Unraveling Molecular Collisions in Protoplanetary Disks

Rovibrational transitions in HCCH and CO_2 involving the ν_3 IR active modes induced by collisions with He atoms

Taha Selim MSc.

tselim@science.ru.nl

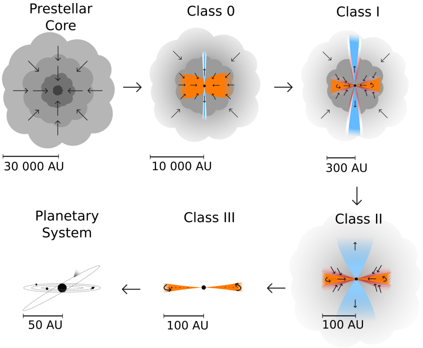
Theoretical Chemistry
Institute for Molecules and Materials
Radboud University Nijmegen

DAN II Network Meeting
November 28th, 2018
Leiden

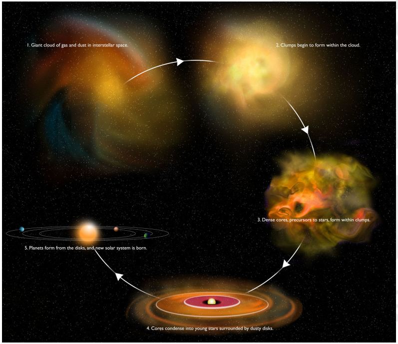
Introduction: Astrochemistry and Protoplanetary Disks

The quest to understand the formation of planets and origin of life!

Circumstellar/Protoplanetary Disks

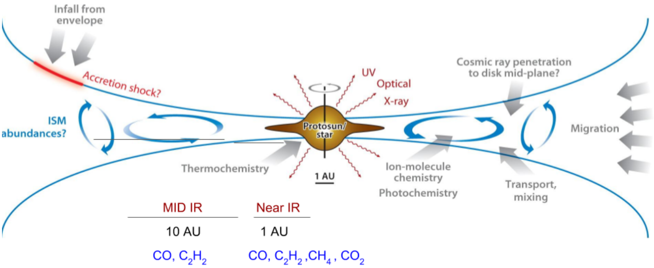


– Persson, Magnus Vilhelm (2014)



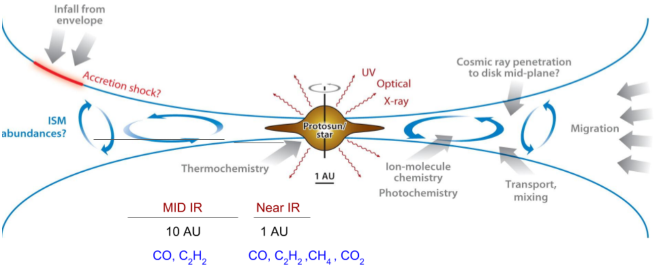
– Bill Saxton, NRAO/AUI/NSF

Temperature range ~
100 K to 1500 K
Collision energies (KE) ~
1 to 10 000 cm^{-1}.



Organic Molecules: important constituents of the protoplanetary disks

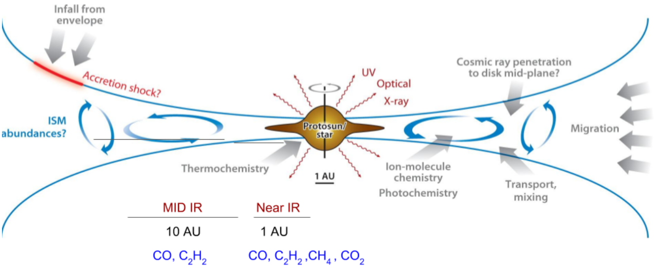
Temperature range ∼ 100 K to 1500 K
Collision energies (KE) ∼ 1 to 10 000 cm^{-1}.



Organic Molecules: important constituents of the protoplanetary disks

Examples: C_2H_2, CO_2, CH_4 . . . with dominant collisions partners: He & H_2

Temperature range $\sim$ 100 K to 1500 K
Collision energies (KE) $\sim$
1 to 10 000 cm^{-1}.

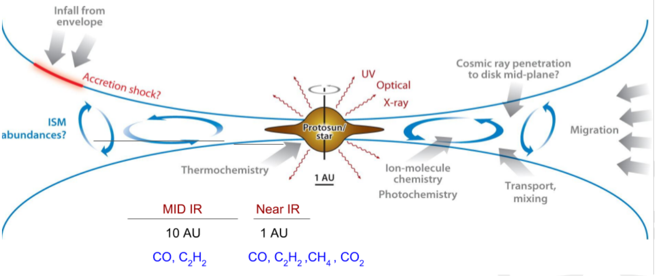


Organic Molecules: important constituents of the protoplanetary disks

Examples: C_2H_2, CO_2, CH_4 . . . with dominant collisions partners: He & H_2

- Mid & near IR rovibrational lines: probing the chemistry

Temperature range ∼
100 K to 1500 K
Collision energies (KE) ∼
1 to 10 000 cm^{-1}.

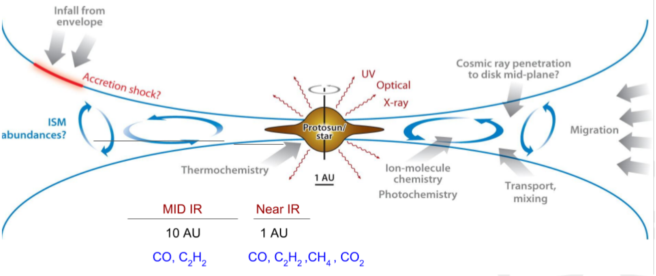


Organic Molecules: important constituents of the protoplanetary disks

Examples: C_2H_2, CO_2, CH_4 . . . with dominant collisions partners: He & H_2

- Mid & near IR rovibrational lines: probing the chemistry
- Understanding: Temperature, densities & molecular abundances

Temperature range ∼
100 K to 1500 K
Collision energies (KE) ∼
1 to 10 000 cm^{-1}.

