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## Chlorine Addition/elimination to Butenes Exclusively Proceeds via Roaming

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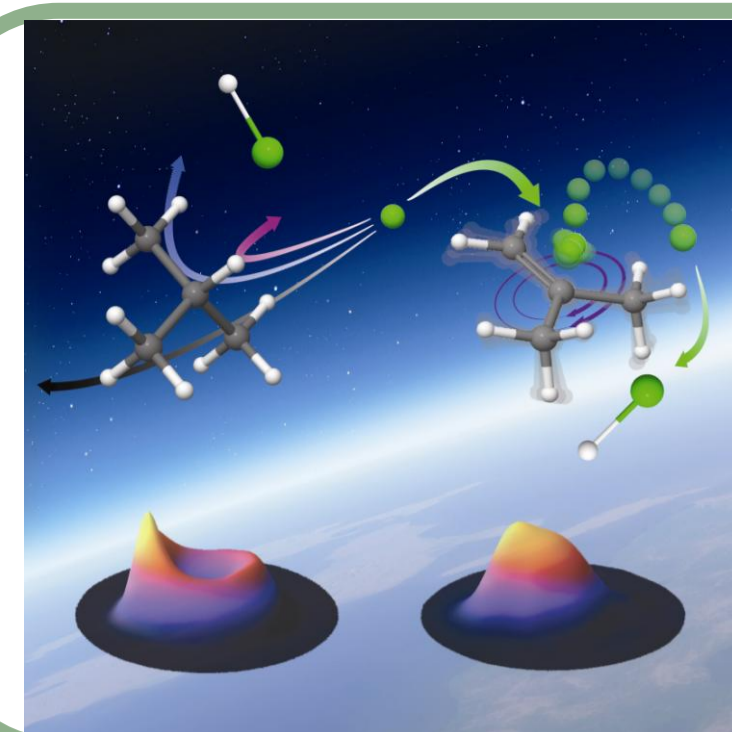
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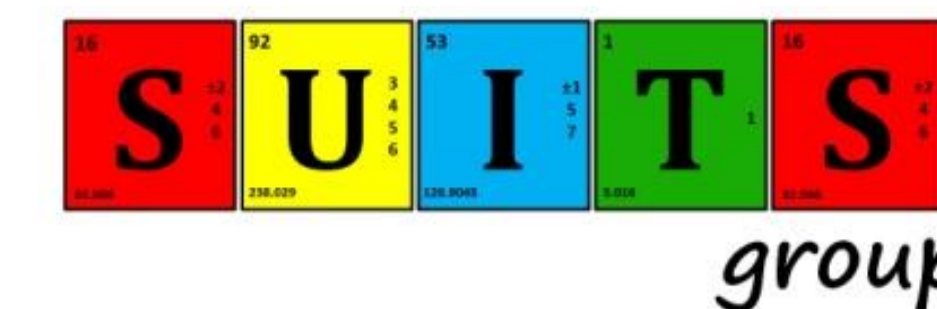
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# Cl Addition/elimination to Butenes Exclusively Proceeds via Roaming



