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Unraveling the Isoprene-Argon Complex: Insights from Pulsed Nozzle Fourier Transform Microwave Spectroscopy and Computational Analysis

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Abstract

The study of various weakly bound complexes in the interstellar medium has posed significant challenges. Isoprene which is a fundamental organic molecule, and Argon which is a noble gas, form a complex that serves as an essential model system for examining molecular interactions in space. This research investigates the isoprene-Argon complex through the combination of Pulsed Nozzle Fourier Transform Microwave (PNFTMW) spectrometry and advanced computational methods. Utilizing a PNFTIR spectrometer, the study focuses on rotational transitions of both the Isoprene monomer and Isoprene-Argon complex, providing valuable insights into their vibrational and rotational characteristics. The discussion encompasses rotational constants (A, B, C) and dipole moment components (|μa|/D, |μb|/D, |μc|/D), shedding light on the complex's rotational behaviour and charge distribution along principal axes. The observed variations in rotational constants across diverse quantum chemical methods highlight the importance of method selection, while differences in dipole moments show the complex's sensitivity to computational nuances. The findings contribute to a better understanding of the Isoprene-Argon complex's molecular structure and its potential implications in interstellar chemistry. This multidisciplinary approach lays the groundwork for future investigations into molecular interactions and the refinement of computational models for improved predictive accuracy in describing complex molecular properties.

Keywords: Isoprene, Argon, Pulsed Nozzle Fourier Transform Microwave, Interstellar Medium, Computational analysis.

Introduction

In the expansive realm of the interstellar medium (ISM), where molecular interactions occur under extreme conditions, the investigation of weakly bound complexes has become a pivotal pursuit (Whitfield et al., 2013; Keutsch et al., 2013; Etim et al., 2023; Shinggu, et al., 2023). Microwave spectroscopic studies have played a crucial role in unravelling the intricate structures and bonding of such complexes, primarily focusing on hydrogen-bonded and van der Waals interactions (Andrew et al., 2018; Oladimeji et al., 2022). The historical journey began in 1972 when Klemperer and colleagues observed the groundbreaking (HF) complex, initiating an era of exploration into the complexities of molecular bonding (Benjamin et al., 2023). The classification of weakly bound complexes as hydrogen-bonded or van der Waals has stirred debate, with recent studies challenging traditional notions (Obaidulla et al., 2024; Etim et al., 2023). The term "non-covalent interactions" has emerged to encompass both hydrogen bonding and van der Waals interactions, showcasing the evolving landscape of molecular understanding (Samuel et al., 2023; Samuel et al., 2024; Samuel et al., 2023). Amidst these complexities, questions arise regarding the essence of a hydrogen bond, prompting further exploration (Mohsen et al., 2023; Fan et al., 2021). The rotational spectra reveal structural similarities, hinting at a common nature of interaction within these complexes (Nhlabatsi, 2017). Moving into the vast expanse of the ISM, the study of molecular species becomes a fascinating exploration, offering insights into exotic chemistry thriving under extreme conditions (Qu et al., 2016; Suman et al., 2021; Etim, et al., 2021; McCarthy, & McGuire, 2021). The uncharted territory of NH_3–H_2 complexes, contributes to the refinement of our comprehension of interstellar chemistry. The elucidation of bound states and the understanding of molecular dynamics contribute to bridging the gap between theoretical predictions and experimental validations (Zamirri et al., 2019; Shinggu et al., 2023; Etim, & Arunan 2016; Mondal et al., 2021).

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Simultaneously, in a parallel exploration of the ISM, the search for novel molecular species continues through rotational spectroscopy (Melli, 2023; Etim et al., 2018; Belloche et al., 2017). Furonitrile, with its potential significance in astrochemistry, emerges as a promising candidate for detection in the ISM (Etim et al., 2021; Grogan, 2021; Etim et al., 2017). This research aims to characterize the rotational spectra of isolated 2- and 3-furonitrile and their complexes with water, providing crucial insights into their interactions. In the pursuit of understanding the rich chemistry of the ISM, these preliminary investigations mark the initial steps towards unravelling the mysteries of isoprene...Ar complexes (Etim, 2023; Asuquo et al., 2017; Etim, & Arunan, 2015; Samuel et al., 2023). They offer a glimpse into the diverse molecular landscapes that adorn the cosmic canvas, promising to expand our knowledge of the intricate dance of molecules in the interstellar medium (Chandler et al., 1983; Zewail, 2000; Sandoval, & Hyster, 2020). In the vast expanse of the interstellar medium, where molecular interactions defy conventional norms, the exploration of weakly bound complexes becomes a compelling endeavour (Zhu et al., 2022; Messinger, 2021; Brice, 2019).

