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Case Study

Computational Approach for Architecture, Tailoring, and Advancements in Perfluorinated Compounds: Synthesis, Characterization, and Future Directions in Fire Suppression Technology

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Abstract: The demand for effective fire extinguishants has spurred investigation into novel perfluorinated molecules due to their exceptional properties, including high thermal stability, low toxicity, and eco-friendliness. This study presents a computational framework for designing and tailoring perfluorinated compounds as potential alternatives to traditional extinguishing agents. The research centers on elucidating the synthesis, molecular architecture, and characterization of these compounds to enhance their fire suppression capabilities while mitigating environmental impact. By employing computational methods, molecular modeling, and advanced spectroscopic techniques, the structural intricacies and potential applications of perfluorinated compounds in fire suppression are investigated. Additionally, future research directions aimed at addressing challenges and advancing the development of environmentally sustainable fire extinguishants are discussed. This manuscript contributes to the ongoing efforts to replace conventional extinguishing agents with safer and more environmentally friendly alternatives.

***Keywords*:** computational approach, tailoring, advancements, perfluorinated compounds, fire suppression technology

1. Introduction

Fire extinguishants are indispensable for safeguarding lives and property from the destructive impacts of fires. However, traditional extinguishing agents present significant environmental hazards, including ozone depletion and contributions to global warming. In response to these challenges, researchers have turned their attention to exploring alternative solutions, with particular interest in perfluorinated molecules.[1] These compounds offer unique properties, including high thermal stability, low toxicity, and environmental friendliness, making them promising candidates for fire suppression.[2-4] Perfluorinated molecules, characterized by carbon chains entirely substituted by fluorine atoms, present distinct advantages in combating fires effectively and sustainably.[5] With a growing emphasis on environmental sustainability, there is a pressing need for extinguishants that minimize ozone depletion and greenhouse gas emissions. Perfluorinated compounds represent a significant advancement in addressing these concerns, offering safer and more environmentally friendly fire suppression solutions. New approaches, and requirements, for the synthesis and structural characterization of different stereochemistry-containing perfluorinated frameworks are crucial in current scientific

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endeavors.

The widespread use of ozone-depleting substances (ODSs) and compounds with high Global Warming Potentials (GWPs) in various applications for decades has posed significant risks to environmental sustainability and human health.[6,7] Given the adverse effects of ODSs, there is an urgent need to transition towards more environmentally friendly alternatives. Perfluorinated substances, commonly used in fluorotelomers, emerge as promising replacements for ODSs due to their advantageous properties, including thermal stability, low toxicity, and negligible impact on ozone depletion.[8] Fluorotelomers serve multiple purposes, either as standalone active components, such as in firefighting foams or as integral parts of more intricate formulations, such as impregnating agents.[9] Their versatile applications encompass firefighting foams, water-repellent and dirt-repellent textiles and mats, grease-repellent papers, and surface treatments for tiles and flooring materials.[9] In contrast, the uses of perfluoroalkyl carboxylic acids (PFCA) are more limited, with one notable application being their utilization as process aids in the production of various fluoropolymers like polytetrafluoroethylene (PTFE).[10] They offer a viable solution to mitigate the adverse effects associated with traditional ODSs. Moreover, the development of environmentally friendly alternatives aligns with global initiatives aimed at addressing climate change and promoting sustainable practices. By transitioning away from ODSs towards perfluorinated compounds, industries can contribute to reducing their carbon footprint and fostering environmental stewardship. Furthermore, advancements in computational design and synthesis play a pivotal role in accelerating the development of perfluorinated alternatives. Computational techniques enable researchers to predict the behavior and properties of these molecules, facilitating the design of tailored compounds with enhanced efficacy and reduced environmental impact.[11]

In this context, this research discussion focuses on the design, synthesis, and molecular modeling of perfluorinated frameworks to create optimal fire extinguishants. This endeavor is critical not only for addressing environmental concerns but also for meeting the diverse needs of various industrial applications.[11] The textile industry is a significant consumer of perfluorinated substances, primarily for treating items such as sun-blocking textiles, car textiles, and work clothes.[12] Additionally, perfluorinated compounds find diverse applications in areas like firefighting foams, water-repellent textiles, grease-repellent papers, and surface treatments for tiles and flooring materials.[13,14] Despite their wide-ranging use, the foundational principles guiding the design and synthesis of perfluorinated compounds are still evolving. There is a need for more quantitative analysis of perfluorinated compound processing, especially concerning their effectiveness as fire extinguishants, to enhance design efficiency. Mathematical frameworks rooted in molecular models offer an integrated perspective on these systems, aiding their development. Moreover, there are descriptions of compositions for fire extinguishing and methods for fire control or prevention, utilizing fluorinated ketones with up to two hydrogen atoms as extinguishing agents. These agents can be used independently or alongside co-extinguishing agents like hydrofluorocarbons, hydrochlorofluorocarbons, hydrofluoroethers, iodofluorocarbons, chlorofluorocarbons, bromofluorocarbons, hydrobromofluorocarbons, and mixtures thereof. Thus, a thorough exploration of computational design strategies is essential for developing safer and more sustainable fire extinguishing solutions.