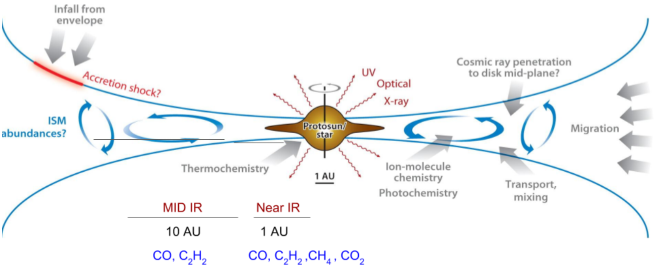


Organic Molecules: important constituents of the protoplanetary disks

Examples: C_2H_2, CO_2, CH_4 . . . with dominant collisions partners: He & H_2

- Mid & near IR rovibrational lines: probing the chemistry
- Understanding: Temperature, densities & molecular abundances
- Low densities: Non Local Thermodynamical Equilibrium (LTE)

Temperature range ∼
100 K to 1500 K
Collision energies (KE) ∼
1 to 10 000 cm^{-1}.



Organic Molecules: important constituents of the protoplanetary disks

Examples: C_2H_2, CO_2, CH_4 . . . with dominant collisions partners: He & H_2

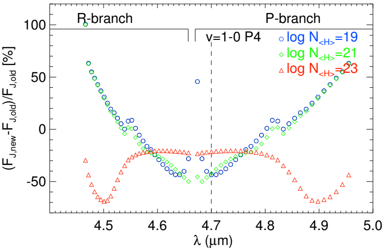
- Mid & near IR rovibrational lines: probing the chemistry
- Understanding: Temperature, densities & molecular abundances
- Low densities: Non Local Thermodynamical Equilibrium (LTE)

State-to-state ICSs & rate coefficients of rovibrational (de)excitation

Simon Bruderer Daniel Harsono, and Ewine F. van Dishoeck, *A & A J.*, **A94**, *19 (2015)*

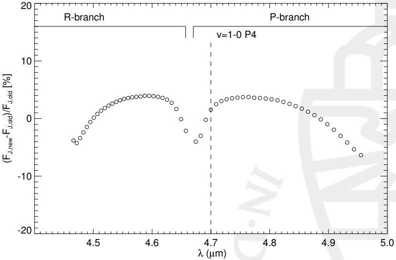
Slab model

$T = 200K$, $\log n_{H,H_2} = 9$, $\log n_{He} = 8$, $\log n_e = 5$



Disk model

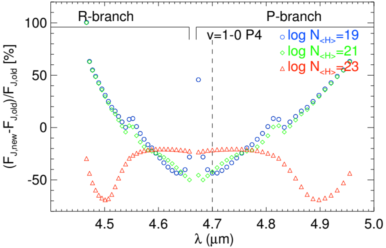
2.2 $M_{\odot}$ Herbig Ae star



Lei Song, N. Balakrishnan, Kyle Walker, Phillip Stancil, Wing-Fai Thi, Inga Kamp, Ad van der Avoird, Gerrit C. Groenenboom , *Astrophys. J.*, **813**, 96 (2015)

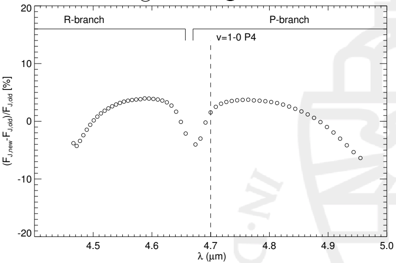
Slab model

$T = 200K$, $\log n_{H,H_2} = 9$, $\log n_{He} = 8$, $\log n_e = 5$



Disk model

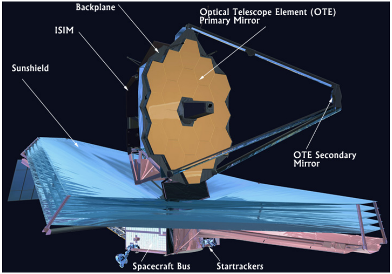
$2.2\ M_\odot$ Herbig Ae star



Lei Song, N. Balakrishnan, Kyle Walker, Phillip Stancil, Wing-Fai Thi, Inga Kamp, Ad van der Avoird, Gerrit C. Groenenboom , *Astrophys. J.*, **813**, 96 (2015)

Accurate rate coefficients yields highly reliable astrochemical models!

JAMES Webb Space Telescope(JWST)



Credit: NASA

- **Rovibrational** Transitions/Spectra
- Large IR telescope: 6.5 m mirror
- $0.6 - 28\ \mu m \sim 350 - 16\,500\ cm^{-1}$
- Observations are expensive!

DAN II: polyatomic molecules C_2H_2 and CO_2

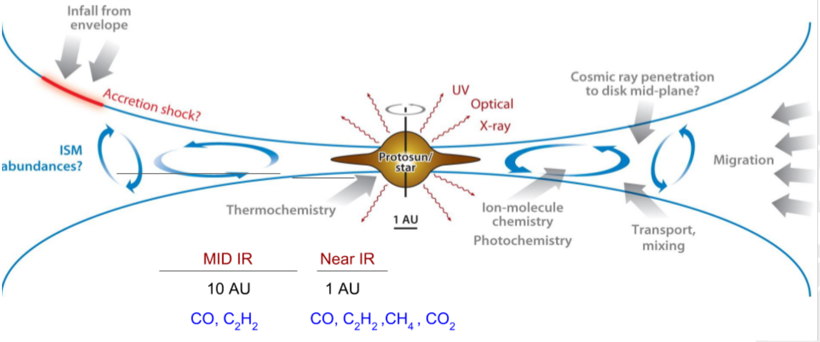


figure adopted from: Mumma et al, Annual Review of A & A 2011

- Polyatomic Molecules: normal modes
- 3N-6 for nonlinear molecules CH_4 $\rightarrow$ 9 normal modes
- 3N-5 for linear molecules: C_2H_2 $\rightarrow$ 7 & CO_2 $\rightarrow$ 4 normal modes

