**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 how they are formed in different areas of the interstellar medium. Only recently, McGuire et al. detected the simple aromatic molecule benzonitrile in Taurus Molecular Cloud-1. Applying quantum chemistry and ab initio molecular dynamics, we suggest 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 in a similar manner. The results presented make an essential contribution to a better understanding of the formation mechanism of benzonitrile at the molecular level. These results also offer new insights that can guide astronomers in their search for aromatic molecules.

**Significance Statement**

Understanding how aromatic molecules are formed in the harsh environment of the interstellar medium has long been a puzzle to scientists. This paper investigates how small aromatic molecules and aromatic nitrogen heterocycles (as well as non-aromatic molecules) are formed from ionized van der Waals clusters. Applying ab initio molecular dynamics, we demonstrate that when the clusters contain acetylene and cyanoacetylene — some of 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 astronomy’s 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]. To date, approximately 175 molecules have been identified in the gas phase [2]. Additionally, different organic molecules have been identified in meteorites and comets, including carboxylic and amino acids, purine and pyrimidine bases, sugars, and hydrocarbons [3-6], with demonstrated interstellar origins. While only relatively small molecules of 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). These include 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), or observed emission bands that appear at 3.3, 3.4, 6.2, 7.7, 8.6, and 11.3 $μm$ in the infrared (IR) spectra [14, 15]. The presence of the UIBs, also referred to as aromatic infrared bands (AIBs), demonstrate the generality of the PAH hypothesis [16].

Polycyclic aromatic nitrogen heterocycles (PANHs), the ring structures of which include a nitrogen atom, are also believed to contribute to the observed IR spectra, with a shift in the 6.2-$μm$ peaks having been suggested as an indicator of their presence [17-19]. In order to understand the chemical evolution of prebiotic molecules, and for enhanced insights in the field of astrophysics, astrobiology, and astrochemistry, it is essential to clarify PANHs possible formation routes [20].

Although the presence of complex organic molecules such as PAHs and PANHs in different areas of the ISM is generally accepted, the mechanisms of 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 relative ubiquity, the detection of a specific PAH or PANH molecule is challenging, due to their low rotational constant. In fact, only recently was the aromatic molecule benzonitrile identified in the cold-core Taurus Molecular Cloud-1 (TMC-1) via its hyperfine structure [21].

It is known that dense molecular clouds possess rich chemical compositions, as 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, internally, it is shielded from most of the radiation. While this protection prevents the destruction of molecules from radiation, some ionizing radiation can still penetrate the cloud’s internal areas and lead to the formation of ionized species [23]. Spectral measurements reveal that a number of different molecules (mostly small molecules with fewer than 12 atoms) can be found in dense molecular clouds. For example, in TMC-1, over 60 molecules have been identified, including cyanopolyynes (HCnN; n=odd) [24, 25]. Due to the fact that molecular collisions are rare under the prevailing cloud conditions, and since the reaction of two neutral species is likely to require activation energy, most such collisions will not be reactive. Consequently, to date, the astrochemistry field has focused on reactions between ions and neutral molecules, as well as on radical reactions, as these do not have activation energies, and are therefore far 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], and as the rare occurrence of ionizing radiation enables the growth of clusters. When the cluster finally encounters ionizing radiation, it can lead to intra-cluster polymerization, a process that, in our opinion, despite possibly playing an essential role in the chemistry of molecular clouds, is often overlooked.

Intra-cluster ionic polymerization has been shown to generate molecular growth. For example, acetylene is the basic building block of complex organic molecules, such as PAHs, formed in a number of 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 have demonstrated that radical ions of the form (C2H2)n+ resulted from the ionization of these clusters. Covalently bonded cyclic structures, such as cyclobutadiene cation and benzene cation, have been identified among the resulting structures [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+. Based on mass-selected ion dissociation and ion mobility measurements, they further demonstrated that the larger structures are covalently bonded [41]. Zhen et al. studied the photodissociation processes of pyrene clusters, and found that small PAHs can convert into larger ones when undergoing laser irradiation [42].

Recently, using ab initio molecular dynamics (AIMD) to model ionization of small neutral acetylene clusters, we demonstrated the potential of this conversion mechanism for forming aromatic molecules.[26, 39, 43] This process can lead to molecular growth, whereby 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 three and four 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 [44], which is particularly important due to its prebiotic nature.