2. Current research

Synthesis of organic molecules/compounds and their architecture and tailoring, especially fluorine-containing atoms in their topology, has significance in current science and textile developments. Fluorinated substances have been used since the 1950s due to their unique properties such as thermal stability, water, dirt, and grease repellency.[15-16] Perfluorinated molecules belong to a group of organic compounds characterized by a carbon chain in which all hydrogen atoms have been replaced with fluorine atoms.[5] Figure 1 depicts the molecular structure of linear/branched/cyclic frameworks of perfluorinated molecules/compounds, highlighting their diverse architectural possibilities. The perfluorinated molecules serve as physical agents[17] and can also function as chemically active counter radicals for H, OH, and O in the flame zones of fires after thermal degradation.[18] Making changes in the structures of molecular designs, and flame suppression effectiveness of perfluorinated compounds are of significance in fire protection science.

The methodologies for selective functionalization and synthesis of fluorinated compounds are crucial aspects of current research. These methods encompass a diverse range of techniques, including fluorination of phenylsulfanyl esters using difluoroiodotoluene,[19] development of novel fluorinated block copolymer architectures,[20] synthesis of fluorinated

copolymers via copper-mediated living radical polymerization,[21] investigation into the kinetics of homopolymerization of fluorinated acrylates,[22] exploration of the synthesis and properties of new fluorinated esters and thioesters,[23] and the fluorination of sulfanyl amides using difluoroiodoarene reagents.[24] Additionally, chemical modifications of fluorinated polyimides and other techniques have been reported, along with the preparation and characterization of fluorinated and hydrocarbon ester functionalized poly(p-phenylenes) and partially bridged-fluorinated dimethyl bicyclo[1.1.1] pentane-1,3-dicarboxylates, including their solubility in supercritical fluids. These methodologies aimed to achieve tailored structures of fluorinated compounds, which are essential for their efficacy as fire extinguishants and in textile engineering.