DAN II: polyatomic molecules C_2H_2 and CO_2

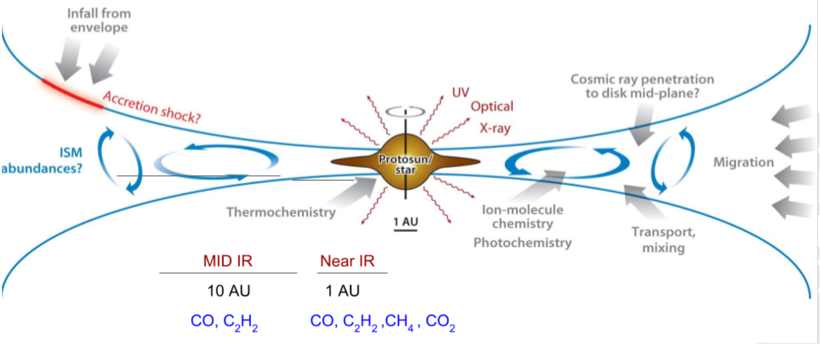


figure adopted from: Mumma et al, Annual Review of A & A 2011

- Polyatomic Molecules: normal modes
- 3N-6 for nonlinear molecules CH_4 $\rightarrow$ 9 normal modes
- 3N-5 for linear molecules: C_2H_2 $\rightarrow$ 7 & CO_2 $\rightarrow$ 4 normal modes
- Some modes are IR active: C_2H_2 $\rightarrow$ 3 & CO_2 $\rightarrow$ 2 normal modes

DAN II: polyatomic molecules C_2H_2 and CO_2

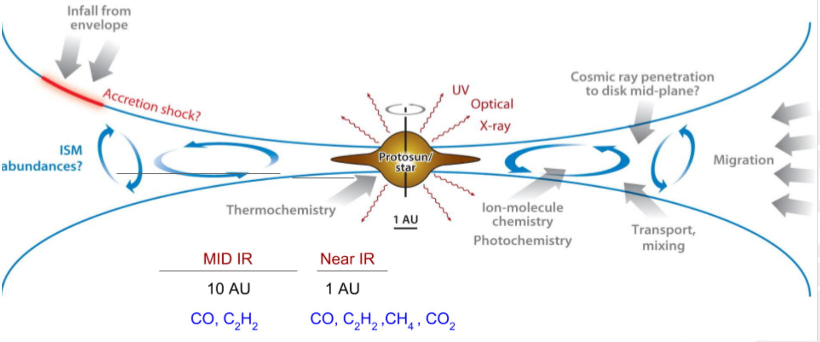


figure adopted from: Mumma et al, Annual Review of A & A 2011

- Polyatomic Molecules: normal modes
- 3N-6 for nonlinear molecules CH_4 → 9 normal modes
- 3N-5 for linear molecules: C_2H_2 → 7 & CO_2 → 4 normal modes
- Some modes are IR active: C_2H_2 → 3 & CO_2 → 2 normal modes

First: one normal mode at a time

DAN II: polyatomic molecules C_2H_2 and CO_2

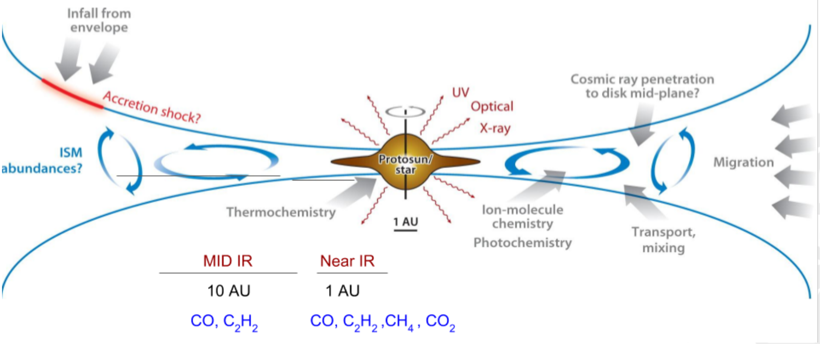
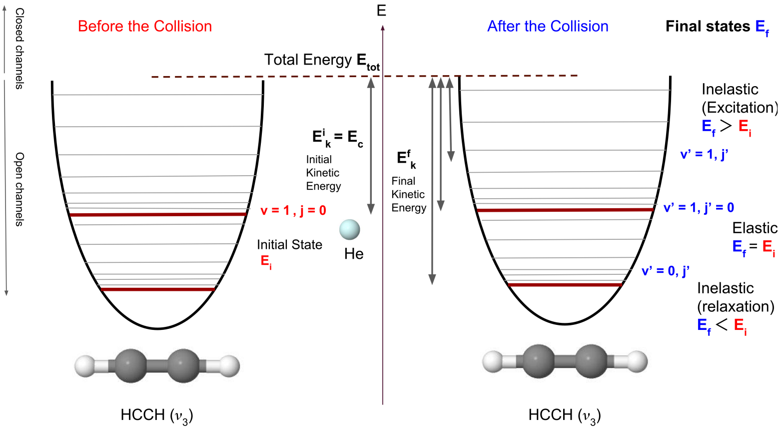


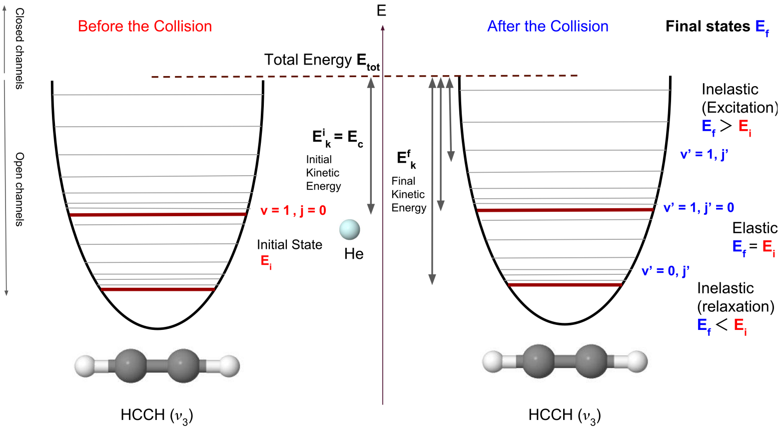
figure adopted from: Mumma et al, Annual Review of A & A 2011