In this paper, we establish the strong relevance of the intra-cluster growth mechanism on the molecular formation in molecular cloud environments. By applying this mechanism to acetylene and cyanoacetylene mixed clusters, we were able to successfully predict benzonitrile radical cation formation. This result is significant, as the benzonitrile molecule was recently identified experimentally in TMC-1. Moreover, the intra-cluster growth mechanism perceive 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. Moreover, our results show the formation of additional nitrogenous organic molecules, which can serve as the basis of future astrophysical research studies.

This paper is organized as follows: Section II.a introduces the subject of neutral van der Waals structures of pure cyanoacetylene clusters, and includes a discussion of their stability and the stability of the ionized clusters. AIMD simulations were performed to study the resulting condition of the clusters upon ionization. The AIMD results of pure and mixed clusters are presented in Sections II.b.i and II.b.ii, respectively. Section II.c reviews the mechanism for benzonitrile formation from a mixed trimer cluster. Details of our calculations are presented in Section III, followed by the Conclusion in Section IV.

1. Tielens, A.G.G.M., *The molecular universe.* Reviews of Modern Physics, 2013. **85**(3): p. 1021-1081.

2. Agúndez, M. and V. Wakelam, *Chemistry of Dark Clouds: Databases, Networks, and Models.* Chemical Reviews, 2013. **113**(12): p. 8710-8737.

3. Kvenvolden, K., J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnamperuma, I.R. Kaplan, and C. Moore, *Evidence for Extraterrestrial Amino-acids and Hydrocarbons in the Murchison Meteorite.* Nature, 1970. **228**(5275): p. 923-926.

4. Mullie, F. and J. Reisse. *Organic matter in carbonaceous chondrites*. 1987. Berlin, Heidelberg: Springer Berlin Heidelberg.

5. Cooper, G., N. Kimmich, W. Belisle, J. Sarinana, K. Brabham, and L. Garrel, *Carbonaceous meteorites as a source of sugar-related organic compounds for the early Earth.* Nature, 2001. **414**(6866): p. 879-883.

6. Irvine, W.M., *Extraterrestrial Organic Matter: A review.* Origins of life and evolution of the biosphere, 1998. **28**(4): p. 365-383.

7. Sellgrem, K., *The near-infrared continuum emission of visual reflection nebulae.* Astrophysical Journal, Part 1 1984. **277**: p. 623-633.

8. Tielens, A.G.G.M., *Interstellar Polycyclic Aromatic Hydrocarbon Molecules.* Annual Review of Astronomy and Astrophysics, 2008. **46**(1): p. 289-337.

9. Allamandola, L.J., A.G.G.M. Tielens, and J.R. Barker, *Interstellar polycyclic aromatic hydrocarbons - The infrared emission bands, the excitation/emission mechanism, and the astrophysical implications.* Astrophysical Journal Supplement Series, 1989. **71**: p. 733-775.

10. Leger, A. and J.L. Puget, *Identification of the 'unidentified' IR emission features of interstellar dust?* Astronomy and Astrophysics, 1984. **137**(1): p. L5 - L8.

11. Joblin, C. and G. Mulas, *Interstellar polycylic aromatic hydrocarbons: from space to the laboratory.* Interstellar Dust from Astronomical Observations to Fundamental Studies, 2009. **35**: p. 133-152.

12. Rhee, Y.M., T.J. Lee, M.S. Gudipati, L.J. Allamandola, and M. Head-Gordon, *Charged polycyclic aromatic hydrocarbon clusters and the galactic extended red emission.* Proceedings of the National Academy of Sciences of the United States of America, 2007. **104**(13): p. 5274-5278.

13. Ehrenfreund, P. and M.A. Sephton, *Carbon molecules in space: from astrochemistry to astrobiology.* Faraday Discussions, 2006. **133**(0): p. 277-288.

14. Allamandola, L.J., A.G.G.M. Tielens, and J.R. Barker, *Polycyclic aromatic hydrocarbons and the unidentified infrared emission bands: auto exhaust along the milky way.* The Astrophysical Journal, 1985. **290**: p. L25.