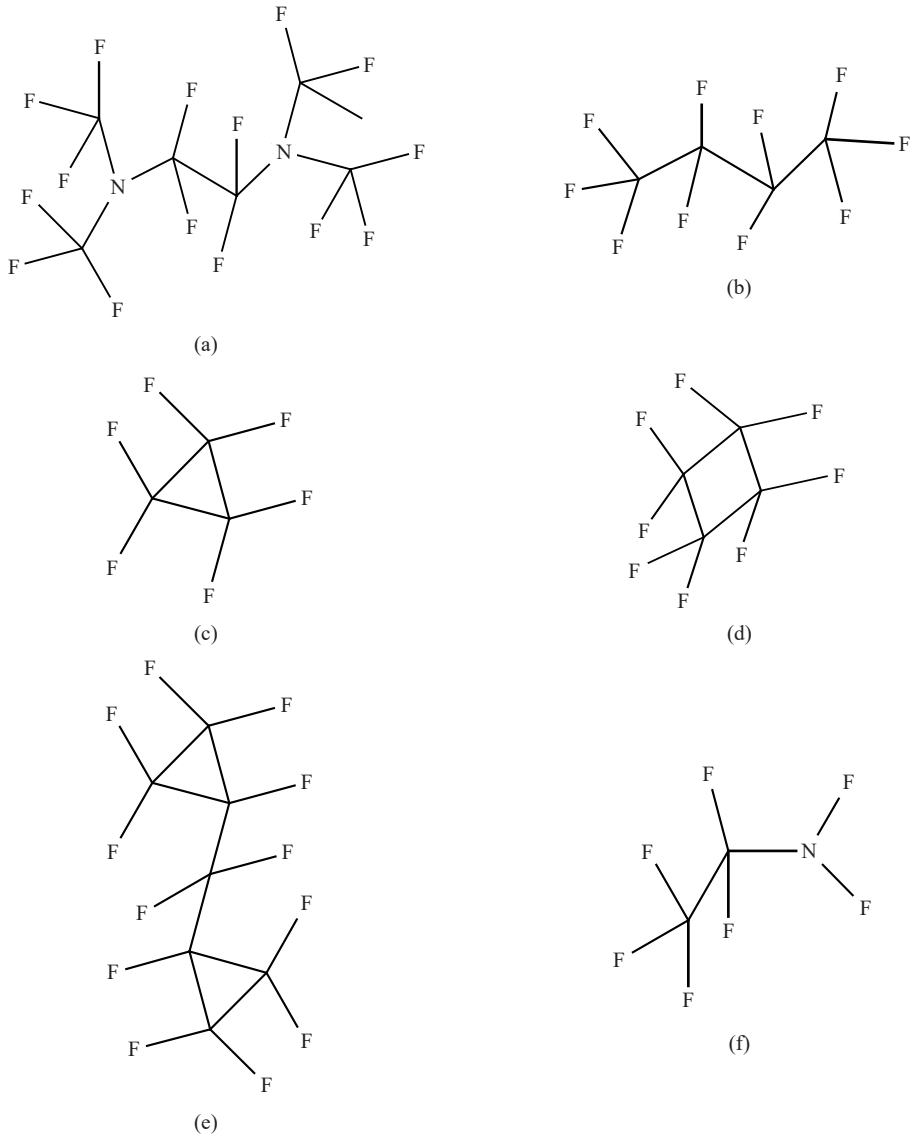


Figure 1. An illustration of the molecular structure of linear/branched/cyclic frameworks of perfluorinated molecules/compounds

Our main objective is to focus on the architecture and tailoring of perfluorinated compounds; such topologically predefined and modified structures have played an important role in the development of fire extinguishants and advancing textile engineering. Further development in this area requires innovative approaches to manufacturing procedures under various experimental conditions. One of the ways to achieve this target is by using molecular

modeling, a computational approach, which will further help in architecture and tailoring by manipulating atomic locations within target molecular frameworks. For the designing of linear/branched/cyclic frameworks of perfluorinated molecules/compounds, molecular modeling has provided a theoretical model through computational calculations.[25] Firstly, the different models of target molecules were obtained by changing hydrocarbon into perfluorinated frameworks. Secondly, we can achieve the same by increasing or decreasing the chain lengths of these perfluorinated molecules. After that, the cyclic moieties of proposed molecules were examined. The interrelationship among the linear/branched/cyclic network of perfluorinated compounds was designed by a structural change, which further helped in the modifications of our target molecules. The positive results will be a promise for the future, which could be extended for a noble solution for the universe.

Recognizing the importance of computational approaches, Kumar and Johar[26] designed models for perfluorinated compounds critical for developing potential fire-extinguishing agents. Through computational science, they innovated new organic compounds as substitutes for halons, aiming for attributes like low Global Warming Potentials (GWP), short Atmospheric Lifetimes (ALT), zero Ozone Depletion Potential (ODP), and minimal toxicity. This effort aligns with global efforts to replace Ozone Depleting Substances (ODSs) and compounds with high Global Warming Potentials (GWPs). Addressing this challenge requires the scientific community to devise innovative perfluorinated compounds using diverse methodologies.

Molecular modeling also permits us to understand their efficiency as fire extinguishing agents through mathematical models. The development of better analytical methods for the study of perfluorinated substances is the main consideration while writing this article. Unfortunately, to date, there is no satisfactory process developed to understand the difficulties that come during the design of such compounds and help to avoid certain serious problems in tailoring and synthesis of perfluorinated molecules. Molecular modeling played a pivotal role in planning by making suitable alterations in their synthesis as well as their utilization as potential fire extinguishants. It is only possible by producing mathematical models with this computational approach, which is a better solution for the tailoring of perfluorinated molecules. Therefore, we designed a new methodology with a special focus on the synthesis, modeling, and modification of reaction mechanisms and their related processes. Characterization of these linear, branched, and cyclic organic frameworks of perfluorinated compounds by modern spectroscopic techniques is the key objective.

In short, we always tried to develop an advanced tactic, computational study, with a special feature about perfluorinated compounds for their utilization as potential fire extinguishants in the future. Theoretical and experimental views related to the aim increase our knowledge about the design and development of perfluorinated compounds which will act as a better prospective for the replacement of halons as fire extinguishants. These results are readily applicable to perfluorinated compound architecture and tailoring. The synthesis and characterization of perfluorinated compounds, which will serve as key ingredients and components in the development of fire suppression technologies, will take these test results into account.