- Polyatomic Molecules: normal modes
- 3N-6 for nonlinear molecules CH_4 $\rightarrow$ 9 normal modes
- 3N-5 for linear molecules: C_2H_2 $\rightarrow$ 7 & CO_2 $\rightarrow$ 4 normal modes
- Some modes are IR active: C_2H_2 $\rightarrow$ 3 & CO_2 $\rightarrow$ 2 normal modes

First: one normal mode at a time   Later: **FR** in CO_2 $\rightarrow \nu_1$ & ν_3

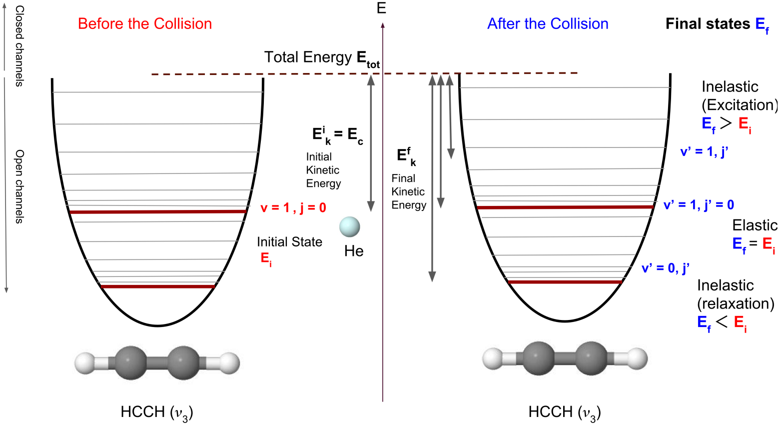

Closed channels
Open channels
Before the Collision
E
After the Collision
Final states E_f
Total Energy E_tot
E^i_k = E_c
Initial
Kinetic
Energy
E^f_k
Final
Kinetic
Energy
v = 1 , j = 0
Initial State
E_i
He
Inelastic
(Excitation)
E_f > E_i
v' = 1, j'
v' = 1, j' = 0
Elastic
E_f = E_i
v' = 0, j'
Inelastic
(relaxation)
E_f < E_i
HCCH (ν3)
HCCH (ν3)

DAN II: polyatomic molecules C_2H_2 and CO_2



ν_3 for HCCH $= 3289\ cm^{-1}$ $\quad$ ν_3 for $CO_2 = 2349\ cm^{-1}$ $\quad$ IR active

$$\text{He} + \text{HCCH}(v=1, j=0) \rightarrow \text{He} + \text{HCCH}(v'=0, j')$$



ν_3 for HCCH $= 3289\ cm^{-1}$ ν_3 for $CO_2 = 2349\ cm^{-1}$ IR active

He + HCCH(v=1,j=0) →He + HCCH(v'=0,j')

Rovibrational transitions in HCCH and CO_2 by collision with He

Scattering Recipe

Scattering Recipe

Molecules are treated as waves: incoming He as “plane waves“

Scattering Recipe

Molecules are treated as waves: incoming He as "plane waves"

① Monomer's Hamiltonian:

$$\hat{H}_Q = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial Q^2} + \frac{\hat{j}^2}{2I} + \underbrace{V_{monomer}(Q)}_{1D\ pot.\ for\ a\ normal\ mode}$$

Scattering Recipe

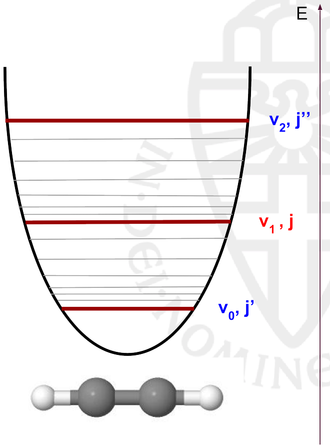
Molecules are treated as waves: incoming He as "plane waves"

① Monomer's Hamiltonian:

$$\hat{H}_Q = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial Q^2} + \frac{\hat{j}^2}{2I} + \underbrace{V_{monomer}(Q)}_{1D\ pot.\ for\ a\ normal\ mode}$$

where

$$I = \sum_i^4 m_i(Z_i^0 + Qdz_i)^2$$



② Total Hamiltonian of the complex:

$$\hat{H} = \underbrace{\hat{H}_Q}_{Monomer's\ Hamiltonian} - \frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{L}^2}{2\mu R^2} + \underbrace{V_{int}(Q, R, \theta)}_{3D\ pot\ responsible\ for\ the\ coupling}$$

② Total Hamiltonian of the complex:

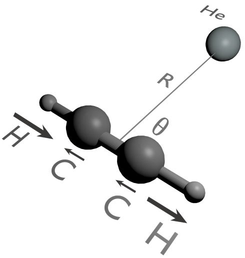
$$\hat{H} = \underbrace{\hat{H}_Q}_{Monomer's\ Hamiltonian} - \frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{L}^2}{2\mu R^2} + \underbrace{V_{int}(Q, R, \theta)}_{3D\ pot\ responsible\ for\ the\ coupling}$$

3D potential: to do the dynamics.

② Total Hamiltonian of the complex:

$$\hat{H} = \underbrace{\hat{H}_Q}_{Monomer's\ Hamiltonian} - \frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2} R + \frac{\hat{L}^2}{2\mu R^2} + \underbrace{V_{int}(Q, R, \theta)}_{3D\ pot\ responsible\ for\ the\ coupling}$$

3D potential: to do the dynamics.

