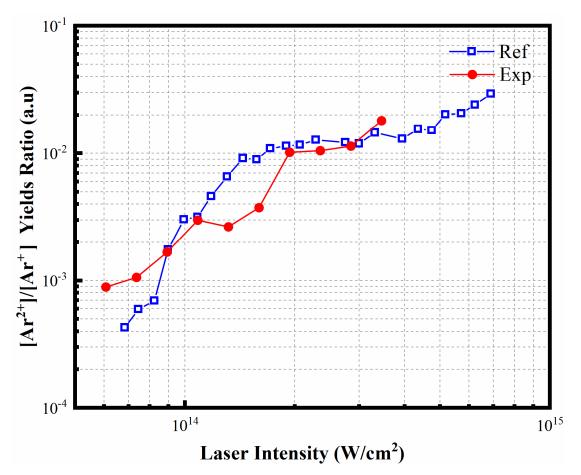
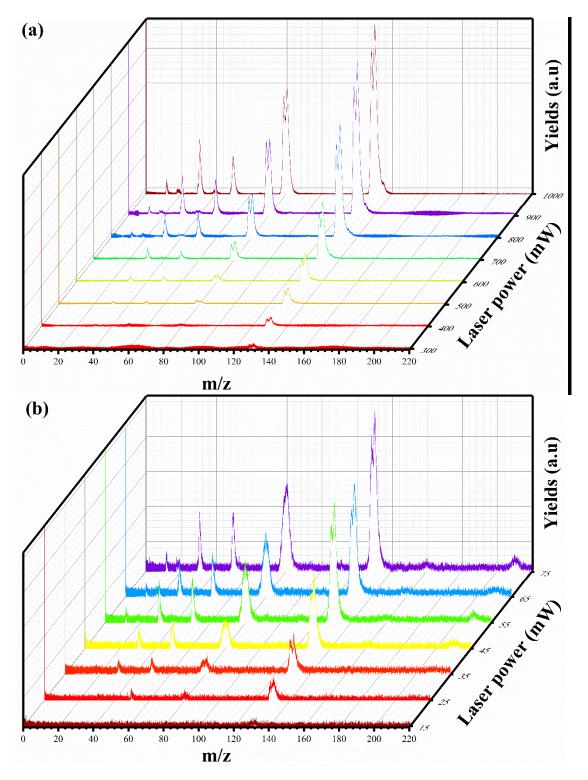




## **Supplementary Materials**



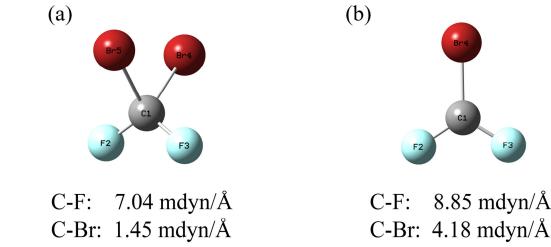
**Figure S1.** The yield ratio of [Ar<sup>2+</sup>]/[Ar<sup>+</sup>] of our measurement comparing with the same ratio in literatures Ref [1]. The red solid square is the experimental results.



**Figure S2.** The time-of-flight mass spectra under different laser power, in the (a) 800nm laser field; (b) 400nm laser field, respectively.

Bond	$CF_2Br_2^+$				CF <sub>2</sub> Br⁺		
	C-F(2)	C-F(3)	C-Br(4)	C-Br(5)	C-F(2)	C-F(3)	C-Br(4)
C-F(2)	0.142				0.113		
C-F(3)	-0.012	0.142			-0.012	0.113	
C-Br(4)	-0.033	-0.033	0.688		-0.016	-0.012	0.239
C-Br(5)	-0.033	-0.033	-0.212	0.688			

**Table S1.** The compliance matrix of singly charged ion CF<sub>2</sub>Br<sub>2</sub><sup>+</sup> and CF<sub>2</sub>Br<sup>+</sup>, which is calculated by B3LYP level of theory using 6-31G\* basis set.



**Figure S3.** (a) the optimized structure of singly charged ion CF<sub>2</sub>Br<sub>2</sub><sup>+</sup> at the B3LYP/6-31G\* level and the related C-F and C-Br bonds strength calculated by the relax force constant (b) the optimized structure of singly charged ion CF<sub>2</sub>Br<sup>+</sup> at the B3LYP/6-31G\* level and the related C-F and C-Br bonds strength calculated by the relax force constant[2].

## Reference

- 1. Guo, C.; Li, M.; Nibarger, J. P.; Gibson, G. N., Physical Review A 1998, 58, R4271-R4274.
- 2. Brandhorst, K.; Grunenberg, J., Chemical Society Reviews 2008, 37, 1558.