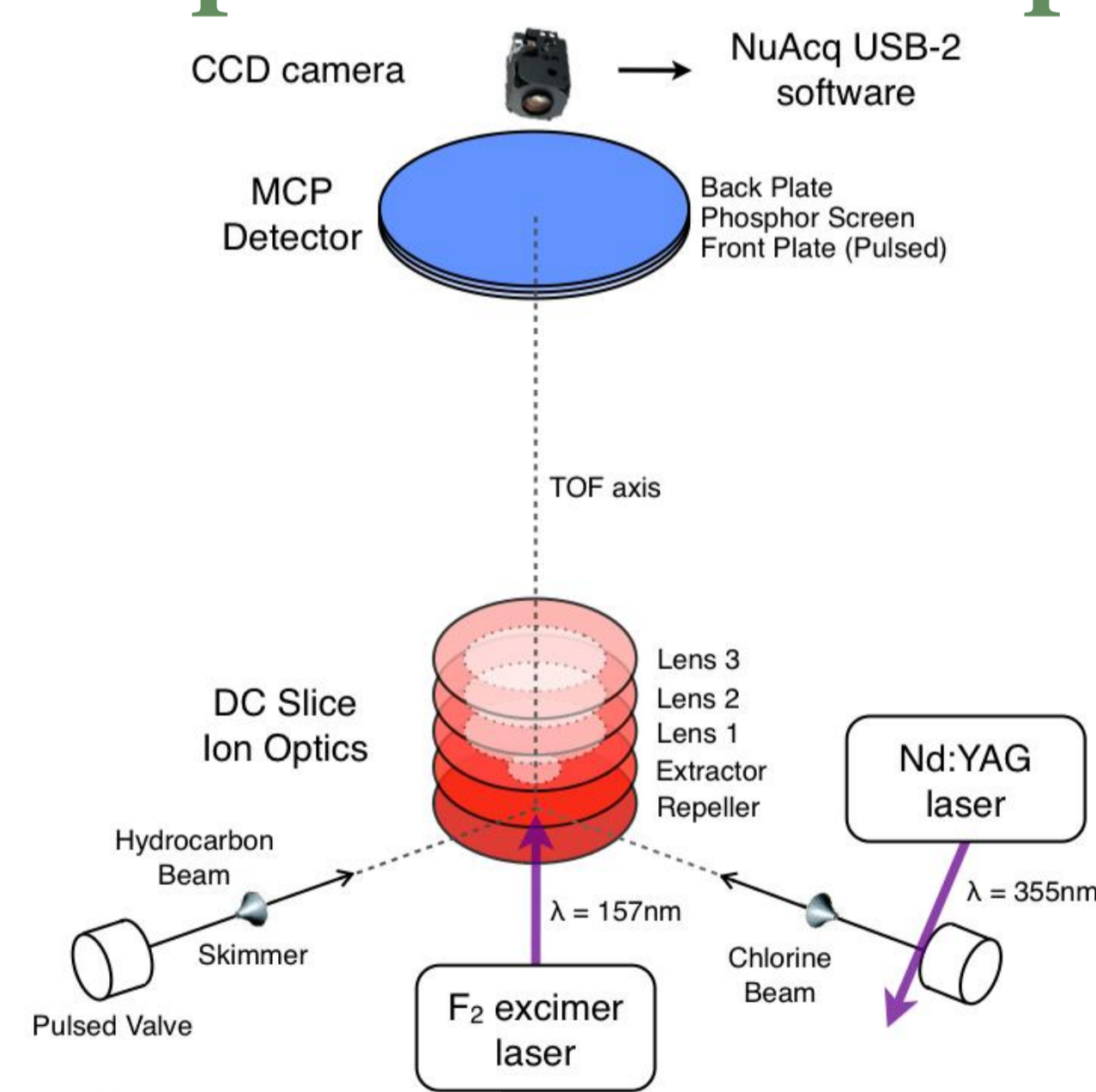
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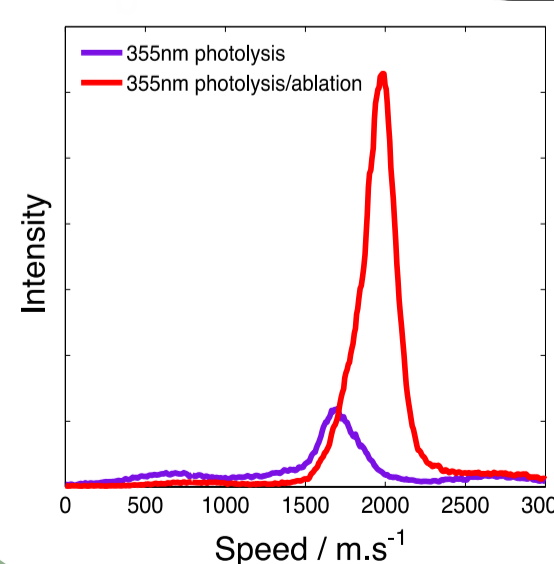
## Abstract