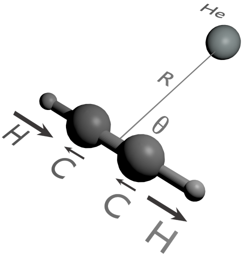


He-HCCH vdW over v_3 normal mode of HCCH

② Total Hamiltonian of the complex:

$$\hat{H} = \underbrace{\hat{H}_Q}_{Monomer's\ Hamiltonian} - \frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{L}^2}{2\mu R^2} + \underbrace{V_{int}(Q,R,\theta)}_{3D\ pot\ responsible\ for\ the\ coupling}$$

3D potential: to do the dynamics.



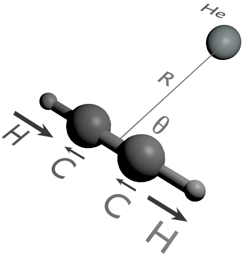
One normal mode at a time.

He-HCCH vdW over v_3 normal mode of HCCH

② Total Hamiltonian of the complex:

$$\hat{H} = \underbrace{\hat{H}_Q}_{Monomer's\ Hamiltonian} - \frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{L}^2}{2\mu R^2} + \underbrace{V_{int}(Q, R, \theta)}_{3D\ pot\ responsible\ for\ the\ coupling}$$

3D potential: to do the dynamics.



He-HCCH vdW over v_3 normal mode of HCCH

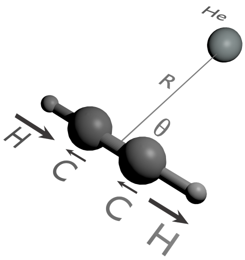
One normal mode at a time.

V is 3D potential:
(Normal mode Q, Radial grid R, Angle θ)

② Total Hamiltonian of the complex:

$$\hat{H} = \underbrace{\hat{H}_Q}_{Monomer's\ Hamiltonian} - \frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{L}^2}{2\mu R^2} + \underbrace{V_{int}(Q, R, \theta)}_{3D\ pot\ responsible\ for\ the\ coupling}$$

3D potential: to do the dynamics.



He-HCCH vdW over v_3 normal mode of HCCH

One normal mode at a time.

V is 3D potential:
(Normal mode Q, Radial grid R, Angle θ)

$He + HCCH$ and $He + CO_2 \rightarrow$ van der Waals (vdW) interactions.

$He - HCCH$ ($^1\Sigma$) and $He - CO_2$ ($^1\Sigma$) PES

CCSD(T): the **"gold standard"** of computational chemistry.

$He - HCCH$ ($^1\Sigma$) and $He - CO_2$ ($^1\Sigma$) PES

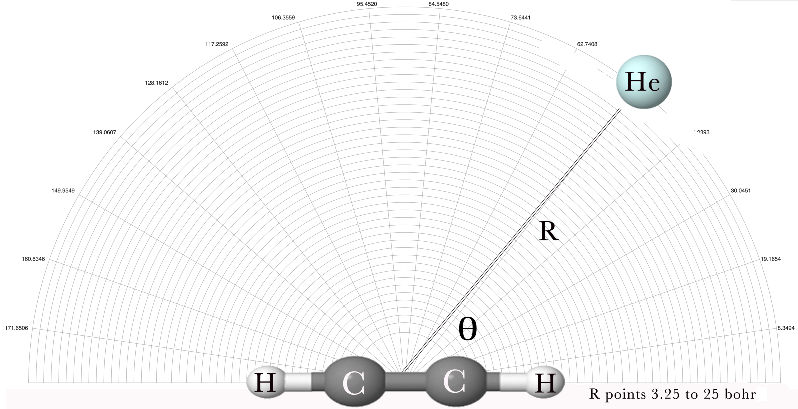
CCSD(T): the **"gold standard"** of computational chemistry.

ab initio: CCSD(T)/aug-cc-pVTZ+ MidBond functions (MB)

CCSD(T): the **"gold standard"** of computational chemistry.

ab initio: CCSD(T)/aug-cc-pVTZ+ MidBond functions (MB)

$He - HCCH$ is highly anisotropic: a dense grid to probe the anisotropy.
2304 points.



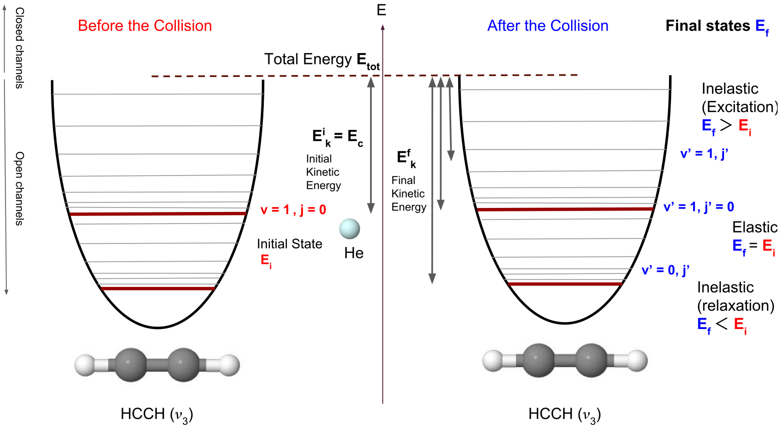
③ Solving Coupled Channels (CC) Eqs & calculate Integral Cross Sections (ICS):

③ Solving Coupled Channels (CC) Eqs & calculate Integral Cross Sections (ICS):

$$\sigma_{v,j\rightarrow v',j'}(E_{v,j}) = \frac{\pi}{(2j+1)k_{v,j}^2}\sum_J (2J+1)\sum_{l=|J-j|}^{J+j}\sum_{l'=|J-j'|}^{J+j'}|\delta_{vv'}\delta_{jj'}\delta_{ll'}-S^J_{vjl,v'j'l'}|^2$$