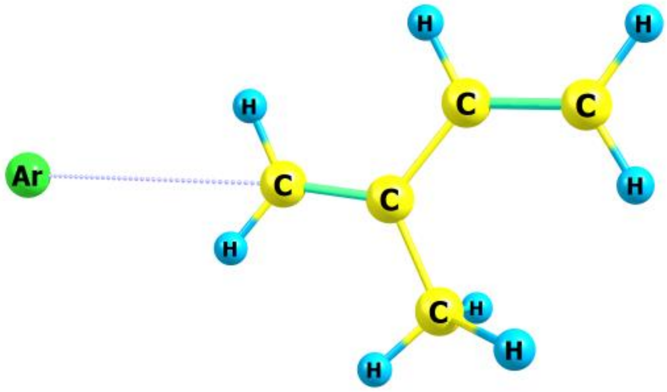

Figure 1: Isoprene----Argon Complex (Gaussian 09 suite software)

The classification debate between hydrogen bonding and van der Waals interactions, spurred by studies on Rg-HX complexes, adds a layer of complexity. Recent investigations challenge traditional notions, expanding the repertoire of potential proton acceptors (Ramphal, 2021; Ditler, & Luber 2022; Domingos et al., 2018). The evolving landscape prompts introspection into the essence of a hydrogen bond, with rare gases even considered as acceptors under specific conditions (Shinggu et al., 2023; Magaji et al., 2022; Etim et al., 2022). This research navigates through microwave spectroscopic and ab initio results, focusing on isoprene argon complexes formed in the interstellar medium (Chen et al., 2022; Kurdziel, 2004; Wickramasinghe, & Bauval 2017). As this research describes the rotational spectra of C_5H_8-H_2X complexes, structural insights emerge, hinting at common interaction patterns. The study extends to asymmetric tops, posing challenges in the assignment but offering crucial perspectives into molecular dynamics (Arunan et al., 2004). In parallel, the search for novel molecular species persists, guided by rotational spectroscopy principles (Becucci, & Melandri 2016). Isoprene and isoprene---Argon complexes with their potential significance in the ISM, remain largely unexplored. As these preliminary investigations unfold, they mark the initial steps in unravelling the mysteries of isoprene Argon complexes (Asvany, & Schlemmer 2021; Etim et al., 2018). The diverse molecular species uncovered offer a glimpse into the cosmic chemistry that adorns the celestial canvas, paving the way for deeper exploration and understanding (Francis, 2022; Etim et al., 2018; Vogiatzis, et al., 2018).

Materials and Methods

Pulsed Nozzle Fourier Transform Microwave (PN-FTMW) Spectrometry

The methodology employed in this study utilized a Pulsed Microwave Fourier Transform Infrared (PNFTIR) spectrometer to investigate Argon-isoprene complexes in the interstellar medium (ISM). Isoprene...argon had 10 transitions in the frequency range of 7 to 14.2GHz (Gorai et al., 2017). Sample preparation involved careful selection and characterization of samples to ensure their purity and stability during analysis. The supersonic expansion technique introduced the gas-phase molecular complexes into the spectrometer, forming a supersonic molecular beam crucial for well-defined rotational spectra (Etim et al., 2017; Nasrollahzadeh et al., 2018). Pulsed microwave excitation-induced rotational transitions, and Fourier Transform Infrared (FTIR) detection probed the resulting molecular states, providing information about vibrational and rotational characteristics (Chimiak & Eiler, 2024; Mani, 2018; Etim et al., 2020). The high-resolution capabilities of the PNFTIR spectrometer, both in the time and frequency domains, enabled precise determination of transition frequencies and intensities (Shinggu et al., 2023). Advanced computational methods were then applied for data analysis, allowing for the identification of molecular species and their complexes (Jelínek, 2017).