We present a crossed-beam dc slice imaging study of the reactions of chlorine atom with selected unsaturated hydrocarbons. Single-photon ionization at 157nm is used to record the velocity-flux contour maps of the radical products at various collision energies in single-collision conditions. These experimental investigations are augmented with ab initio calculations which, taken together, reveal trends in product energy and angular momentum partitioning and offer deep insight into the reaction mechanisms. By focusing on a series of butene isomer targets, we show that the differential cross-sections corresponding to the formation of HCl and alkenyl radicals reflect the competition between direct and indirect reactions, the latter being mediated by Cl addition prior to HCl elimination. A careful analysis of the potential energy surfaces show that, to decompose, the highly frustrated  $\pi$  adducts must undergo near-dissociation before eliminating HCl at the adjacent saturated sites. Hence, our results suggest that roaming radical dynamics, now widely recognized in unimolecular reactions, may play a central role in a broad class of bimolecular reactions as well.

## Experimental Setup

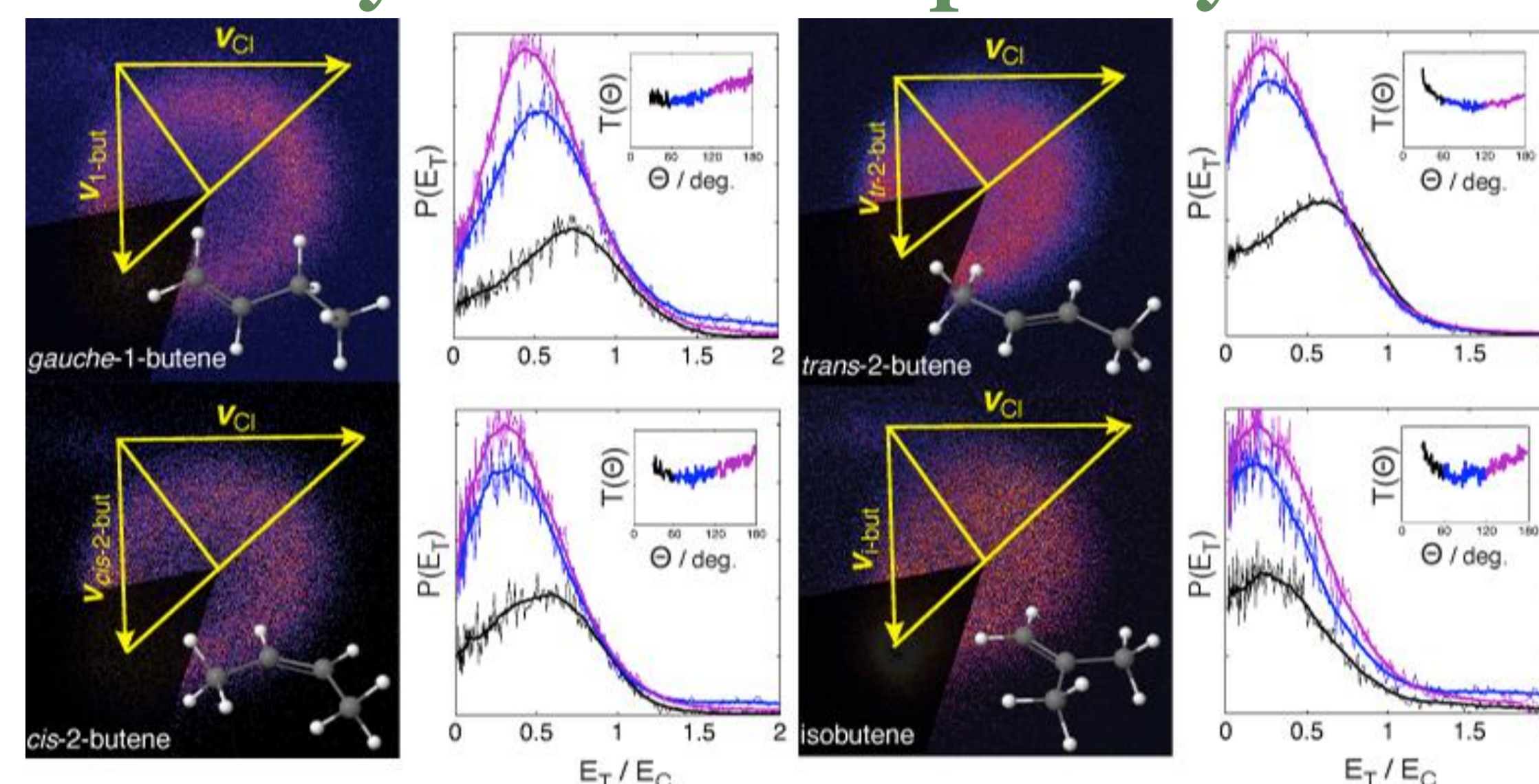


The machine is composed of two perpendicular source chamber and one main chamber. The scattered radical products are ionized with a F2 excimer laser (157 nm, 7.9 eV) as soon as the products exit the interaction region. The ions are then accelerated via a four-electrode dc slice ion optics assembly to impact on a dual microchannel plate (MCP) detector coupled to a fast phosphor screen. The resulting images are recorded using a charged-coupled device (CCD) camera, and the megapixel acquisition program IMACQ-2 is used to accumulate the raw images containing centroided data.

