***Ab Initio* Molecular Dynamics Reveals Formation Path of Benzonitrile and Other Molecules in Conditions Relevant to the Interstellar Medium**

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**Abstract**

Polycyclic aromatic hydrocarbons and polycyclic aromatic nitrogen heterocycles are believed to be widespread in different areas of the interstellar medium. However, the astronomical detection of specific aromatic molecules is extremely challenging. As a result, no specific aromatic molecules have yet been identified, and very little is known about their formation routes in different areas of the interstellar medium. Only recently, McGuire *et al.* detected the simple aromatic molecule benzonitrile in Taurus Molecular Cloud 1. By means of quantum chemistry and *ab initio* molecular dynamics, we present a mechanism that elucidates the formation of small aromatic molecules from the ionization of van der Waals clusters in conditions prevalent in molecular clouds, such as Taurus Molecular Cloud 1. This mechanism predicts benzonitrile formation in acetylene and cyanoacetylene mixed clusters. Additional aromatic molecules may also form similarly. The results presented here are essential for gaining a molecular-level understanding of the formation mechanism of benzonitrile. They also provide new insights that can guide astronomers in their search for aromatic molecules.

**Significance Statement**

Understanding the formation routes of aromatic molecules in the harsh environment of the interstellar medium has been a long-standing puzzle. In this manuscript we report formation routes for small aromatic molecules and aromatic nitrogen heterocycles (as well as non-aromatic molecules) from ionized van der Waals clusters. We demonstrate, via *ab initio* molecular dynamics, that when the clusters contain acetylene and cyanoacetylene—the building blocks found in Taurus Molecular Cloud 1—the model predicts the formation of benzonitrile cation. Our results predict the formation of other important compounds, including a bicyclic structure, and can help facilitate the astronomical search for additional aromatic molecules.

1. **Introduction**

Despite the harsh conditions in space, such as low density, extreme temperatures, shock waves, and radiation, radio astronomy measurements are able to reveal the universe’s rich molecular nature.[1] Thus far, about 175 molecules have been identified in the gas phase.[2] Additionally, different organic molecules have been identified in meteorites and comets; among them are carboxylic and amino acids, puric and pyrimidic bases, sugars, and hydrocarbons,[3-6] with demonstrated interstellar origins. While only relatively small molecules (up to 12 atoms) have been identified in the gas phase, it is commonly believed that much more complex molecules are present in the interstellar medium (ISM). An example is polycyclic aromatic hydrocarbons (PAHs), which are considered widely prevalent in the ISM, and constitute 20% of the carbon in the ISM.[7-13] The well-accepted PAH hypothesis[9, 10] suggests that PAHs (including their derivatives and ionic form) are responsible for the unidentified infrared bands (UIBs)—observed emission bands that appear at 3.3, 3.4, 6.2, 7.7, 8.6, and 11.3 in the IR spectra.[14, 15] The UIBs, also referred to as aromatic infrared bands (AIBs), demonstrate the generality of the PAH hypothesis.[16]

Polycyclic aromatic nitrogen heterocycles (PANHs), in which a nitrogen atom is part of the ring structures, are also believed to contribute to the observed IR spectra. A shift in the 6.2- peaks has been suggested as an indicator of their presence.[17-19] PANHs and their possible formation routes are essential for understanding the chemical evolution of prebiotic molecules, and for astrophysics, astrobiology, and astrochemistry.[20]

Although the presence of complex organic molecules such as PAHs and PANHs in different areas of the ISM is generally accepted, the mechanisms for their formation from smaller precursor molecules in areas such as dense molecular clouds are still elusive, and have been the subject of much study and debate. Moreover, despite their high abundance, the detection of a specific PAH or PANH molecule is challenging, due to their low rotational constant. Only recently was the aromatic molecule benzonitrile identified in the cold-core Taurus Molecular Cloud 1 (TMC-1) via its hyperfine structure.[21]