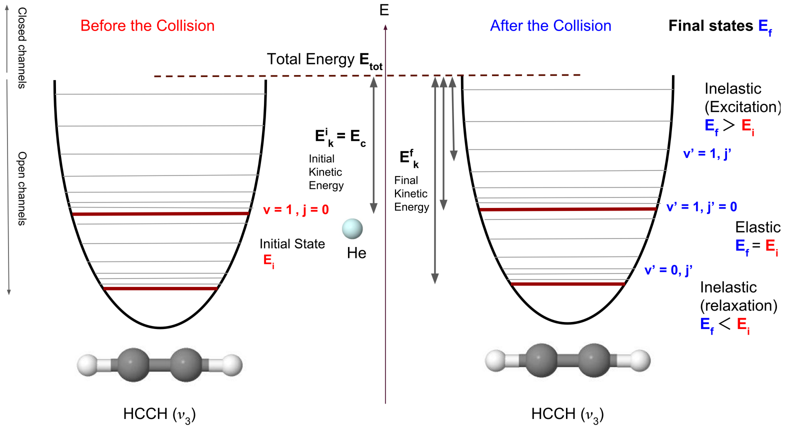
③ Solving Coupled Channels (CC) Eqs & calculate Integral Cross Sections (ICS):

$$\sigma_{v,j\rightarrow v',j'}(E_{v,j}) = \frac{\pi}{(2j+1)k^2_{v,j}} \sum_J (2J+1) \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |\delta_{vv'}\delta_{jj'}\delta_{ll'} - S^J_{vjl,v'j'l'}|^2$$



③ Solving Coupled Channels (CC) Eqs & calculate Integral Cross Sections (ICS):

$$\sigma_{v,j\rightarrow v',j'}(E_{v,j}) = \frac{\pi}{(2j+1)k^2_{v,j}} \sum_J (2J+1) \sum_{l=|J-j|}^{J+j} \sum_{l'=|J-j'|}^{J+j'} |\delta_{vv'}\delta_{jj'}\delta_{ll'} - S^J_{vjl,v'j'l'}|^2$$



④ Convergence Test

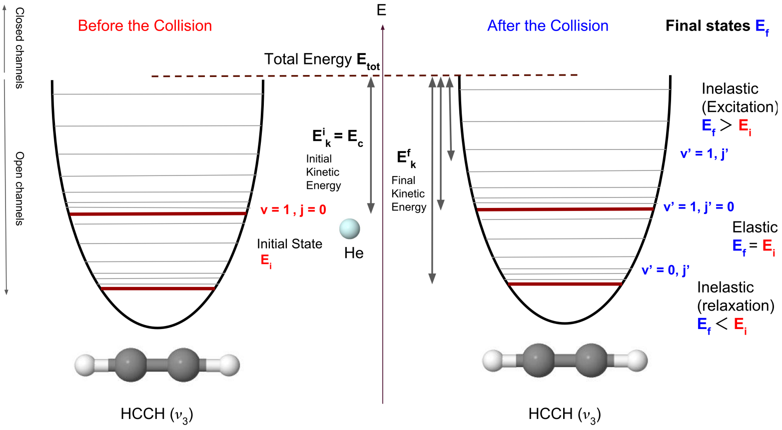
We converge each parameter used in the calculations:

- Ro-vibrational basis/energy levels v, j
- Total angular momentum J: partial waves
- Scattering radial grid R & angular grid θ

④ Convergence Test

We converge each parameter used in the calculations:

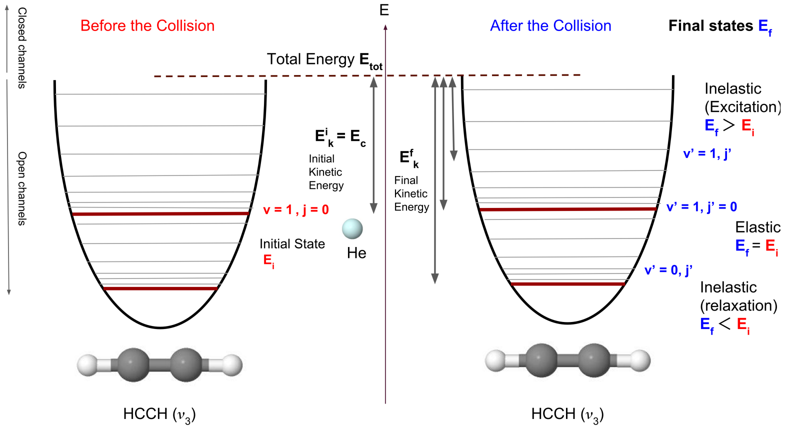
- Ro-vibrational basis/energy levels v, j
- Total angular momentum J: partial waves
- Scattering radial grid R & angular grid θ



④ Convergence Test

We converge each parameter used in the calculations:

- Ro-vibrational basis/energy levels v, j
- Total angular momentum J: partial waves
- Scattering radial grid R & angular grid θ



Higher collisional energies → more accessible states

Born approximation: for vibrational coupling

$$\langle \psi_{v=1,j=0} | \Delta V(R,\theta,Q) | \psi_{v'=0,j'} \rangle$$

Born approximation: for vibrational coupling

$$\langle \psi_{v=1,j=0} | \Delta V(R, \theta, Q) | \psi_{v'=0,j'} \rangle$$

- Cheaper (4 times faster) than full CC calculations
- Half the memory = more runs in parallel

Born approximation: for vibrational coupling

$$\langle \psi_{v=1,j=0} | \Delta V(R,\theta,Q) | \psi_{v'=0,j'} \rangle$$

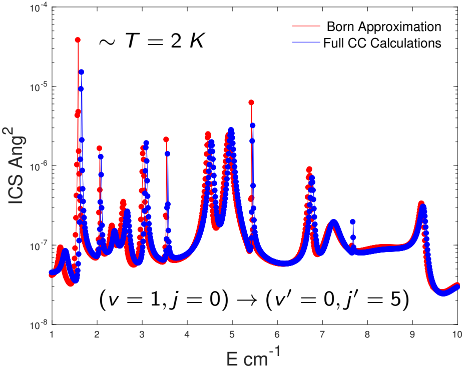
- Cheaper (4 times faster) than full CC calculations
- Half the memory = more runs in parallel