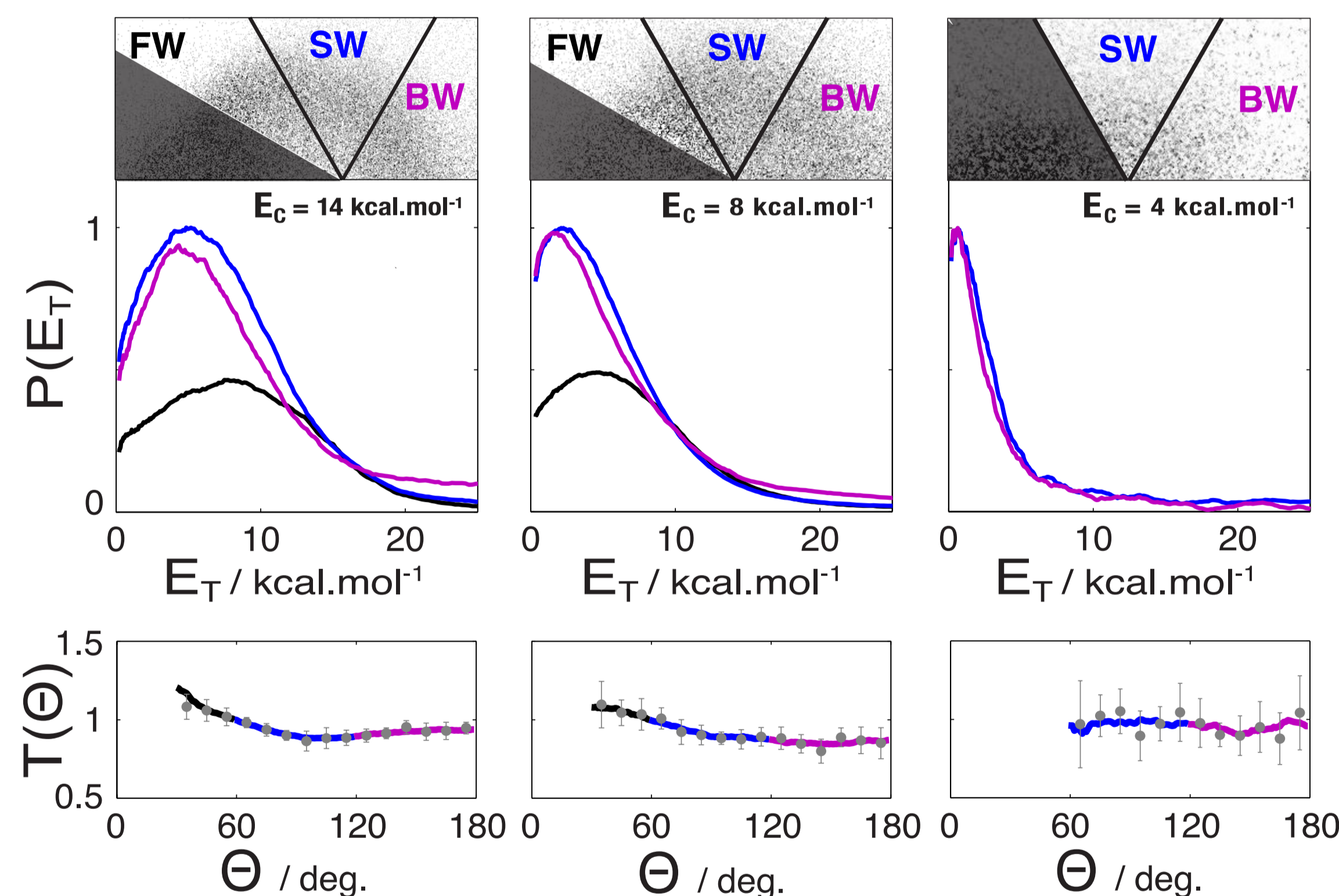


Chlorine beam profiles extracted from dc slice raw images recorded at  $m/z = 35$  with and without confinement/ablation. Speed ratios are equal to 9 and 6, respectively. The effective Cl atom population reaching the interaction region is increased by a factor of 5 when an aluminum ablation plume is generated in an cylindrical extension tube.