15. Russell, R.W., B.T. Soifer, and S.P. Willner, *The 4 to 8 micron spectrum of NGC 7027.* The Astrophysical Journal, 1977. **217**: p. L149.

16. Sandford, S.A., M. Nuevo, P.P. Bera, and T.J. Lee, *Prebiotic Astrochemistry and the Formation of Molecules of Astrobiological Interest in Interstellar Clouds and Protostellar Disks.* Chemical Reviews, 2020.

17. Mattioda, A.L., L. Rutter, J. Parkhill, M. Head‐Gordon, T.J. Lee, and L.J. Allamandola, *Near‐Infrared Spectroscopy of Nitrogenated Polycyclic Aromatic Hydrocarbon Cations from 0.7 to 2.5 μm.* The Astrophysical Journal, 2008. **680**(2): p. 1243-1255.

18. Peeters, E., S. Hony, C. Van Kerckhoven, A.G.G.M. Tielens, L.J. Allamandola, D.M. Hudgins, and C.W. Bauschlicher, *The rich 6 to 9 $\vec\mu$m spectrum of interstellar PAHs\*.* A&A, 2002. **390**(3): p. 1089-1113.

19. Hudgins, D.M., C.W. Bauschlicher, Jr., and L.J. Allamandola, *Variations in the Peak Position of the 6.2 μm Interstellar Emission Feature: A Tracer of N in the Interstellar Polycyclic Aromatic Hydrocarbon Population.* The Astrophysical Journal, 2005. **632**: p. 316.

20. Bera, P.P., T. Stein, M. Head-Gordon, and T.J. Lee, *Mechanisms of the Formation of Adenine, Guanine, and Their Analogues in UV-Irradiated Mixed NH3:H2O Molecular Ices Containing Purine.* Astrobiology, 2017. **17**(8): p. 771-785.

21. McGuire, B.A., A.M. Burkhardt, S. Kalenskii, C.N. Shingledecker, A.J. Remijan, E. Herbst, and M.C. McCarthy, *Detection of the aromatic molecule benzonitrile (&lt;em&gt;c&lt;/em&gt;-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CN) in the interstellar medium.* Science, 2018. **359**(6372): p. 202.

22. Benson, P.J. and P.C. Myers, *A Survey for Dense Cores in Dark Clouds.* The Astrophysical Journal Supplement Series, 1989. **71**: p. 89.

23. Prasad, S.S. and S.P. Tarafdar, *UV radiation field inside dense clouds - Its possible existence and chemical implications.* The Astrophysical Journal, 1983. **267**: p. 603-609.

24. McGuire, B.A., A.M. Burkhardt, C.N. Shingledecker, S.V. Kalenskii, E. Herbst, A.J. Remijan, and M.C. McCarthy, *Detection of Interstellar HC 5 O in TMC-1 with the Green Bank Telescope.* The Astrophysical Journal, 2017. **843**(2): p. L28.

25. Gratier, P., L. Majumdar, M. Ohishi, E. Roueff, J.C. Loison, K.M. Hickson, and V. Wakelam, *A NEW REFERENCE CHEMICAL COMPOSITION FOR TMC-1.* The Astrophysical Journal Supplement Series, 2016. **225**(2): p. 25.

26. Stein, T. and J. Jose, *Molecular Formation upon Ionization of van der Waals Clusters and Implication to Astrochemistry.* Israel Journal of Chemistry, 2020. **60**: p. 1-9.

27. Klemperer, W. and V. Vaida, *Molecular complexes in close and far away.* Proceedings of the National Academy of Sciences, 2006. **103**(28): p. 10584-10588.

28. Ono, Y. and C.Y. Ng, *A study of the unimolecular decomposition of the (C2H2)3+ complex.* Journal of the American Chemical Society, 1982. **104**(18): p. 4752-4758.

29. Shinohara, H., H. Sato, and N. Washida, *Photoionization mass spectroscopic studies of ethylene and acetylene clusters: intracluster excess energy dissipation.* The Journal of Physical Chemistry, 1990. **94**(17): p. 6718-6723.