Born approximation: for vibrational coupling

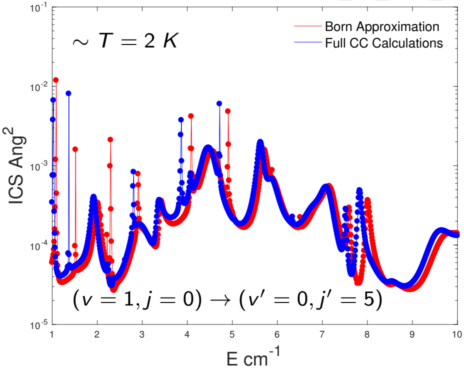
$$\langle \psi_{v=1,j=0} | \Delta V(R,\theta,Q) | \psi_{v'=0,j'} \rangle$$

- Cheaper (4 times faster) than full CC calculations
- Half the memory = more runs in parallel

He-C_2H_2 (ν_3 IR active)$\sim 3289\ cm^{-1}$



He-CO_2 (ν_3 IR active)$\sim 2349\ cm^{-1}$

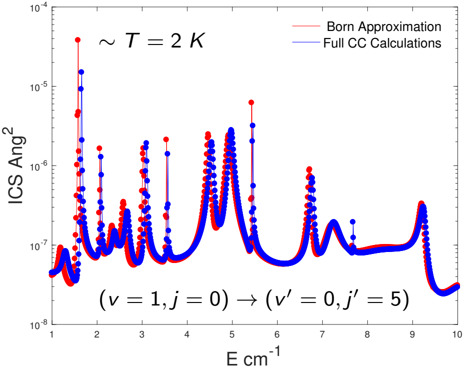


Born approximation: for vibrational coupling

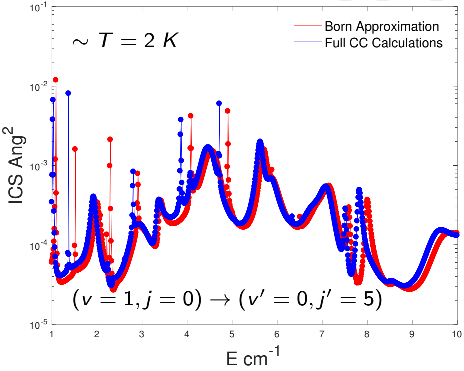
$$\langle \psi_{v=1,j=0} | \Delta V(R, \theta, Q) | \psi_{v'=0,j'} \rangle$$

- Cheaper (4 times faster) than full CC calculations
- Half the memory = more runs in parallel

He-C_2H_2 (ν_3 IR active)$\sim$ 3289 cm^{-1}



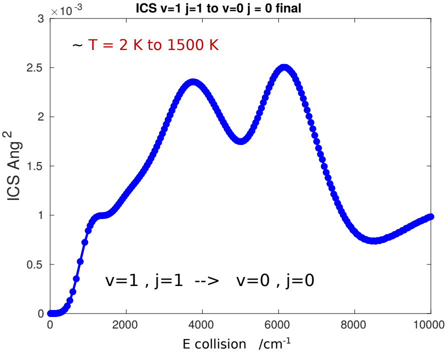
He-CO_2 (ν_3 IR active)$\sim$ 2349 cm^{-1}

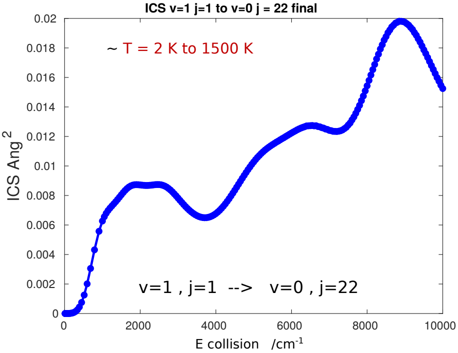


- Very sharp resonances
- Long lifetime of the complex

State-to-State Cross Sections: preliminary results

$He - C_2H_2$ (ν_3 IR active) $\quad B \approx 1.177\ cm^{-1}$

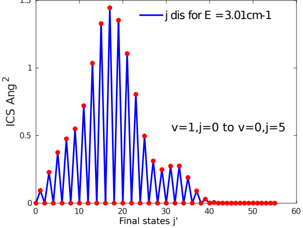


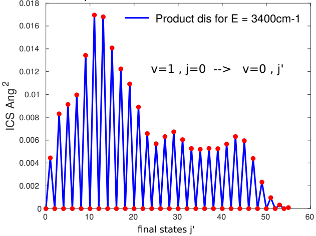


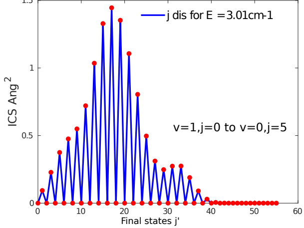
symmetry:

$v = 1, j = 1 \rightarrow v' = 0, j' = even$

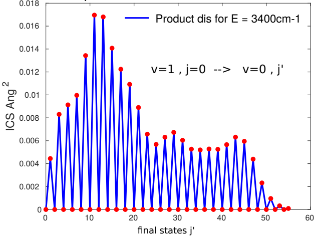
$v = 1, j = 0 \rightarrow v' = 0, j' = odd$


j dis for E =3.01cm-1
v=1,j=0 to v=0,j=5
ICS Ang ^{2}
Final states j'

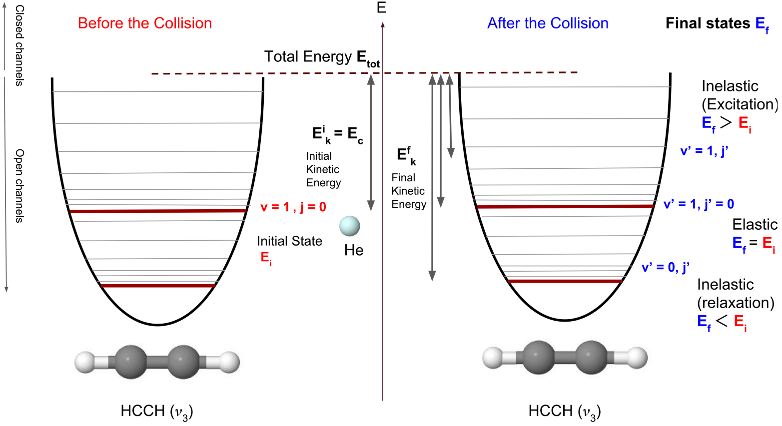

Product dis for E = 3400cm-1
v=1 , j=0 --> v=0 , j'
ICS Ang ^{2}
final states j'



j dis for E =3.01cm-1
v=1,j=0 to v=0,j=5
ICS Ang 2
Final states j'
0
0.5
1
0
10
20
30
40
50
60