## Velocity Contour-map Analysis

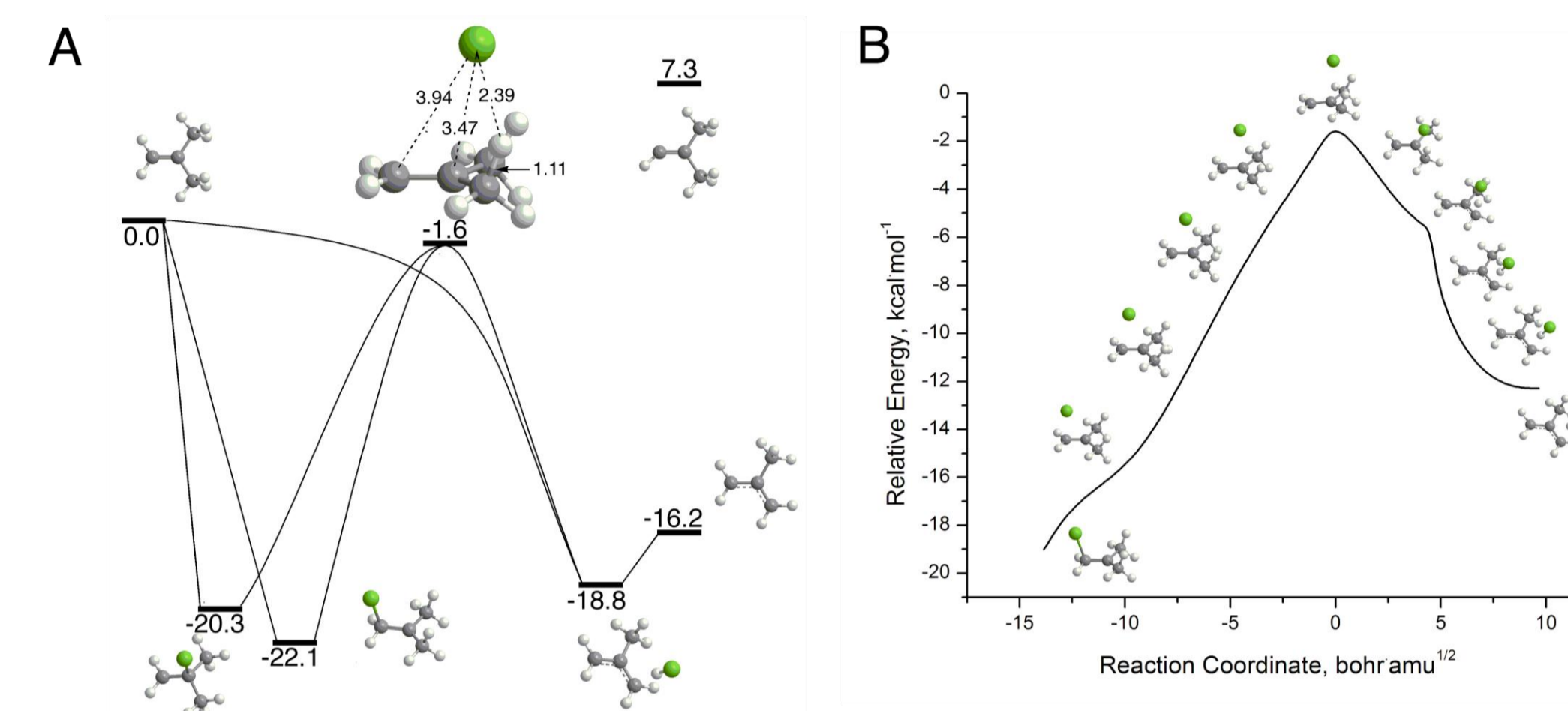


DC slice images and reduced center-of-mass distributions for the reactions of chlorine with 1-butene, cis-2-butene, trans-2-butene, and isobutene at collision energies of  $\sim 12$  kcal.mol<sup>-1</sup>. Forward component is represented in black (30–60°), sideways in blue (60–120°), and backward in purple (120–180°).