3. Computational methodology and novel perfluorinated molecules

We propose to explore the importance and newer possibilities of perfluorinated compounds with their utilization in the development of fire extinguishants by using various modern spectroscopic characterization techniques. For this purpose, our approach involves refining synthetic methods to prepare perfluorinated compounds with various linear, branched, and cyclic frameworks, ensuring precise molecular structures. Modern spectroscopic characterization techniques are a broad range of analytical applications, which can be successfully applied for the study of interfacial phenomena along with conformational changes of the proposed models of fire extinguishants. Besides all these, to get potential fire extinguishants, molecular modeling is further helping in the architecture and tailoring of such compounds, which have better fire extinguishing properties. After considering all that, we utilized all these modern approaches in the development of perfluorinated molecules, which may provide a suitable solution, as a whole, as potential fire extinguishants. From the proposed designs fewer topologies are specified below.

To scrutinize the conformational changes after thermal decomposition pathways, three-dimensional conformations of perfluorinated compounds are very important. These structures profoundly influence stability, physical attributes, and chemical behaviors, all of which impact their efficacy as fire extinguishants.

4. Designing, modeling, synthesis, and characterization of fluorinated compounds

Our research proposal centers on the exploration of designing, modeling, synthesizing, and characterizing fluorinated compounds, particularly focusing on their potential as fire extinguishants. We aim to investigate the contributions of modern spectroscopic techniques, thermal decomposition pathways, and molecular modeling to the development of perfluorinated compounds for fire suppression applications. Illustrations depicting chemical reactions for the synthesis of hexafluorocyclopropane and perfluorocyclobutane (Figure 2 and Figure 3) underscore our examination of various stereochemistries of linear, branched, and cyclic perfluorinated compounds and their influence on fire extinguishing capabilities. How did modern spectroscopic, thermal decomposition pathways, and molecular modeling play a prominent and attractive role in the development of perfluorinated compounds or fire extinguishing agents? This is our main intention to investigate through this research proposal. The determination of their structures and the need for a deeper understanding of their modes of action were studied for the preparation of perfluorinated compounds and the development of potential fire extinguishants.

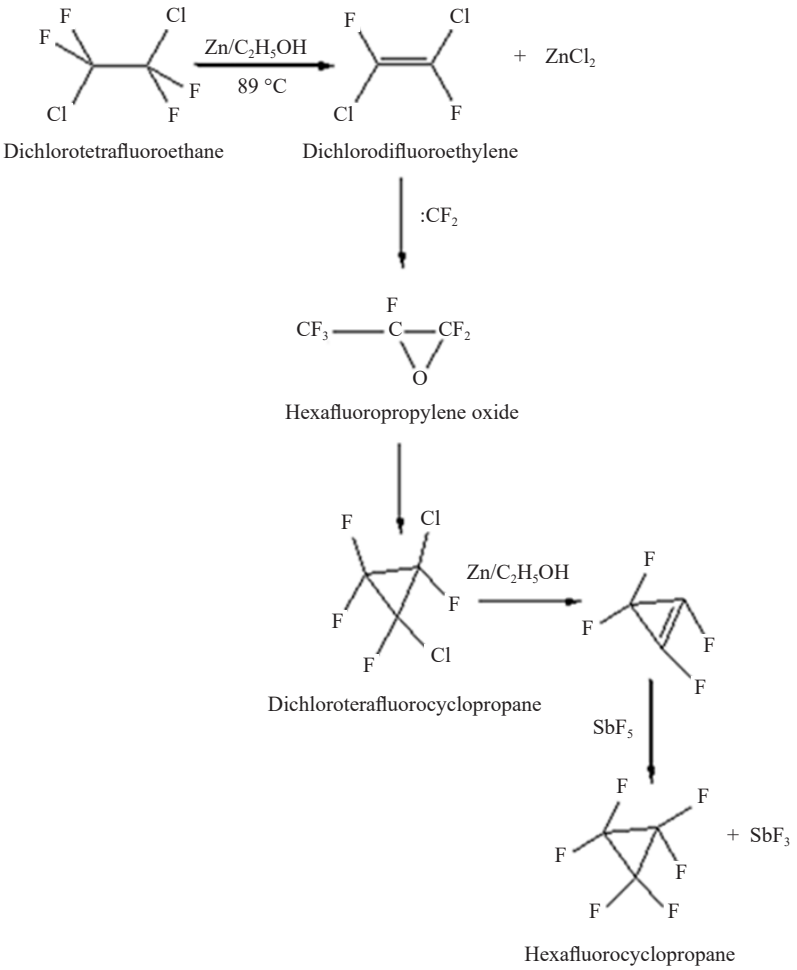


Figure 2. An illustration of the chemical reaction for the preparation of hexafluorocyclopropane

Molecular modeling is undoubtedly used, first of all, to speed up the process of identifying the most potent synthetic perfluorinated compounds as halons alternates, thus facilitating the development of better fire extinguishants. Therefore, a detailed description of the structural variety as well as their synthetic counterparts played a significant role in developing halon alternatives. Some of the important points to be covered under the proposed project are:

1. Design and synthesis of perfluorinated compounds/molecules.
2. Molecular modeling of proposed molecules (A-F) to be synthesized.
3. Structural characterization of the proposed organic frameworks.
4. Implement selective modifications in the skeletons up to the desired lengths.
5. Develop synthetic protocols for fragment-related processes.
6. Establish a structure stability relationship for proposed perfluorinated molecules.
7. Explore the use of nitrogen as building blocks.
8. Investigate the thermal decomposition pathways to understand structural changes.
9. Analyze the Global Warming Potential (GWP) effects and impregnating properties.
10. Evaluate the fire suppression efficacy of synthesized compounds through bench-scale fire tests.

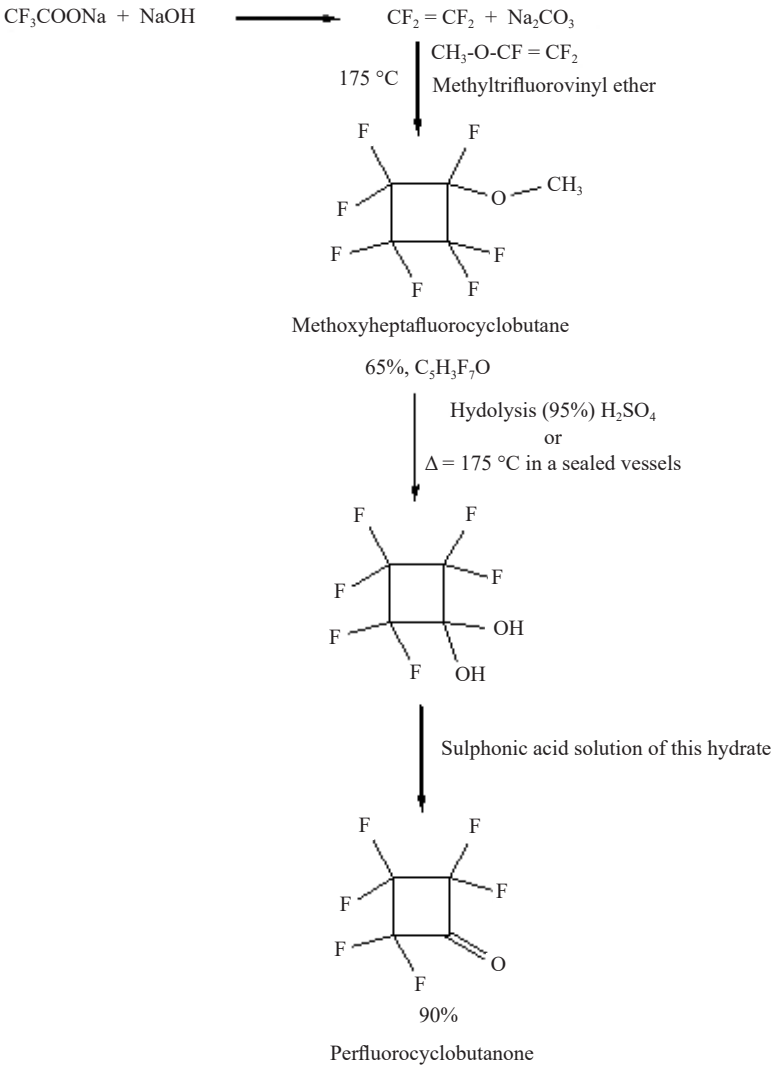


Figure 3. An illustration of the chemical reaction for the preparation of perfluorocyclobutane

On the basis of the above important points/aims that we developed for perfluorinated compounds, these will serve as starting points for our research endeavors. Through this preliminary investigation, we aim to obtain structural insights crucial for understanding the chemical significance and potential utilization of these compounds as fire extinguishants. Characterization measurements of potential fire extinguishants will be derived from the insights gained through

molecular modeling and other analytical techniques.