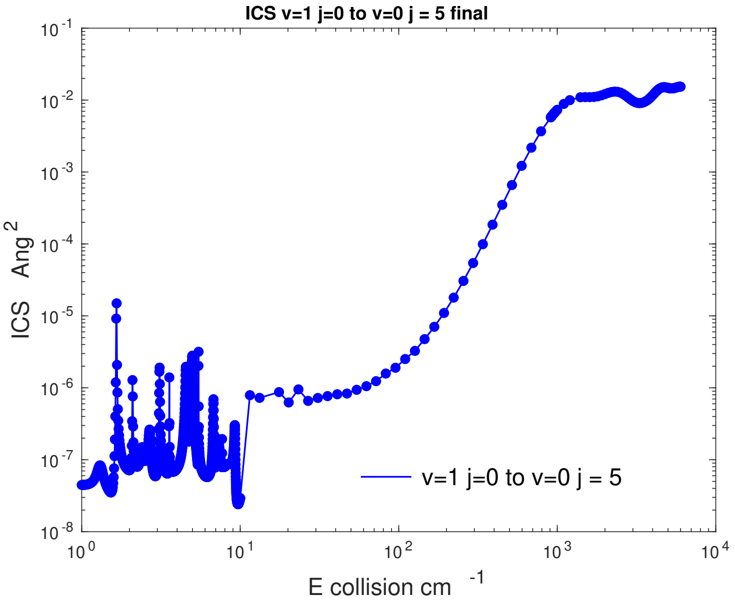


Product dis for E = 3400cm-1
v=1 , j=0 --> v=0 , j'
ICS Ang 2
final states j'
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
0.018
0
10
20
30
40
50
60



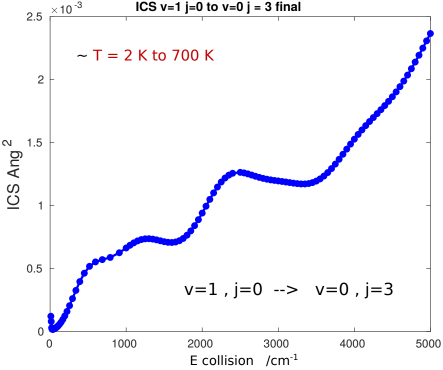
Closed channels
Open channels
Before the Collision
E
After the Collision
Final states E_f
Total Energy E_{tot}
$E^i_k = E_c$
Initial
Kinetic
Energy
E^f_k
Final
Kinetic
Energy
v = 1 , j = 0
Initial State
E_i
He
Inelastic
(Excitation)
$E_f > E_i$
v' = 1, j'
v' = 1, j' = 0
Elastic
$E_f = E_i$
v' = 0, j'
Inelastic
(relaxation)
$E_f < E_i$
HCCH (ν_3)
HCCH (ν_3)

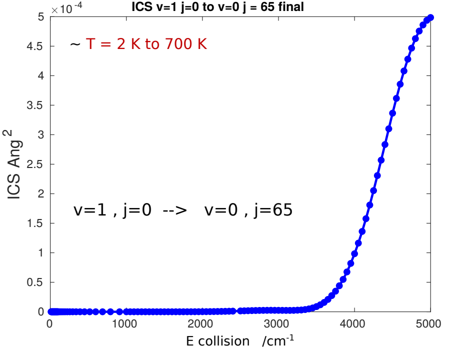
$T \sim 0\ K$ to $800\ K$



State-to-State Cross Sections: preliminary results

$He - CO_2$ (ν_3 IR active) $B \approx 0.39\ cm^{-1}$





symmetry:

$v = 1, j = 1 \rightarrow v' = 0, j' = even$

$v = 1, j = 0 \rightarrow v' = 0, j' = odd$

The collision energies (KE): 1 cm^{-1} to 10 000 cm^{-1}.

Boltzmann averaging of the cross sections:

$$r_{vj \leftarrow v'j'}(T) = \left(\frac{8k_B T}{\pi\mu}\right)^{1/2} \int_0^\infty \sigma_{vj \leftarrow v'j'}(E) e^{-E/k_B T} E dE$$

Vibrational quenching:

$$r_{v \leftarrow v'}(T) = \frac{\sum_{j,j'} g_j e^{-E_{vj}/k_B T} r_{vj \leftarrow v'j'}(T)}{\sum_j g_j e^{-E_{vj}/k_B T}}$$

Current and future work

Now: **calculating rate coefficients**

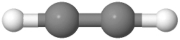
100 K to 1500 K $\sim$ $1\ cm^{-1}$ to $10\ 000\ cm^{-1}$

ν_3 for HCCH $= 3289\ cm^{-1}$ $\quad \nu_3$ for $CO_2 = 2349\ cm^{-1}$ $\quad$ IR active

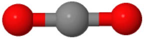
Future

4D & 5D PES + QM scattering by collision with:

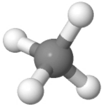
He / H_2



bending mode ν_5
IR active
HCCH



bending mode ν_2
IR active (FR)
CO_2



bending mode ν_4 & ν_4
IR active
CH_4

Acknowledgments

My supervisors:

Prof. Gerrit C. Groenenboom

Prof. Ad van der Avoird

My Colleagues:

Arthur Christianen

MSc. Matthieu Besemer

Funding: NWO / DAN II

NWO Netherlands Organisation for Scientific Research

Thank You!