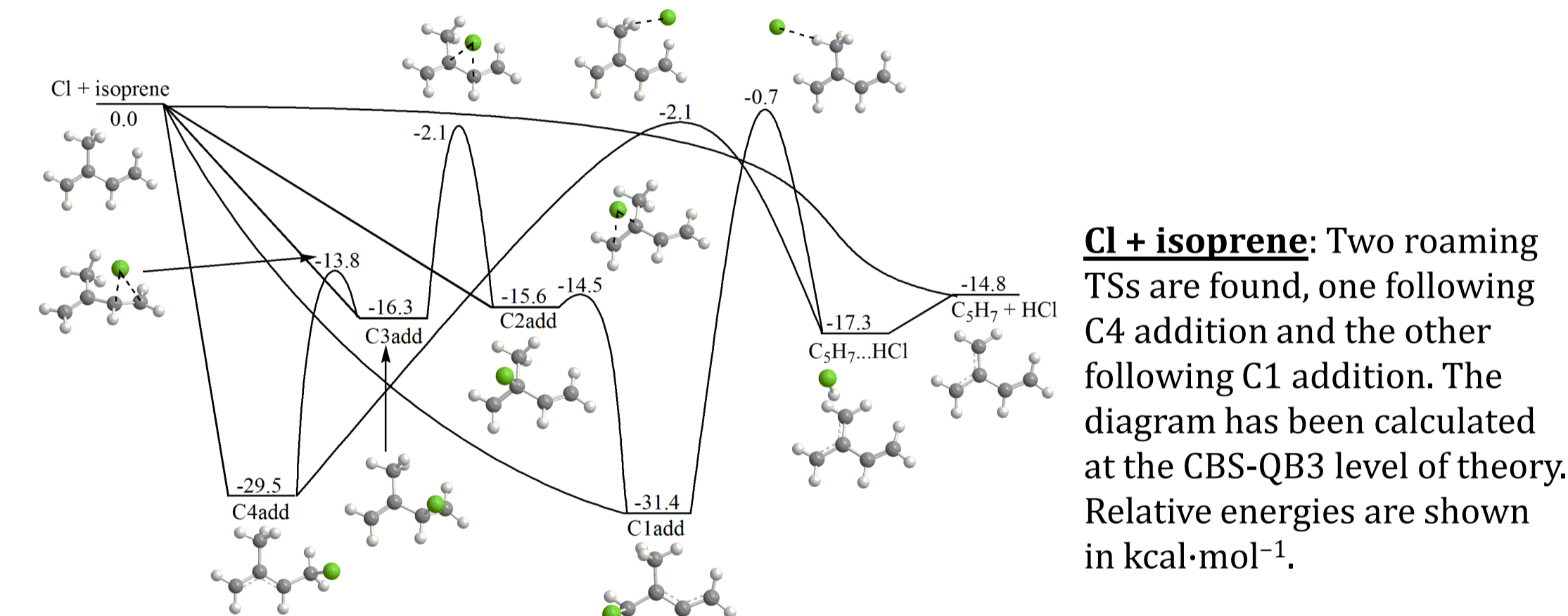


Center-of-mass distributions of the isobutenyl C<sub>4</sub>H<sub>7</sub> radical for different collision energies. The velocity-flux contour maps are shown with the photochemical background masked in the forward direction. Error bars were estimated each 10° via single standard deviation.

## Ab Initio Calculations



**Cl + isobutene:** (A) Key points on the potential energy surface of the reaction. Direct H abstraction is a barrierless pathway with a van der Waals complex in the exit channel. The two addition complexes undergo near dissociation to reach a unique roaming-type transition state (TS-C3roam) before eliminating HCl. The diagram has been calculated at the CBS-QB3 level of theory. Relative energies are shown in kcal.mol<sup>-1</sup>. (B) Minimal energy profile and structures along the ClCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub> → CH<sub>2</sub>C(CH<sub>3</sub>)(CH<sub>2</sub>)...HCl pathway via the roaming transition state, extracted from IRC calculations at the B3LYP/6-311G(2d,d,p) level.



**Cl + isoprene:** Two roaming TSs are found, one following C<sub>4</sub> addition and the other following C<sub>1</sub> addition. The diagram has been calculated at the CBS-QB3 level of theory. Relative energies are shown in kcal.mol<sup>-1</sup>.