Because perfluoro compounds have special characteristics and uses, molecular modeling methods are essential. These applications require a realistic prospective model to be modeled. A model has been created and described for perfluorinated chemicals, but there isn't one for non-perfluorinated compounds. Using ab initio calculations and Gibbs ensemble phase equilibrium simulations, this work created a tentative model for single perfluorinated molecules. Next, utilizing all vapor-liquid phase equilibrium data for perfluorinated compounds that were accessible, a realistic unified atom potential model was created and refined. The Columbic interaction for long-range interaction, the Lennard-Jones potential for van der Waals interaction, the partial charge, the harmonic function for bond bending potential, and the seventh order polynomial function of cosine for torsional potential are all included in the model. It does a fair job of replicating the essential characteristics and phase envelope of perfluorinated compounds. To supply the intramolecular force field and partial charge for the electrostatic potential, ab initio calculations were carried out. In order to automate parameterization in the construction of potential models, the Gibbs-Duhem integration approach was extended to the development potential model for a group of complicated molecules. A generalized partial charge set is proposed for chain molecules of perfluorinated chemicals. Because perfluorinated chemicals are stable in water, this study might potentially be used to replicate reverse micelle systems with them as surfactants, which would be more applicable to the industry. Furthermore, by estimating viscosity characteristics under shear, this prospective model might be utilized to explore lubrication with perfluorinated substances. While it is not anticipated that simulations using this potential model can reproduce experimental transport parameters quantitatively, they should yield qualitative insights. It is necessary to have an explicit vi-atom model for dynamic attributes; the ab initio results can be utilized immediately in this endeavor. A helpful method for improving the model would be to compare it with spectroscopic data from experiments.

5. Investigation methods

Physiochemical characterization methods were used to investigate potential fire extinguishants and their efficiency. Spectroscopic spectral studies were conducted at low concentrations of macromolecules, mimicking physiological environments. On the other hand, for heterogeneous systems, as is the case of proposed complexes, where multiple interactions are possible, other substrates on which the organic network of potential fire extinguishing agents is strongly dependent. Therefore, the synthesis and design of a novel network of organic compounds containing fluorine atoms and their use as better fire extinguishants were proposed in this paper.

Various spectroscopic techniques are commonly utilized for the structural characterization of fire extinguishing agent's potential. Elemental analysis, including carbon, hydrogen, and nitrogen content determination, is performed using elemental analyzers such as the Carlo-Erba 1106.[27] Mass spectrometry, particularly the electron ionization (EI) technique, offers insights into the molecular composition and fragmentation patterns.[28] Nuclear magnetic resonance (NMR) spectroscopy, including proton and carbon-13 NMR, provides information on molecular structure and connectivity.[29] Fourier-transform infrared (FTIR) spectroscopy is employed for functional group identification,[30,31] while ultraviolet-visible (UV-Vis) spectroscopy and fluorescence spectroscopy offer insights into electronic transitions and complex formations.[32] C/MS was also applied to detect fragment details of the studied frameworks.[33,34]

Modern spectroscopic characterization methods were applied to investigate thermal stability. Techniques such as differential scanning calorimetry (DSC), atomic force microscopy (AFM), and light scattering provided insights into thermal behavior, surface morphology, and molecular size distribution, respectively, and the nature of changes in the frameworks of perfluorinated molecules, that is, conformational changes, stability factors to heat, and the size and shape of these molecules. The overall thermodynamical parameters of the decomposition event of these perfluorinated molecules were followed by the enthalpy of the used fire extinguishants. Comparison of the thermodynamic parameters helped to understand the thermal factors associated with small exothermic enthalpy changes and the overall binding processes of perfluorinated compounds and their potential as fire suppressants. Furthermore, UV-visible and fluorescence spectroscopy enabled the characterization of cationic complexes in solution, offering valuable information on bonding parameters within the polymeric network of perfluorinated molecules. Suggested condensation of perfluorinated compounds into globule conformation was observed to provide additional insights into the structural transformations of these compounds under varying conditions.

6. Future aspects

The phased-out use of halon extinguishants due to their harmful effects on the stratospheric ozone layer[35,36] necessitates the exploration of alternative fire suppression technologies. While fluorinated alkanes like HFC-227ea (CF_3CHFCF_3), HFC-236fa ($CF_3CH_2CF_3$), and PFC-218 ($CF_3CF_2CF_3$) have emerged as transitional halon replacements,[37] their efficacy and environmental impact remain under scrutiny. It is essential to examine how the hydrogen content of fluoroalkanes influences their pyrolytic and fire-extinguishing mechanisms. Recent investigations have shown that increasing hydrogen content increases the energy barrier of the fire-extinguishing free radical $CF_3^{\bullet}$ produced by these fluorinated alkanes,[38] (Figure 4). Notably, the PFC-218 agent exhibits the highest fire-extinguishing concentration (FEC) while demonstrating minimal corrosive product release and limited combustion promotion.[39] These findings provide insights for molecular engineering and screening of effective and environmentally benign Halon replacements.