30. Booze, J.A. and T. Baer, *The photoionization and dissociation dynamics of energy‐selected acetylene dimers, trimers, and tetramers.* The Journal of Chemical Physics, 1993. **98**(1): p. 186-200.

31. Coolbaugh, M.T., S.G. Whitney, G. Vaidyanathan, and J.F. Garvey, *Intracluster polymerization reactions within acetylene and methylacetylene clusters ions.* The Journal of Physical Chemistry, 1992. **96**(23): p. 9139-9144.

32. Hrouda, V., M. Roeselová, and T. Bally, *The C4H4•+ potential energy surface. 3. The reaction of acetylene with its radical cation.* The Journal of Physical Chemistry A, 1997. **101**(21): p. 3925-3935.

33. Momoh, P.O., S.A. Abrash, R. Mabrouki, and M.S. El-Shall, *Polymerization of ionized acetylene clusters into covalent bonded ions:  evidence for the formation of benzene radical cation.* Journal of the American Chemical Society, 2006. **128**(38): p. 12408-12409.

34. Momoh, P.O. and M.S. El-Shall, *Stepwise hydration of ionized acetylene trimer. Further evidence for the formation of benzene radical cation.* Chemical Physics Letters, 2007. **436**(1–3): p. 25-29.

35. Momoh, P.O., A.-R. Soliman, M. Meot-Ner, A. Ricca, and M.S. El-Shall, *Formation of Complex Organics from Acetylene Catalyzed by Ionized Benzene.* Journal of the American Chemical Society, 2008. **130**(39): p. 12848-12849.

36. Momoh, P.O., A.M. Hamid, A.-R. Soliman, S.A. Abrash, and M.S. El-Shall, *Structure of the C8H8•+ radical cation formed by electron impact ionization of acetylene clusters. Evidence for a (Benzene•+·Acetylene) complex.* The Journal of Physical Chemistry Letters, 2011. **2**(19): p. 2412-2419.

37. Momoh, P.O., A.M. Hamid, S.A. Abrash, and M. Samy El-Shall, *Structure and hydration of the C4H4•+ ion formed by electron impact ionization of acetylene clusters.* The Journal of Chemical Physics, 2011. **134**(20): p. 204315.

38. Relph, R.A., J.C. Bopp, J.R. Roscioli, and M.A. Johnson, *Structural characterization of (C2H2)1–6+ cluster ions by vibrational predissociation spectroscopy.* The Journal of Chemical Physics, 2009. **131**(11): p. 114305.

39. Stein, T., B. Bandyopadhyay, T.P. Troy, Y. Fang, O. Kostko, M. Ahmed, and M. Head-Gordon, *Ab initio dynamics and photoionization mass spectrometry reveal ion-molecule pathways from ionized acetylene clusters to benzene cation.* Proc Natl Acad Sci U S A, 2017. **114**(21): p. E4125-E4133.

40. Ahmed, M. and O. Kostko, *From atoms to aerosols: probing clusters and nanoparticles with synchrotron based mass spectrometry and X-ray spectroscopy.* Physical Chemistry Chemical Physics, 2020. **22**(5): p. 2713-2737.

41. Momoh, P.O., I.K. Attah, M.S. El-Shall, R.P.F. Kanters, J.M. Pinski, and S.A. Abrash, *Formation of covalently bonded polycyclic hydrocarbon ions by Intracluster polymerization of ionized ethynylbenzene clusters.* The Journal of Physical Chemistry A, 2014. **118**(37): p. 8251-8263.

42. Junfeng, Z., C. Tao, and G.G.M.T. Alexander, *Laboratory Photochemistry of Pyrene Clusters: An Efficient Way to Form Large PAHs.* The Astrophysical Journal, 2018. **863**(2): p. 128.

43. Tamar, S., B. Partha P., L. Timothy J., and H.-G. Martin, *Molecular Growth upon Ionization of Van Der Waals Clusters Containing HCCH and HCN is a Pathway to Prebiotic Molecules*. 2020.

44. Stein, T., P.P. Bera, T.J. Lee, and M. Head-Gordon, *Molecular growth upon ionization of van der Waals clusters containing HCCH and HCN is a pathway to prebiotic molecules.* Physical Chemistry Chemical Physics, 2020. **22**(36): p. 20337-20348.