Atomic and Molecular Collisions

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Introduction

Inelastic collisions, e.g.

$$\mathrm{H} + \mathrm{CO}(\nu, j) \longrightarrow \mathrm{H} + \mathrm{CO}(\nu', j')$$

- Vibrational quantum number: $\nu = 0, 1, \ldots$
- Rotational quantum number: $j = 0, 1, \ldots$

$$\begin{array}{cccc} \frac{d}{dt} n_{\mathrm{CO}(\nu',j')} = & k_{\nu,j\to\nu' j'}(T) & n_{\mathrm{H}} & n_{\mathrm{CO}(\nu,j)} \\ (m^{-3}s^{-1}) & (m^3/s) & (m^{-3}) & (m^{-3}) \end{array}$$

Interstellar medium:

- Dominant species: $\mathrm{H}, \mathrm{He}, \mathrm{H}_2$, $n \approx 10^6\,\mathrm{cm}^{-3}$
- About 200 molecules observed: $\mathrm{CO}, \mathrm{CN}, \mathrm{CH}_4, \mathrm{H}_2\mathrm{CO}, \ldots$
- $\Rightarrow$ lectures Pierre Hily-Blant and Inga Kamp

Types of collisions

- Elastic: only direction of motion changes

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{A} + \mathrm{B}$$

- Inelastic: internal state of molecules changes

$$\mathrm{A} + \mathrm{BC}(\nu, j) \rightarrow \mathrm{A} + \mathrm{BC}(\nu', j')$$

- Reactive: chemical composition changes

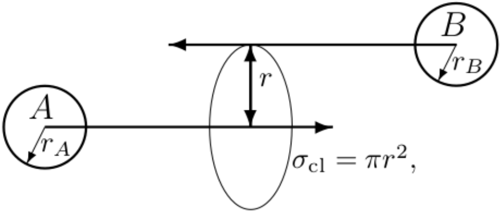
$$\mathrm{A} + \mathrm{BC}(\nu, j) \rightarrow \mathrm{AB}(\nu', j') + \mathrm{C}$$

$\Rightarrow$ Here: only 2 body collisions

Overview of lecture

- Classical hard sphere collision
  - Cross section
  - Collision rates
- Classical central force problem: atom-atom elastic
  - Classical Hamiltonian
  - Classical trajectories
  - Impact parameter and orbital angular momentum
- Quantum scattering in 1 dimension
  - Flux
- Quantum scattering in 3 dimensions, elastic and inelastic
  - Coupled channels method

Classical hard spheres, cross section



The classical collisional cross section $\sigma_{\rm cl}$ for for hard spheres with diameters r_A and r_B is given by

$$\sigma_{\rm cl} = \pi(r_A + r_B)^2.$$

If the relative velocity is v than the collision rate is given by

$$r_{\rm cl} = v\ \sigma_{\rm cl}$$
$$(m^3/s) \quad (m/s)\ (m^2)$$

Two particles A and B: masses m_A and m_B, positions in $\mathbb{R}^3$: $\boldsymbol{r}_A$ and $\boldsymbol{r}_B$
Center-of-mass coordinates:

$$\boldsymbol{R}_{CM} = \frac{m_A \boldsymbol{r}_A + m_B \boldsymbol{r}_B}{m_A + m_B}$$
$$\boldsymbol{r} = \boldsymbol{r}_B - \boldsymbol{r}_A, \qquad r \equiv |\boldsymbol{r}|.$$

Classical Hamiltonian: $H(\boldsymbol{r}, \dot{\boldsymbol{r}}) = T + V(r)$

$$T = \frac{1}{2} m_A \dot{\boldsymbol{r}}_A \cdot \dot{\boldsymbol{r}}_A + \frac{1}{2} m_B \dot{\boldsymbol{r}}_B \cdot \dot{\boldsymbol{r}}_B = \frac{1}{2} M \dot{\boldsymbol{R}} \cdot \dot{\boldsymbol{R}} + \frac{1}{2} \mu \dot{\boldsymbol{r}} \cdot \dot{\boldsymbol{r}}.$$