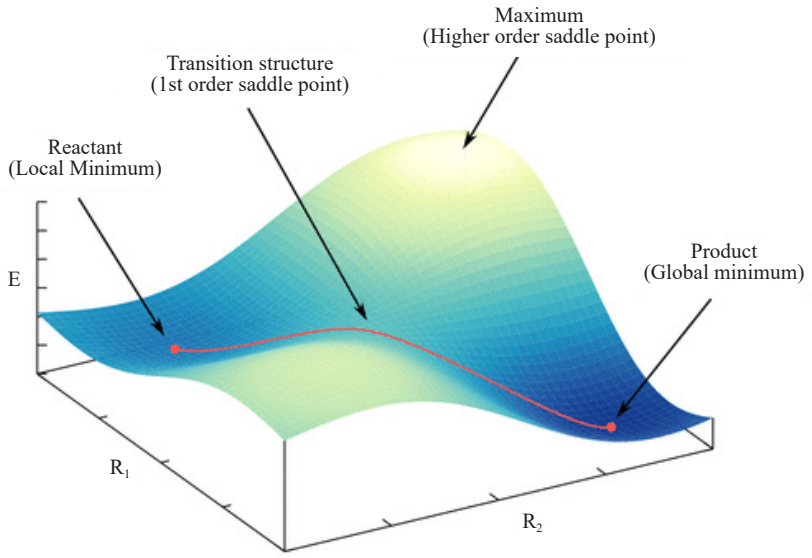
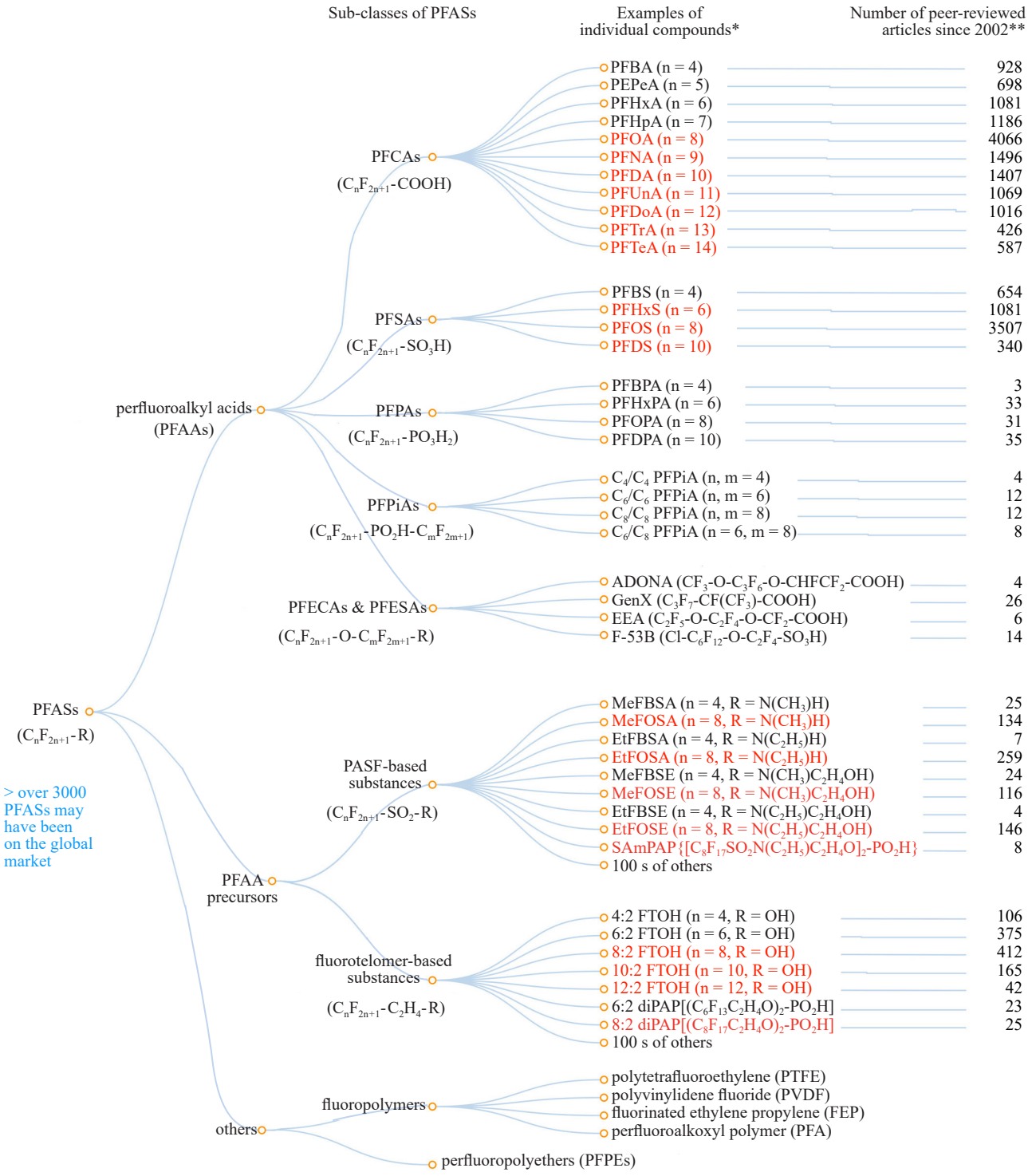


