Dynamic separability demonstrated for competing reaction pathways

Scientific Achievement

New theory demonstrates that reaction pathways associated with different kinds of nuclear motion are dynamically separable, even when they are not energetically separable.

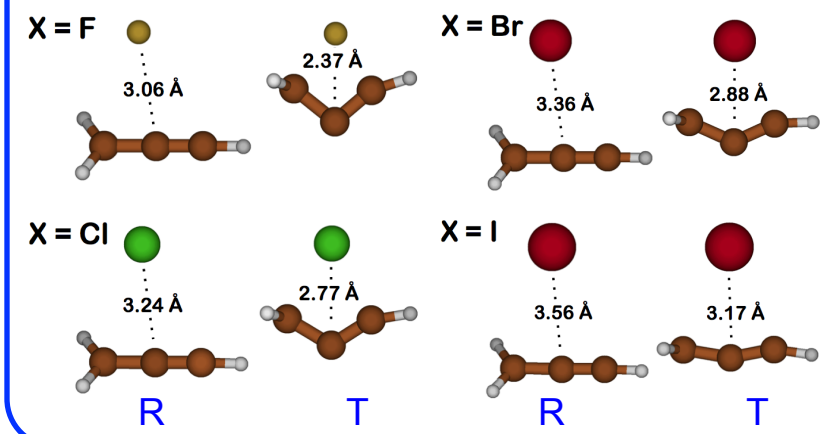
Significance and Impact

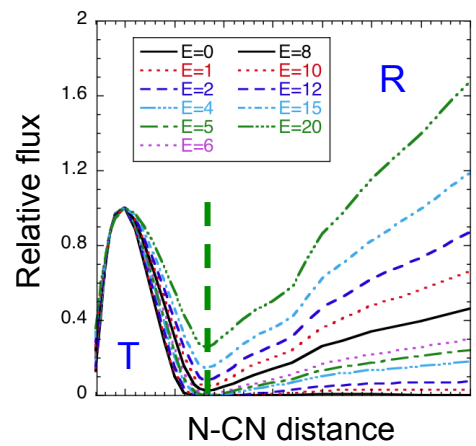
Dynamic separability enables broad applicability of existing theoretical methods (developed for isolated reaction pathways) to reactions with complex mechanisms.

Research Details

- Competition between tight (T) and roaming (R) pathways for molecular elimination and isomerization was characterized theoretically.
- The T and R transition state regions together comprise a single global transition state but require different dynamical methods for accurate dynamics calculations.
- Dynamic separability allows these transition state regions to be treated independently, resulting in more accurate calculations as well as a useful conceptual model for interpreting the resulting chemistry.

Saddle points for isomerization of propargyl halides (CH_2XCCH) to haloallenes (CH_2CCHX). As X gets larger the two saddle points look more similar, demonstrating that these saddle points are part of a single global transition state.





The R and T regions are dynamically separable, as shown here for NCN isomerization.

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L. B. Harding, S. J. Klippenstein, A. W. Jasper, J. Phys. Chem. A **116**, 6967 (2012).

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