Total mass: $M = m_A + m_B$, reduced mass: $\mu^{-1} = m_A^{-1} + m_B^{-1}$.
Conjugate momenta:

$$p_i \equiv \frac{\partial T}{\partial \dot{r}_i} = \mu \dot{r}_i, \quad i = 1, 2, 3$$

Hamiltonian for relative motion:

$$H(\boldsymbol{r}, \boldsymbol{p}) = \frac{p^2}{2\mu} + V(r)$$

Classical Hamilton-Jacobi equations

$$\dot{r}_i = \frac{\partial H}{\partial p_i} = p_i, \qquad \dot{\boldsymbol{r}} = \mu^{-1}\boldsymbol{p}$$

$$\dot{p}_i = -\frac{\partial H}{\partial r_i} = -\frac{\partial V(r)}{\partial r_i} = -\frac{\partial r}{\partial r_i}\frac{\partial V(r)}{\partial r}, \qquad \dot{\boldsymbol{p}} = -\hat{\boldsymbol{r}}\frac{\partial V(r)}{\partial r}$$

The total angular momentum of the system, $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p}$, is *conserved*:

$$\dot{\boldsymbol{\ell}} = \dot{\boldsymbol{r}} \times \boldsymbol{p} + \boldsymbol{r} \times \dot{\boldsymbol{p}} = \mu^{-1}\boldsymbol{p} \times \boldsymbol{p} - r\frac{\partial V(r)}{\partial r}\hat{\boldsymbol{r}} \times \hat{\boldsymbol{r}} = \boldsymbol{0}.$$

Rewrite Hamiltonian using:

$$\ell^2 = \boldsymbol{\ell}\cdot\boldsymbol{\ell} = (\boldsymbol{r}\times\boldsymbol{p})\cdot(\boldsymbol{r}\times\boldsymbol{p}) = (\boldsymbol{r}\cdot\boldsymbol{r})(\boldsymbol{p}\cdot\boldsymbol{p}) - (\boldsymbol{r}\cdot\boldsymbol{p})(\boldsymbol{r}\cdot\boldsymbol{p}) = r^2p^2 - (\boldsymbol{r}\cdot\boldsymbol{p})^2$$

or

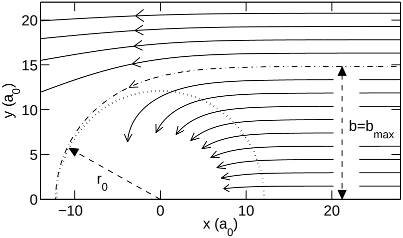
$$r^2p^2 = \ell^2 + r^2p_r^2,$$

so

$$H = \frac{p^2}{2\mu} + V(r) = \frac{p_r^2}{2\mu} + \frac{\ell^2}{2\mu r^2} + V(r)$$

Classical trajectories for central force problem

$\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{p} \quad \Rightarrow \boldsymbol{\ell} \perp \boldsymbol{r}$ and $\boldsymbol{\ell} \perp \boldsymbol{p}$: scattering plane



$$\text{Hamiltonian radial problem: } H = \frac{p_r^2}{2\mu} + \overbrace{\underbrace{\frac{l^2}{2\mu r^2}}_{\text{centrifugal term}} + V(r)}^{\text{Effective 1-D potential}}$$

ℓ related to impact parameter b: $\ell = \mu v b$

Solution for the angle: $\varphi(t) = \varphi(0) + \int_0^t \frac{\ell}{\mu r(t)^2} dt.$

Classical to quantum

Observables become operators

$$p_i \rightarrow \hat{p}_i = \frac{\hbar}{i}\frac{\partial}{\partial r_i}, \qquad \boldsymbol{\ell} \rightarrow \hat{\boldsymbol{\ell}} = \boldsymbol{r} \times \hat{\boldsymbol{p}}, \qquad \hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2} r + \frac{\hat{\ell}^2}{2\mu r^2} + V(r)$$

