Electron-impact dissociation dynamics for modelling of plasma technologies

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Motivation

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- Search for environmentally-friendly (low GWP) organofluorines for use in semiconductor plasma technologies.
- Predict dissociation products after electron impact and determine the chemical composition of plasma.

Industrial organofluorines

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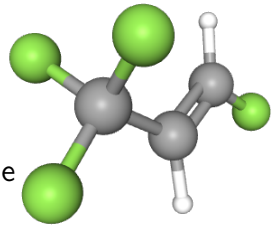
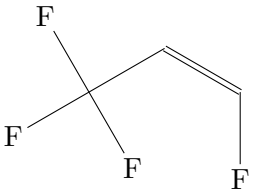
$C_3H_2F_4$

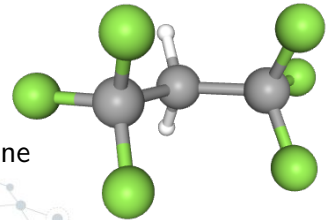
Tetrafluoropropene

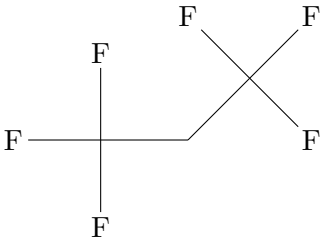




$C_3H_2F_6$

Hexafluoropropane





Dissociation via electron-impact excitation

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- Electron-impact excitation of molecule M^* into excited state(s) M^*.

$$e^- + M \longrightarrow e^- + M^* \longrightarrow e^- + A + B$$

- Molecular dynamics simulations determine dissociation channels and their branching ratios (ab initio multiple cloning method).
- Excitation cross sections determine which excited states required (R-matrix method, Quantemol Electron Collisions software).

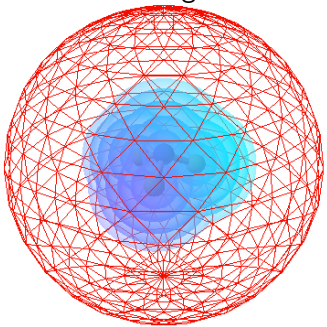
Quantemol Electron Collisions (QEC)

- User-friendly interface for calculating electron-molecule collisions.
- Molpro quantum chemistry package provides molecular target orbitals.
- Molecular R-matrix (UKRmol+) code calculates excitation cross sections.

R-matrix theory

- Space divided into inner, outer and asymptotic regions.
- Inner region confines the N-electron molecular target.

inner region



outer region

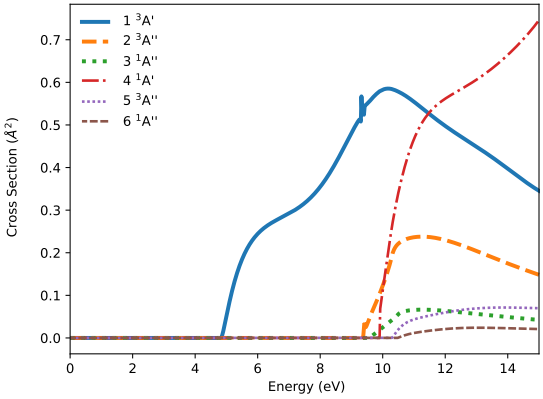
connection to asymptotic forms

Single outgoing electron

Exchange, correlation with inner electrons neglected

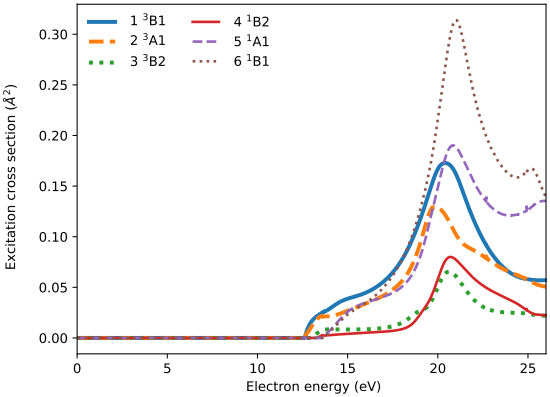
- Outer region wavefunction extends to large distances.
- Connection to asymptotic forms allows calculation of cross sections.