**Preliminary RRKM results:** The statistical lifetimes of the Cl-butene complexes are too long (72, 10 and 2ns at  $E_c = 4, 8$  and 14 kcal.mol<sup>-1</sup>) to account for the onset of the FW component when compared with the rotational period ( $\sim 30$  ps) of the complex. For Cl-isoprene complexes, the lifetimes appear to be significantly slower; with lifetimes equal to 6.0, 0.8, and 86ns, at  $E_c = 4, 8$ , and 14 kcal.mol<sup>-1</sup>. Interestingly, we do not observe experimentally any H abstraction products, but we do observe the complex formation...

## Conclusions

In Cl + alkene reactions, the overall dynamics is profoundly modified by the presence of the CC double bond. The experimental results suggest in particular that complex-mediated addition-elimination reactions play a prominent role at low collision energies. A careful scan of the potential energy surfaces demonstrate that HCl elimination from C<sub>4</sub>H<sub>8</sub>Cl intermediates can occur exclusively via a Cl atom roaming excursions.

## References:

- A.D. Estillere, L. M. Visger, and A. G. Suits, "Imaging the dynamics of chlorine atom reactions with alkenes" *J. Chem. Phys.* 133, 074306 (2010)  
 B. Joalland, R.D. Van Camp, Y. Shi, N. Patel, and A.G. Suits, "Crossed-Beam Slice Imaging of Cl Reaction Dynamics with Butene Isomers," *J. Phys. Chem. A* (2013)  
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