For stationairy states, solve time independent Schrödinger equation:

$$\hat{H}\Psi(\boldsymbol{r}) = E\Psi(\boldsymbol{r}), \quad \text{condition: } \int |\Psi(\boldsymbol{r})|^2 d\boldsymbol{r} = 1 \text{ (Hilbert space)}$$

For moving particles, solve time-dependent Schrödinger equation:

$$i\hbar\frac{\partial\Psi(\boldsymbol{r},t)}{\partial t} = \hat{H}\Psi(\boldsymbol{r},t), \quad \text{initial condition: } \Psi(\boldsymbol{r}, t=0)$$

Weird tricks:

- Use time-independent Schrödinger equation for scattering (fixed E)
- Drop normalization condition (leave Hilbert space)
- Use complex wave functions to describe moving particles (have flux)
- Set up boundary conditions that correspond to colliding particles

Flux in one dimension

Probability for particle to be in interval $[a, b]$:

$$P_{ab}(t) = \int_a^b |\Psi(x,t)|^2 \, dx = \int_a^b \Psi(x,t)^* \Psi(x,t) \, dx$$

Use time-dependent Schrödinger equation to derive:

$$\begin{aligned}
\dot{P}_{ab}(t) &= \int_a^b \Psi(x,t)^* \, \dot{\Psi}(x,t) \, dx + \int_a^b \dot{\Psi}(x,t)^* \, \Psi(x,t) \, dx \\
&= -\frac{i}{\hbar} \int_a^b \left[\Psi(x,t)^* \hat{H} \Psi(x,t) - \Psi(x,t) \hat{H} \Psi(x,t)^* \right] dx \\
&= \frac{i\hbar}{2\mu} \int_a^b \left[\Psi(x,t)^* \frac{d^2}{dx^2} \Psi(x,t) - \Psi(x,t) \frac{d^2}{dx^2} \Psi(x,t)^* \right] dx \\
&= \frac{i\hbar}{2\mu} \int_a^b \frac{d}{dx} \left[\Psi(x,t)^* \frac{d}{dx} \Psi(x,t) - \Psi(x,t) \frac{d}{dx} \Psi(x,t)^* \right] dx \\
&= j_b - j_a
\end{aligned}$$

Flux: $\quad j_x = \frac{\hbar}{\mu} \mathrm{Im} \left[\Psi(x,t)^* \frac{\partial}{\partial x} \Psi(x,t) \right]$

Example in 1D: $\Psi(x) = Ne^{ikx}$, flux:

$$j = \frac{\hbar}{\mu} \mathrm{Im} \left[N^* e^{-ikx} \frac{d}{dx} N e^{ikx} \right] = |N|^2 \frac{\hbar k}{\mu} = \rho \frac{p}{\mu} = \rho v$$

In 3D:

$$\boldsymbol{j} = \frac{\hbar}{\mu} \mathrm{Im} \left[\Psi(\boldsymbol{r}, t)^* \, \boldsymbol{\nabla} \Psi(\boldsymbol{r}, t) \right]$$

Beam of free particles in 3D (a plane wave):

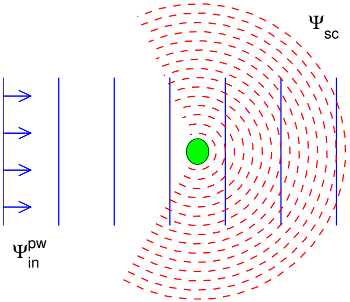
$$\Psi(\boldsymbol{r}) = N e^{i \boldsymbol{k} \cdot \boldsymbol{r}}, \qquad \text{flux:} \quad \boldsymbol{j} = |N|^2 \frac{\hbar \boldsymbol{k}}{\mu} = \rho \boldsymbol{v}$$

In spherical polar coordinates (r, θ, ϕ):

$$\boldsymbol{\nabla} = \hat{\boldsymbol{r}} \frac{\partial}{\partial r} + \hat{\boldsymbol{f}}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\boldsymbol{f}}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$$