The PNFTIR spectrometer's applications in previous investigations, including the study of phenylacetylene and propargyl alcohol, demonstrated its versatility in exploring complex molecular structures. Phenylacetylene, an intermediate in the formation of soot particles in interstellar space, exemplified the spectrometer's efficacy in unravelling the molecular intricacies of the cosmos. This methodology contributes to ongoing efforts to understand the chemical diversity of the ISM, particularly in the exploration of isomeric counterparts and branched-chain molecules (Öberg, 2016; Etim et al., 2024; Samuel et al., 2024). The detailed experimental setup, sample preparation, and data analysis provide a comprehensive framework for utilizing the PNFTIR spectrometer in advancing our knowledge of interstellar molecular complexes. The homebuilt PN-FTMW spectrometer in our laboratory has been used for the preliminary studies on the Isoprene. Argon weakly bound complex. Details of the working principles and components of this instrument can be found in the review of its advances and application (Magaji et al., 2022).

PN-FTMW spectroscopy is a technological marvel, that takes centre stage in molecular analysis. It facilitates the study of organic molecules, weakly bound complexes, and reaction intermediates with unparalleled resolution and sensitivity. The successful implementation of this technique, demonstrated through the examination of standard interstellar molecules like OCS, showcases its high resolution and sensitivity, unveiling the intricacies of molecular transitions (Shinggu et al., 2023; Samuel et al., 2023).

Computational Methodology

The computational methodology employed in this research involves the use of quantum chemical calculations to analyze the molecular properties of the isoprene-Argon complex. Specifically, electronic structure calculations were performed using various quantum chemical methods, including MP2/6-31G*, HF/6-311++G(d,p), MP4/6-311G+(d,p), and B3LYP/6-311+G(d,p). These calculations aimed to predict rotational constants and dipole moment components of the complex, providing insights into its structural characteristics (Frisch et al., 2009; Etim et al., 2021). The initial step involved geometry optimization of the isoprene-Argon complex using the chosen quantum chemical methods. The optimized geometry was then utilized to calculate rotational constants (A, B, C) and dipole moment components ($|\mu a|/D$, $|\mu b|/D$, $|\mu c|/D$) for the complex. The selection of various quantum chemical methods allowed for the exploration of different levels of electronic structure theory and their impact on the accuracy of the computed molecular properties.

Benchmarking calculations were performed to compare the results obtained from different methods and to assess their agreement with experimental data. This iterative process helped refine the computational model and enhance the reliability of predictions regarding the Isoprene-Argon complex's molecular structure. The computational methodology combined geometry optimization and quantum chemical calculations to predict key molecular properties, contributing to a comprehensive understanding of the isoprene-Argon complex. The insights gained from these calculations complemented experimental findings obtained through Pulsed Nozzle Fourier Transform Microwave (PNFTMW) spectrometry, providing a multidimensional perspective on the complex's structural and chemical characteristics (Etim et al., 2020; Etim et al., 2021; Ushie et al., 2019).

Results

Search for the Isoprene Monomer and Isoprene...Argon Rotational Spectra

Although the microwave spectrum of isoprene is known in the frequency range mentioned above in searching for the transitions for the isoprene...argon complex, we began by for the monomer transitions within the frequency range of our spectrometer. In searching for both the isoprene monomer and isoprene...argon complex transitions, argon was used as the carrier gas. The gas was bubbled through the isoprene sample. The mixture was expanded from a stagnation pressure of 1.1 bar and a microwave pulse of 1µs time duration was used during the search.

A total of ten (10) transitions in the range of 7 to 14.2GHz were observed which could well fit very well with the theoretically predicted transitions for the monomer. These transitions are shown in Table 1.2. These transitions were shown to be dependent only on isoprene as they were still observed when helium (instead of argon) was used as the carrier gas. Two transitions at 9758.263281MHz and 9920.253516MHz were observed while searching for the 9749.371343 MHz (2_{20}-1_{10} line) and 9919.220000 MHz (2_{21}-1_{11} line) transitions respectively. These transitions were dependent on both isoprene and argon. With helium as the carrier gas, these lines could not be seen, thus they are transitions corresponding to the isoprene...argon weakly bound complex.

