

New insight on the photofragmentation of CH_2I_2

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Synopsis An experimental and theoretical investigation of the VUV photofragmentation of CH_2I_2 molecule is reported. The work focuses on the I-loss channel. The experimental results demonstrate that at energies lower than 12 eV diiodomethane radical cation dissociates only into the CH_2I^+ ion and an I atom while the theoretical calculations show that isomerisation of $[\text{CH}_2\text{I}_2]^+$ into iso-diiodomethane $[\text{CH}_2\text{I-I}]^+$ intermediates can occur before the loss of iodine atom.

Diiodomethane is a halomethane widely studied for its role played in the terrestrial atmosphere as well as in solution chemistry. In the environment CH_2I_2 is a source of iodine atom which affects the ozone chemistry and contributes to the formation of the ultrafine marine aerosol particles, while in photoreaction chemistry this molecule is used for cyclopropanation of alkene. Different studies [1] have demonstrated that in condensed phase diiodomethane molecule under photon irradiation isomerizes into iso-diiodomethane and becomes a source of “ CH_2 ” species. Moreover in the recent literature it has been reported that in the gas phase halo-methane can isomerize into isohalomethane before losing the halogen molecule [2]. In a previous study [3] we have investigated the photofragmentation of dihalomethanes (CH_2X_2 , X=F, Cl, Br, I) and in particular we found that diiodomethane generates different fragment ions and the I-loss channel is the one opening at the lowest energy. In this work we report an experimental and theoretical investigation of VUV photofragmentation of CH_2I_2 molecule with the main focus on I-loss channel, which occurs from the lower electronic ionic states as showed in our PEPICO experiments.

Theoretical calculations have been performed at the MP2/CCSD(T) level of theory to obtain the structures and the energy of each stationary point found for the $[\text{CH}_2\text{I}_2]^+$ ion. The results show that the isomerization of diiodomethane radical cation $[\text{CH}_2\text{I}_2]^+$ into iso-diiodomethane intermediates $[\text{CH}_2\text{I-I}]^+$ is an energetically competing channel with respect to the direct C-I bond breaking (Figure 1).

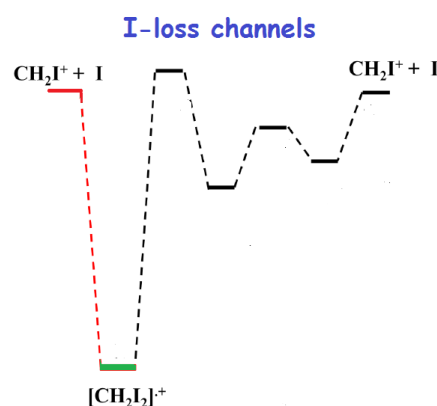


Figure 1. Schematic representation of energetic paths to I atom and CH_2I^+ ion from $[\text{CH}_2\text{I}_2]^+$ through $[\text{CH}_2\text{I-I}]^+$ intermediates (black pattern on the right).

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