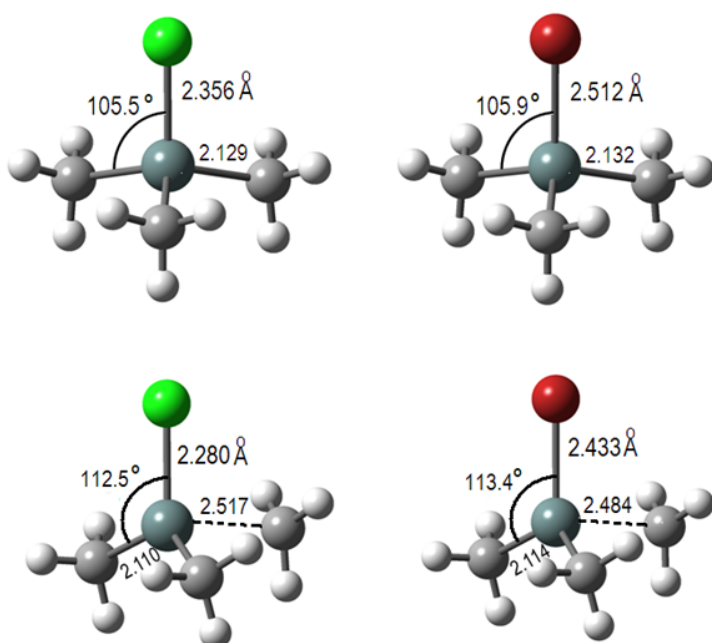


### Supplementary electronic information to

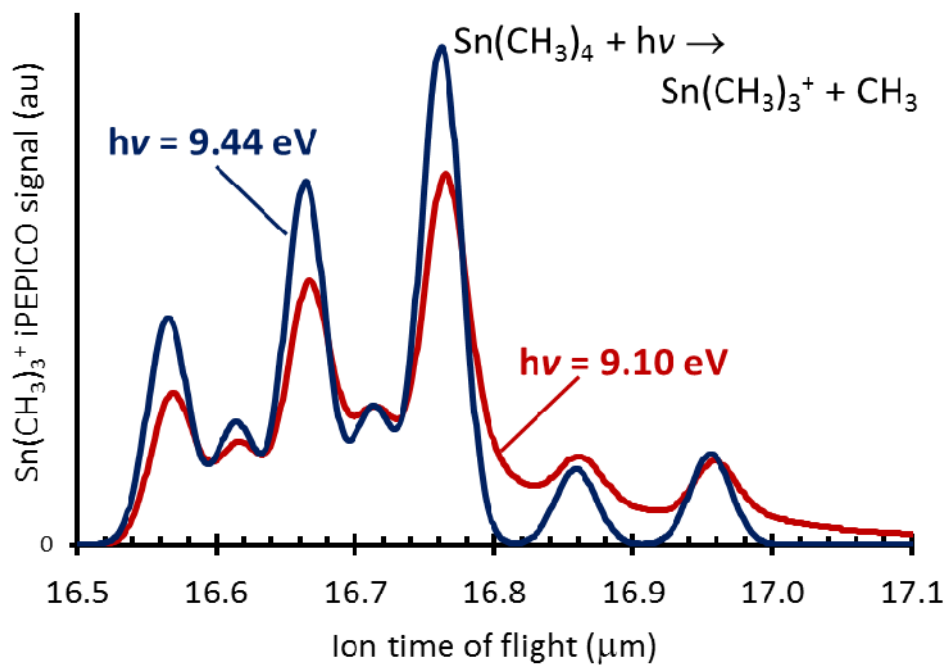
#### Dissociation of energy selected $\text{Sn}(\text{CH}_3)_4^+$ , $\text{Sn}(\text{CH}_3)_3\text{Cl}^+$ , and $\text{Sn}(\text{CH}_3)_3\text{Br}^+$ ions: Evidence for isolated excited state dynamics