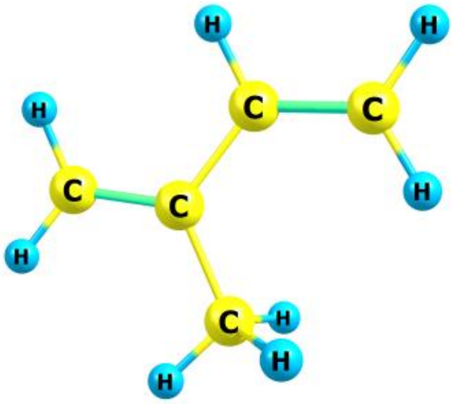

Figure 2: Isoprene Monomer (Gaussian 09 suite software)

Experimental results for Isoprene-Argon Complex

Table 1.1: Rotational constants and dipole moment components along the three Principal axes for the isoprene...Ar complex

Parameter	Value
A/MHz	4,166.8
B/MHz	731.1
C/MHz	624.4
|μa|/D	0.1
|μb|/D	0.0
|μc|/D	0.0

The provided table (Table 1.1) outlines key rotational constants and dipole moment components for the isoprene...Ar complex. The rotational constants A, B, and C elucidate the molecule's rotational behaviour about its principal axes. A high value of A (4,166.8 MHz) suggests significant resistance to rotation about the axis of maximum moment of inertia, reflecting the molecular structure's inherent stability or complexity. The values of B (731.1 MHz) and C (624.4 MHz) provide additional details about rotational dynamics around axes of intermediate and minimum moments of inertia, respectively. These constants collectively contribute to a comprehensive understanding of the complex's rotational properties, offering valuable insights into its structural characteristics and potential implications for its interactions with other molecules.

The dipole moment components, |μa|/D, |μb|/D, and |μc|/D, reveal details about the charge distribution along the three principal axes. Notably, the non-zero value of |μa| (0.1 D) indicates an asymmetric charge distribution along the axis of maximum moment of inertia. This asymmetry may be indicative of specific chemical interactions or structural features within the isoprene...Ar complex. The absence of dipole moment along axes b and c (|μb|/D = 0.0, |μc|/D = 0.0) suggests a certain level of symmetry or cancellation of charges along these directions. Overall, the combined information from rotational constants and dipole moment components enhances our understanding of the isoprene...Ar complex's molecular characteristics, potentially offer valuable insights for applications in chemistry, physics, or related fields.

Table 1.2: Observed Transitions of Isoprene Monomer

Frequency (MHz)	Transition J K_{-1} K_{+1} --	J K_{-1} K_{+1}	Obs-Cal (MHz)
7256.4944	2, 1, 1	2, 0, 2	0.0500
9444.4336	2, 0, 2	1, 1, 1	-0.0040
9830.6563	3, 1, 2	2, 2, 1	-0.1007
10035.2930	3, 1, 2	3, 0, 3	-0.0135
11397.1855	1, 1, 1	0, 0, 0	0.0933
12404.3926	4, 2, 2	4, 1, 3	-0.0940
12484.9121	3, 2, 2	3, 1, 2	0.0400
13313.8613	2, 2, 0	2, 1, 1	0.1189
13353.5801	5, 2, 3	5, 1, 4	0.2793
14207.1348	4, 1, 3	4, 0, 4	-0.0654

Table 1.2 presents observed rotational transitions of the isoprene monomer, providing information on the frequency (in MHz), the specific rotational transition (J, K-1, K+1), and the difference between observed and calculated frequencies (Obs-Cal, in MHz). Each transition is characterized by quantum numbers J, K-1, and K+1, representing rotational and vibrational states. The discrepancies between observed and calculated frequencies (Obs-Cal) offer insights into the accuracy of theoretical predictions for these transitions.

The frequencies associated with each transition provide a detailed view of the rotational behaviour of the isoprene monomer. For instance, the frequency of 7256.4944 MHz corresponds to the transition from the rotational state (J, K-1, K+1) of (2, 1, 1) to (2, 0, 2) with a small observed-calculated difference of 0.0500 MHz. The negative differences in frequencies, such as in the transition at 9444.4336 MHz, indicate that the observed values are slightly lower than the calculated ones. These differences can be attributed to various factors, including experimental error or the influence of external conditions on the molecular structure.