Figure 4. For a hypothetical system with coordinates R_1 and R_2, the Potential Energy Surface (PES) depicts stable states such as equilibrium configurations and reactants or products. Paths can connect minima, and the maximum is a transition state. Transition states, which reflect the least energy needed to transition between two PES minima and are essential to chemical reactions, are first-order saddle points with a maximum in one coordinate and minima in all others[1]

Halon 1211 and Halon 1301 are widely recognized as highly effective fire extinguishants, frequently employed in diverse settings such as museums, airplanes, naval vessels, and aerospace installations.[39] However, the earth's stratospheric ozone layer is continually being destroyed and depleted by $Br^{\bullet}$ and $Cl^{\bullet}$ free radicals generated during the photolysis of halon agents. Halon agents have been outlawed in most cases by the Montreal Protocol and its revisions as a source of significantly ozone-depleting chemicals (ODS).[40] The first generation of Halon replacements discovered during the discovery process are hydrochlorofluorocarbons (HCFCs) and chlorofluorocarbons (CFCs), which have a shorter atmospheric lifetime (ALT) than brominated alkanes.[41,42] Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) were created to mitigate the impacts of ozone depletion, eliminating Br and Cl atoms.[39] However, HFCs and PFC chemicals have significant global warming potential (GWP), for making them less ecologically friendly than HFCs, newer approaches have to be applied.

Hydrofluoroolefins (HFOs) have low GWP and ALT values,[43] but their ability to suppress fire is not as good as halon agents.[44] Moving forward, research efforts should prioritize addressing the limitations of current halon alternatives (Figure 5). For instance, 2-BTP agents containing bromine atoms exhibit promising fire-extinguishing capabilities. However, their effectiveness is tempered by the potential generation of hydrogen bromide (HBr) during firefighting operations, attributed to the presence of bromine. HBr is known to pose health risks to humans and can cause damage to equipment.[39] In conclusion, the Kyoto Protocol designates certain fluorinated alkane fire extinguishing agents as

temporary Halon alternatives.[45]



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* PFASs in RED are those that have been restricted under national/regional/global regulatory or voluntary frameworks, with or without specific exemptions (for details, see OECD (2015), Risk reduction approaches for PFASs. http://oe.cd/iAN)
** The numbers of articles (related to all aspects of research) were retrieved from SciFinder® on Nov. 1, 2016

Figure 5. "Family tree" of PFASs, containing the quantity of peer-reviewed publications published on each since 2002, as well as instances of specific PFASs[1]

While the development of transitional halon alternatives marks progress, there is a pressing need for more effective and environmentally sustainable fire suppression technologies. By leveraging advancements in molecular engineering and screening techniques, researchers can identify novel compounds with improved fire-extinguishing efficacy and minimal environmental impact. Additionally, continued collaboration and adherence to international protocols will be essential to ensure the global adoption of safer and more sustainable fire suppression solutions.

Fluorine, a key component in pharmaceuticals and agrochemicals, has seen significant growth since its introduction in the 1950s. Its use is linked to improved metabolic stability, selectivity, and solubility. However, fluorinated compounds are susceptible to metabolism and liberation of fluoride or low molecular weight fluorinated molecules from fluorine-containing drugs. To avoid potential lethal toxicity, candidates must be monitored. Innovative fluorination reagents and methods have enabled medicinal chemists to install fluorine at various positions in a molecule, but inappropriate placement can lead to stability and toxicity issues. Many fluorinated drugs have excellent stability and safety, but the purpose of collecting examples is to raise awareness of common drug instability and metabolism issues leading to defluorination and resulting reactive/toxic metabolites. Follow-up studies are often necessary, and medicinal chemists must recognize the potential liability of certain fluorine-containing substructures and initiate early profiling before problematic moieties become essential parts of a lead series.

Author contributions

Dr. Rajiv Kumar supervised and wrote this case study. Dr. Chinenye Adaobi Igwegbe suggested some changes in the manuscript, updated the required corrections, and, in the end, approved the manuscript.

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Conflict of interest

The authors declare no conflict of interest, financial or otherwise.

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