Dense molecular clouds are known to possess rich chemistry. They are inhomogeneous, and contain high-density cores (relative to the ISM) and low temperatures of 10–100K.[16, 22] Moreover, while the cloud’s surface is exposed to a large amount of radiation from its surroundings, the inner parts of the cloud are shielded from most of the radiation. Although the shielding prevents the destruction of molecules due to radiation, some ionizing radiation can still penetrate the inner areas and lead to the formation of ionized species.[23] Spectral measurements reveal that different molecules (mostly small molecules with less than 12 atoms) can be found in dense molecular clouds. For example, in TMC-1, over 60 molecules have been identified, among them cyanopolyynes (HCnN; n=odd).[24, 25] The mechanism for the chemical reactions taking place in the clouds is thought to be dictated by molecular collisions. However, under the prevailing conditions in the cloud, molecular collisions are rare and, since the reaction of two neutral species is likely to require activation energy, most collisions will not be reactive. For this reason, the astrochemistry community focused on reactions between ions and neutral molecules, as well as radical reactions, as those reactions do not have activation energies, and are thus much more likely to occur and lead to chemical growth.

While most encounters between neutral species are not reactive, they can result in the formation of molecular clusters, especially in the low temperatures of the cloud environment.[26, 27] The rare occurrence of ionizing radiation allows clusters to grow. When the cluster finally encounters ionizing radiation, it can lead to intra-cluster polymerization, a process that may play an essential role in the chemistry of molecular clouds, yet is often overlooked.

Intra-cluster ionic polymerization has been shown to bring about molecular growth. For example, acetylene is the basic building block of complex organic molecules, such as PAHs, formed in various processes, including those leading to soot formation during combustion, or the creation of interstellar dust. Thus, many experimental studies have focused on clusters of acetylene molecules, and demonstrated that radical ions of the form (C2H2)n+ were obtained by ionization of these clusters. Among the resulting structures, covalently bonded cyclic structures such as cyclobutadiene cation and benzene cation were identified.[28-40] Recently, Momoh et al. showed that ionization of van der Waals clusters of ethynylbenzene (C8H6)n, formed by supersonic beam expansion, led to molecular growth into larger structures, and resulted in radical cations of (C8H6)n+. They demonstrated that the aforementioned structures are covalently bonded, based on mass-selected ion dissociation and ion mobility measurements.[41] Zhen et al. studied the photodissociation processes of pyrene clusters, and found that small PAHs can convert into larger PAHs when undergoing laser irradiation.[42] We recently demonstrated the potential of this mechanism to form aromatic molecules, by modeling ionization of small neutral acetylene clusters via *ab initio* molecular dynamics (AIMD). This process can lead to molecular growth, where structures are formed on the C4 and C6 potential energy surfaces, among them the benzene cation.[39] In addition, upon ionization of mixed HCCH and HCN clusters, growth can occur between 3 and 4 units, forming new C-C and C-N bonds. We showed that cyclic structures can be formed through this mechanism, including the pyridine radical cation,[43] which is extremely important due to its prebiotic nature.

In this manuscript, we establish the high relevance of the intra-cluster growth mechanism to molecular formation in molecular cloud environments. By applying this mechanism to acetylene and cyanoacetylene mixed clusters, we successfully predicted benzonitrile radical cation formation. This result is significant, as the benzonitrile molecule was recently identified experimentally in TMC-1. Moreover, the mechanism predicts the formation of a fused double-ring structure, 2 azabicyclo[4.2.0]octa-1,3,5,7-tetraene cation, emphasizing its importance for astrochemical systems. Promptly after ionization, complex nitrogenous organic molecules are formed, some of which contain fused rings! Moreover, our results show the formation of additional nitrogenous organic molecules, which can be used to focus astrophysical research studies in the future.

This paper is organized as follows: Neutral van der Waals structures of pure cyanoacetylene clusters are introduced in section II.a, which includes a discussion of their stability and the stability of the ionized clusters. To study the fate of the cluster upon ionization, we performed AIMD simulations. The AIMD results of pure and mixed clusters are presented in sections II.b.i and II.b.ii, respectively. Section II.c presents the mechanism for benzonitrile formation from mixed trimer cluster. Details of our calculation are presented in section III, followed by the Conclusion in section IV.