Spherical wave $(r > 0)$:

$$\Psi(r, \theta, \phi) = f(\theta, \phi) \, \frac{1}{r} e^{ikr}, \qquad \text{flux: } \boldsymbol{j} = |f(\theta, \phi)|^2 \tfrac{\hbar k}{\mu} \, \hat{\boldsymbol{r}} + \dots$$



Problem: solve

$$(\hat{H} - E)\Psi(\boldsymbol{r}) = 0$$

with collision energy $E = \frac{\hbar^2 k^2}{2\mu}$ to find scattering amplitude $f(\theta, \phi)$

$$\Psi(\boldsymbol{r}) \underset{(\text{large } r)}{\simeq} \underbrace{v^{-\frac{1}{2}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}}}_{\text{incoming plane wave}} + \underbrace{v^{-\frac{1}{2}} \frac{1}{r} e^{ikr} f(\theta, \phi)}_{\text{outgoing scattered wave}}$$

Observable: differential cross section:

$$\sigma(\theta, \phi) = \frac{\text{outgoing flux}}{\text{incoming flux}} = |f(\theta, \phi)|^2$$

Plane wave expansion

$$\Psi^{\mathrm{pw}} = e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = \sum_{\ell=0}^{\infty} i^{\ell}(2\ell+1)j_{\ell}(kr)P_{\ell}(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{r}})$$

Spherical Bessel functions of the first kind:

$$j_{\ell}(x) \underset{(\text{large } x)}{\simeq} \frac{\sin(x-\ell\pi/2)}{x} = \frac{-e^{-i(x-\ell\pi/2)} + e^{i(x-\ell\pi/2)}}{2ix}$$

Legendre polynomials: $P_0(z) = 1$, $P_1(z) = z$, and for $\ell = 1, 2, \ldots$

Recursion relation: $$(\ell+1)P_{\ell+1}(z) = z(2\ell+1)P_{\ell}(z) - \ell P_{\ell-1}(z)$$

Orthogonality: $$\int_{-1}^{1} P_{\ell'}(z)P_{\ell}(z)dz = \frac{2}{2\ell+1} = \delta_{\ell',\ell}$$

Spherical harmonic addition theorem:

$$P_{\ell}(\hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{r}}) = \frac{4\pi}{2\ell+1}\sum_{m_{\ell}=-\ell}^{\ell} Y_{\ell m_{\ell}}(\hat{\boldsymbol{r}})Y_{\ell m_{\ell}}(\hat{\boldsymbol{k}})^{*}$$

Spherical harmonics $Y_{\ell m}(\theta, \phi)$

Commutation relations angular momentum operators

$$[\hat{\ell}_x, \hat{\ell}_y] = \hat{\ell}_x \hat{\ell}_y - \hat{\ell}_y \hat{\ell}_x = i\hbar \ell_z$$
$$[\hat{\ell}^2, \hat{\ell}_z] = 0$$

Spherical harmonics $Y_{\ell m}(\theta, \phi)$, Dirac notation: $|\ell m\rangle$

$$\hat{\ell}^2 |\ell m\rangle = \hbar^2 \ell(\ell+1)|\ell m\rangle$$
$$\hat{\ell}_z |\ell m\rangle = \hbar m |\ell m\rangle$$

Orthogonality relation:

$$\int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \, Y_{\ell',m}(\theta,\phi)^* Y_{\ell,m}(\theta,\phi) = \langle \ell' m' | \ell m\rangle = \delta_{\ell',\ell}\delta_{m',m}$$

Special cases:

$$Y_{\ell,0}(\theta,\phi) = \sqrt{\frac{2\ell+1}{4\pi}}\, P_\ell(\cos\theta)$$
$$Y_{\ell m}(0,0) = \sqrt{\frac{2\ell+1}{4\pi}}\, \delta_{m,0}$$