Table A1.2 provides a comprehensive overview of rotational transitions in the isoprene monomer, offering valuable data for validating theoretical models and understanding the molecule's behaviour in different energy states. The observed-calculated discrepancies highlight areas where further refinement in theoretical predictions or experimental techniques may be beneficial for a more accurate description of the rotational dynamics of the isoprene monomer.

Table. 1.3 Rotational Constants

MP2/6-31G*		**HF/6-311++g(d,p)**	**MP4/6-311g+ (d,p)**	**B3LYP/6-311+g(d,p)**
Rotational Constant	**GHz**	**GHz**	**GHz**	**GHz**
A	6.3631982	6.7799771	6.3304846	6.7799771
B	1.2988198	0.5289783	0.4124869	0.5289783
C	1.0879708	0.4929358	0.3881753	0.4929358

The examination of rotational constants for the isoprene-Argon complex, derived from diverse quantum chemical methods (MP2/6-31G*, HF/6-311++G(d,p), MP4/6-311G+(d,p), and B3LYP/6-311+G(d,p)), reveals consistent trends and subtle variations, offering valuable insights into the complex's molecular structure. Across methods, the A rotational constant consistently falls within the range of approximately 6.33 to 6.78 GHz, indicating a reliable estimation of the complex's size and symmetry. The B and C rotational constants also display a level of agreement, though with slight variations that highlight the sensitivity of the methods to different aspects of the complex's geometry.

Specifically, the MP2/6-31G* method yields an A constant of 6.3631982 GHz, B constant of 1.2988198 GHz, and C constant of 1.0879708 GHz. The HF/6-311++G(d,p) method produces an A constant of 6.7799771 GHz, B constant of 0.5289783 GHz, and C constant of 0.4929358 GHz. The MP4/6-311G+(d,p) method results in an A constant of 6.3304846 GHz, B constant of 0.4124869 GHz, and C constant of 0.3881753 GHz. Lastly, the B3LYP/6-311+G(d,p) method provides an A constant of 6.7799771 GHz, B constant of 0.5289783 GHz, and C constant of 0.4929358 GHz.

Structural implications of the isoprene-Argon complex become apparent as the consistent A values suggest a larger and less symmetric molecule. Notably, the HF/6-311++G(d,p) method yields lower B and C constants compared to other methods, indicating potential differences in the complex's vibrational motions and symmetry. The observed variations underscore the importance of considering multiple quantum chemical approaches to gain a comprehensive understanding of the complex's molecular features. The choice of quantum chemical method should be tailored to the specific properties under investigation. While HF and B3LYP methods provide similar results, slight differences between MP2 and MP4 methods emphasize the need for careful selection based on the aspects of the complex that are of particular interest. Benchmarking against experimental data becomes crucial for validating the accuracy of computational results, and acknowledging the inherent limitations of quantum chemical methods. In summary, the rotational constants, with their specific values across methods, offer a nuanced perspective on the Isoprene-Argon complex, enriching our understanding of its structural characteristics and providing a foundation for further exploration.

Table 1.4: Dipole Moment

MP2/6-31G*		**HF/6-311++g(d,p)**	**MP4/6-311g+ (d,p)**	**B3LYP/6-311+g(d,p)**
Parameter	**Value (Debye)**	**Value (Debye)**	**Value (Debye)**	**Value (Debye)**
X	0.9227	0.1015	-0.1605	0.0691
Y	0.0416	0.2456	0.2113	0.2742
Z	0.0965	0.0200	0.0000	0.0187
Total	0.9286	0.2665	-0.1605	0.2834

The dipole moments of the Isoprene-Argon complex, computed using multiple quantum chemical methods, exhibit intriguing variations across different computational approaches. In the MP2/6-31G* method, the X component stands at 0.9227 Debye, indicating a significant dipole moment along that axis. This suggests an uneven distribution of charge within the complex, potentially influencing its interactions with surrounding molecules or environments. The Y and Z components contribute 0.0416 and 0.0965 Debye, respectively, to the total dipole moment of 0.9286 Debye.