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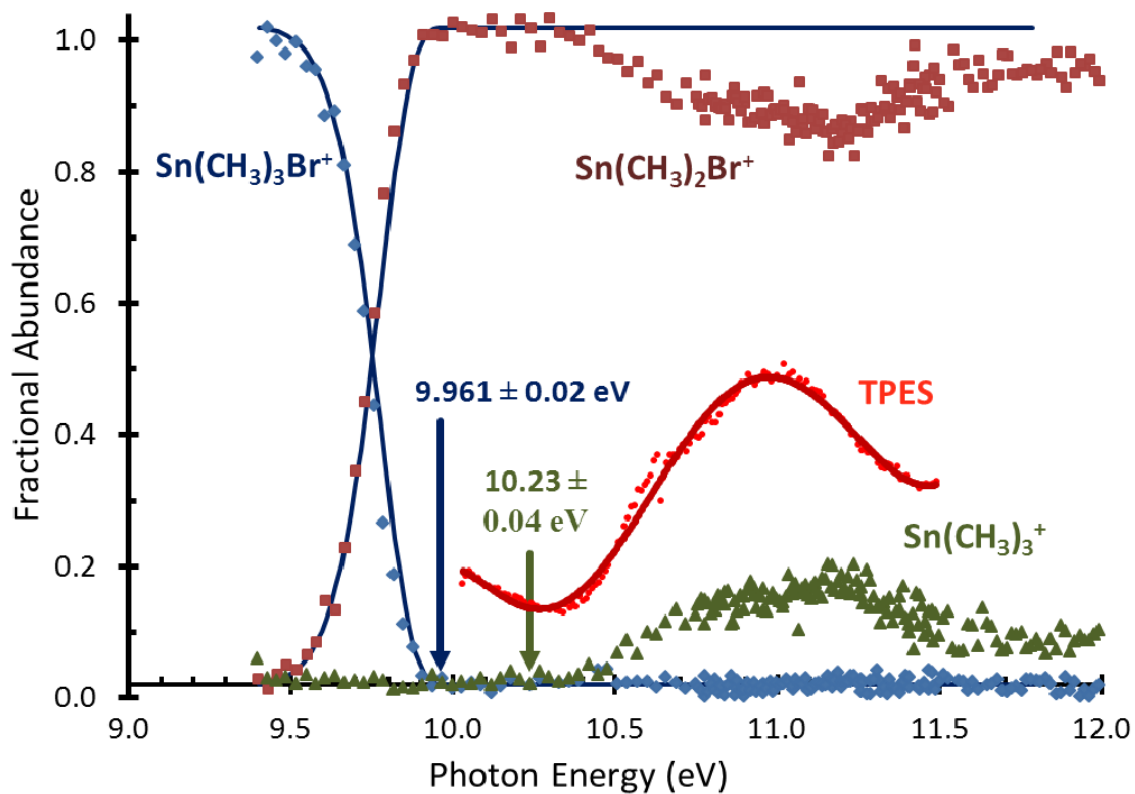
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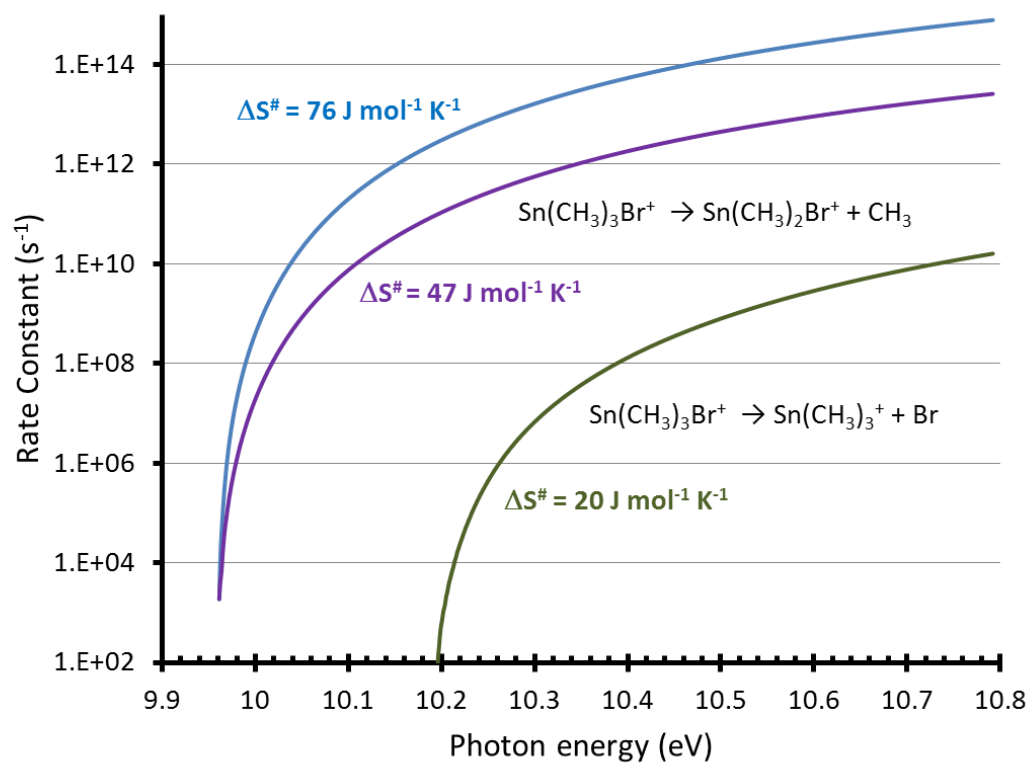
**Figure S1.** Molecular geometry for  $\text{Sn}(\text{CH}_3)_3\text{Cl}$  (left) and  $\text{Sn}(\text{CH}_3)_3\text{Br}$  (right). The neutral molecules (top) and their corresponding ions (down) were optimized at the B3LYP level with 6-311+G(d,p) basis set for C, H, Cl; 6-311G(d,p) for Br and the combination of the SDB-aug-cc-pVTZ basis set and LANL2 effective core potential (ECP) for Sn.



**Figure S2.** Calculated time of flight distributions at two photon energies showing the slight asymmetry due to the slow dissociation at the reaction threshold.



**Figure S3.** Breakdown diagram for  $\text{Sn}(\text{CH}_3)_3\text{Br}$  in the vicinity of the  $\text{CH}_3$  and Br loss onsets. The solid lines are modeled fits for both the  $\text{CH}_3$  and Br loss channels using the RRKM rates shown in Figure 6. Note that the modeling predicts no observable Br loss. However, note the close correspondence between the TPES and the Br loss signal between 10.5 and 11.5 eV.



**Figure S4.** The rate constants for the  $\text{CH}_3$  and  $\text{Br}$  loss channels from  $\text{Sn}(\text{CH}_3)_3\text{Br}^+$  ions. Very loose ( $\Delta S^\ddagger = 76 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and a moderately loose ( $\Delta S^\ddagger = 47 \text{ J mol}^{-1} \text{ K}^{-1}$ ) transition states are assumed for the methyl loss channel. Despite the very loose transition state for the  $\text{Br}$  loss channel, its rate is orders of magnitude too low to compete with the lower energy methyl loss channel.