S-matrix for 3D elastic scattering

Wave function for free particle, $V(r) = 0$, for large r

$$\Psi^{\rm pw} \simeq \frac{2\pi}{ikr} \sum_{\ell m} Y_{\ell m}(\hat{\boldsymbol{r}})[-e^{-i(kr-\ell\pi/2)} + e^{i(kr-\ell\pi/2)}] i^{\ell} Y_{\ell m}(\hat{\boldsymbol{k}})^*$$

A potential $V(r)$ can only affect the outgoing spherical waves,

$$\Psi^{\rm SC} \simeq \frac{2\pi}{ikr} \sum_{\ell m} Y_{\ell m}(\hat{\boldsymbol{r}})[-e^{-i(kr-\ell\pi/2)} + e^{i(kr-\ell\pi/2)} S_\ell] i^{\ell} Y_{\ell m}(\hat{\boldsymbol{k}})^*$$

For free particle, $S_\ell = 1$. Always: conservation of flux $|S| = 1$
Collect change in outgoing wave as result of potential:

$$\Psi_{\rm sc} - \Psi^{\rm pw} = \frac{2\pi}{ikr} \sum_{\ell} \sum_{m} Y_{\ell m}(\boldsymbol{r}) e^{i(kr-\ell\pi/2)} (S_\ell - 1) i^{\ell} Y_{\ell m}(\hat{\boldsymbol{k}})^* \equiv \frac{1}{r} e^{ikr} f(\hat{r})$$

So the scattering amplitude is given by $[T_\ell \equiv 1 - S_\ell$, take $\hat{\boldsymbol{k}} = (0,0)]$:

$$f(\hat{r}) = \frac{2\pi}{ik} \sum_{\ell} \sum_{m} Y_{\ell m}(\hat{\boldsymbol{r}})(S_\ell - 1) Y_{\ell m}(\hat{\boldsymbol{k}})^* = \frac{i}{k} \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2} P_\ell(\cos\theta) T_\ell$$

Integral cross section (ICS) for elastic scattering

Differential cross section (DCS)

$$\sigma(\theta,\phi) = |f(\theta,\phi)|^2$$

The ICS:

$$\sigma = \int_{-1}^{1} d\cos\theta \int_0^{2\pi} d\phi\, |f(\theta,\phi)|^2 = \frac{\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)|T_\ell|^2$$

Fully absorbing hard sphere:

$$|T_\ell|^2 \approx \begin{cases} 1 - S_l \approx 1, & \text{for } \ell < \ell_{\max} = \mu v b_{\max}/\hbar \\ 0, & \text{otherwise} \end{cases}$$

Using

$$\sum_{l=0}^{\ell_{\max}} \ell \approx \frac{1}{2}\ell_{\max}^2$$

$$\sigma \approx \frac{\pi}{k^2}\ell_{\max}^2 = \pi b_{\max}^2$$

Solving elastic scattering for central potential

Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{\hat{\ell}^2}{2\mu r^2} + V(r)$$

Factorize partial wave:

$$\Psi_{\ell,m}(r,\theta,\phi) = \frac{1}{r}\varphi_\ell(r)Y_{\ell,m}(\theta,\phi)$$

Radial equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{\hat{\ell}^2}{2\mu r^2} + V(r) - E\right]\varphi_\ell(r) = 0$$

Boundary condition bound state: $\int |\varphi(r)|^2 dr = 1$

Boundary conditions for elastic scattering:

$$\begin{array}{rcl} \varphi_\ell(r=0) & = & 0 \\ \varphi_\ell(r) & \underset{(\text{large } x)}{\simeq} & N\left(-e^{-ikr} + e^{ikr}S_\ell\right) \end{array}$$

Discretize radial problem

Set up equally spaced radial grid:

$$r_i \equiv r_0 + i\Delta, \quad \text{i=1,2,\dots,N}$$

Potential (may include centrifugal term) is multiplicative operator:

$$V(r)\varphi(r)|_{r=r_i} = V(r_i)\varphi(r_i)$$

Second order derivative using finite difference:

$$\frac{\partial^2}{\partial r^2}\varphi(r)|_{r=r_i} = \frac{\varphi(r_{i-1}) - 2\varphi(r_i) + \varphi(r_{i+1})}{\Delta^2}$$