Comparatively, the hf/6-311++g(d,p) method yields a distinct dipole moment profile, with values of 0.1015 Debye, 0.2456 Debye, and 0.0200 Debye for the X, Y, and Z components, respectively. This method portrays a slightly altered charge distribution, emphasizing the sensitivity of the Isoprene-Argon complex's dipole moments to the intricacies of the computational model. The total dipole moment in this case amounts to 0.2665 Debye, providing an overall measure of the molecular polarity.

The mp4/6-311g+ (d,p) method introduces another perspective, with a notable X component of -0.1605 Debye, suggesting a reversal in the direction of the dipole moment along this axis. The Y and Z components contribute 0.2113 Debye and 0.0000 Debye, resulting in a total dipole moment of -0.1605 Debye. This divergence in the dipole moment values underscores the impact of the chosen quantum chemical method on the representation of the Isoprene-Argon complex's charge distribution.

Lastly, the b3lyp/6-311+g(d,p) method presents a different set of dipole moment values, with 0.0691 Debye, 0.2742 Debye, and 0.0187 Debye for the X, Y, and Z components, respectively. The total dipole moment reaches 0.2834 Debye. These variations across methods emphasize the sensitivity of the isoprene-Argon complex to the computational nuances, showcasing the need for a meticulous choice of quantum chemical approach when assessing molecular properties. The observed deviations in dipole moments from those of Isoprene alone suggest that the presence of Argon induces specific changes in charge distribution, contributing to the complex's overall dipole and influencing its reactivity in diverse environments.

Table. 1.5: Bond Length and Bond Angles

MP2/6-31G*		**HF/6-311++g(d,p)**		**MP4/6-311g+ (d,p)**		**B3LYP/6-311+g(d,p)**	
Parameter	**Value**	**Parameter**	**Value**	**Parameter**	**Value**	**Parameter**	**Value**
R(1-2)	1.466	R(1-2)	1.477	R(1-2)	1.485	R(1-2)	1.467
R(1-3)	1.090	R(1-3)	1.078	R(1-3)	1.094	R(1-3)	1.088
R(1-7)	1.344	R(1-7)	1.324	R(1-7)	1.352	R(1-7)	1.338
R(2-4)	1.347	R(2-4)	1.327	R(2-4)	1.355	R(2-4)	1.342
R(2-10)	1.505	R(2-10)	1.507	R(2-10)	1.522	R(2-10)	1.508
R(4-5)	1.086	R(4-5)	1.076	R(4-5)	1.090	R(4-5)	1.085
R(4-6)	1.086	R(4-6)	1.076	R(4-6)	1.089	R(4-6)	1.084
R(7-8)	1.085	R(7-8)	1.075	R(7-8)	1.089	R(7-8)	1.084
R(7-9)	1.085	R(7-9)	1.076	R(7-9)	1.088	R(7-9)	1.084
R(10-11)	1.095	R(10-11)	1.086	R(10-11)	1.100	R(10-11)	1.095
R(10-12)	1.093	R(10-12)	1.083	R(10-12)	1.098	R(10-12)	1.091
R(10-13)	1.095	R(10-13)	1.086	R(10-13)	1.100	R(10-13)	1.095

Conclusion

This research utilized Pulsed Nozzle Fourier Transform Microwave (PNFTMW) spectrometry and computational methods to comprehensively investigate the Isoprene-Argon complex. The experimental approach, employing a versatile PNFTIR spectrometer, successfully identified rotational transitions for both the Isoprene monomer and Isoprene-Argon complex. The discussion of rotational constants and dipole moment components revealed the complex's rotational behaviour and charge distribution along principal axes. Variations in rotational constants across different quantum chemical methods emphasized the importance of method selection, while differences in dipole moments underscored the sensitivity of the Isoprene-Argon complex to computational nuances. These findings contributed to a nuanced understanding of the complex's molecular structure and its potential implications in interstellar chemistry, highlighting the need for a multidisciplinary approach in studying molecular systems in diverse environments. This research laid the groundwork for future explorations into molecular interactions and the refinement of computational models for enhanced predictive accuracy in describing complex molecular properties.

Recommendation

Future research should explore other computational methods, such as quantum Monte Carlo or coupled-cluster techniques, to provide further information into the electronic structure and energetics of the complex and the results obtained for the isoprene-argon complex should be compared with those of similar systems (e.g., other biomolecule-noble gas complexes) to identify trends and patterns.

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