Electron-impact excitation cross sections for $C_3H_2F_4$



- Lowest triplet state dominates at low energies.

Electron-impact excitation cross sections for $C_3H_2F_6$



- Multiple states contribute.

Ab initio multiple cloning method

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- Direct quantum non-adiabatic molecular dynamics simulations:

$$i\frac{\partial}{\partial t}\Psi(\mathbf{R},\mathbf{r},t) = H\Psi(\mathbf{R},\mathbf{r},t)$$

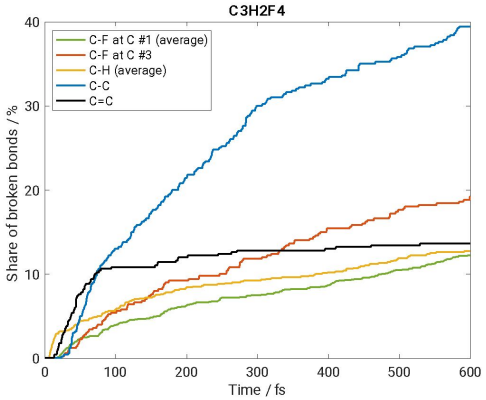
- Includes many Born-Oppenheimer electronic states and non-adiabatic couplings.
- Solve for time-dependent amplitude of electronic states $a_I(t)$:

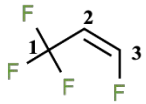
$$\dot{a}_I(t) = -i\sum_{I,J} H_{IJ}a_J(t),$$

where

$$H_{IJ} = \begin{cases} V_I & I = J \\ -i\dot{\mathbf{R}}\cdot\mathbf{C}_{IJ} & I \neq J \end{cases}$$

Dissociation kinetics for $C_3H_2F_4$





- Only lowest triplet excited state included, non-adiabatic coupling not significant.
- C=C bond breaking occurs earliest, likely location of excitation.
- C=C bond breaking stabilizes as excitation transfers to neighbouring bonds.

Dissociation pathways for $C_3H_2F_4$

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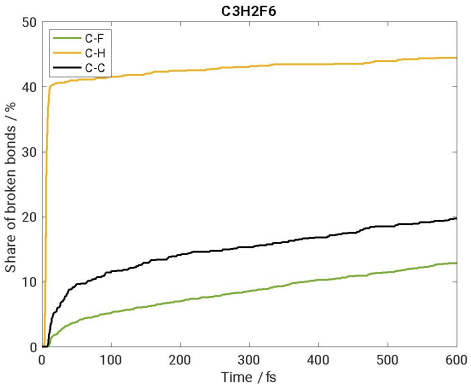
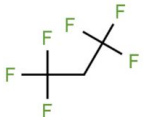
- Probability P of dissociation products.

Product	P
F	0.49
CF_3	0.36
C_2H_2F	0.25
H	0.22
$C_3H_2F_3$	0.20
CHF	0.13

- 23% of $C_3H_2F_4$ molecules remain undissociated after 600 fs.

Dissociation kinetics for $C_3H_2F_6$





- Two triplet excited states included.
- C-H bonds break rapidly, likely location of initial excitation.
- Gradual excitation transfer to C-C and C-F bonds.

Dissociation pathways for $C_3H_2F_6$

- Probability P of dissociation products.

Product	P
H	0.82
F	0.61
C_3HF_6	0.39
C_3HF_5	0.22
CF_2	0.20
CF_3	0.12

- All molecules dissociate within 600 fs.

Conclusions

- Lowest triplet excited state dominates the molecular dynamics.
- Initial bond-breaking indicates the likely location of the initial excitation.
- Subsequent excitation transfer opens other dissociation channels.

Acknowledgements

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- Scientific Consultant position open! **recruitment@quantemol.com**
- Quantemol Database **quantemoldb.com**

Thank you for your attention!