilibrium structures together with their relationships in addition to all dissociation channels^{3,4}.

The SHS method was used with conjunction with B3LYP method with small (3–21G) basis set. The stationary points were calculated at higher levels of theory and/or larger basis sets.

Results and Discussion:

The SHS method successfully found 7 equilibrium structures and 9 transition states along with 5 dissociation channels on $[C_2NP]$ potential energy surface (Fig. 1). It is also found 5 equilibrium structures and 3 transition states along with 3 dissociation channels on $[C_2P_2]$ potential energy surface (Fig. 2).



Investigating the potential surfaces we can say that the global minima of the two potential surfaces are NCCP and PCCP. Although the other low-laying isomers are significantly higher in energy than the minima they seem to lie in reasonably deep potential wells with respect to unimolecular rearrangements and fragmentations hence they might be detectable in the low-pressure interstellar space and planetary atmospheres.

References:

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