Represent wave function as vector $\boldsymbol{c}$ with values on the grid $c_i \equiv \varphi(r_i)$.
Potential operator: diagonal matrix $\boldsymbol{V}$ with elements $V_{i,j} = V(r_i)\delta_{i,j}$
Kinetic energy operator $\Rightarrow$ tridiagonal matrix:

$$\boldsymbol{T} = -\frac{\hbar^2}{2\mu\Delta^2}\begin{pmatrix} -2 & 1 & & \\ 1 & -2 & 1 & \\ & 1 & -2 & 1 \\ & & 1 & \ddots \end{pmatrix}$$

Numerical solution of radial problem

Bound states (vibrational wave functions), matrix eigenvalue problem:

$$\boldsymbol{Hc} = E\boldsymbol{c}, \qquad \text{with } N \times N \text{ Hamiltonian matrix: } \boldsymbol{H} = \boldsymbol{T} + \boldsymbol{V}$$

For scattering problem, rewrite radial Schrödinger equation:

$$\frac{d^2}{dr^2}\varphi_\ell(r) = W(r)\varphi_\ell(r), \qquad \text{with } W(r) = \tfrac{\ell(\ell+1)}{r^2} + \tfrac{2\mu}{\hbar^2}[V(r) - E]$$

Second order finite difference gives three term recursion relation:

$$\frac{c_{i-1} - 2c_i + c_{i+1}}{\Delta^2} = W_i c_i, \qquad \text{with } W_i \equiv W(r_i)$$

Define ratios of wave functions in neighboring points:

$$c_{i-1} \equiv Q_i c_i, \qquad \text{initial condition: } Q_1 = 0$$

to obtain two term recursion relation for Q-matrix

$$Q_{i+1} = (2 + \Delta^2 W_i - Q_i)^{-1}$$

Karman *et al.*, J. Chem. Phys. **141**, 064102 (2014)

Obtain S-matrix by matching to free wave

Match radial wave function to asymptotic form:

$$\varphi_\ell(r) \simeq N(-e^{-ikr} + e^{ikr} S_\ell)$$

For last two points on grid (r_N must be sufficiently large):

$$\varphi_\ell(r_{N-1}) = Q_N \varphi_\ell(r_N)$$

Equation for S-matrix:

$$-e^{-ikr_{N-1}} + e^{ikr_{N-1}} S_\ell = Q_N(-e^{-ikr_N} + e^{ikr_N} S_\ell)$$

Solve S-matrix

$$S_\ell = \frac{e^{-ikr_{N-1}} - Q_N e^{-ikr_N}}{e^{ikr_{N-1}} - Q_N e^{ikr_N}}$$

Summary elastic scattering calculation

- Get potential $V(r)$, choose collision energy E
- Setup grid: r_0, stepsize Δ, number of points: N
- Select partial waves: $\ell = 0, 1, \ldots, \ell_{max}$
- Compute W-matrices: $W_i = \frac{\ell(\ell+1)}{r_i^2} + \frac{2\mu}{\hbar^2}[V(r_i) - E]$
- Set $Q_1 = 0$, use recursion to find Q_N
- Match wave function to find S_ℓ
- Transition matrix: $T_\ell = 1 - S_\ell$
- Get scattering amplitude $f(\theta, \phi)$ and DCS $\sigma(\theta, \phi) = |f(\theta, \phi)|^2$
- Obtain integral cross section $\sigma(E)$ from $T_\ell = 1 - S_\ell$
- Collision rates $k(T)$ from thermal average of $v\sigma$

Renormalised Numerov: 5nd order finite difference instead of 2nd

Jacobi (or scattering) coordinates:

$$\boldsymbol{r} = \boldsymbol{r}_B - \boldsymbol{r}_A$$

$$\boldsymbol{R} = \frac{m_A \boldsymbol{r}_A + m_B \boldsymbol{r}_B}{m_A + m_B} - \boldsymbol{r}_C, \qquad \text{reduced mass: } \mu^{-1} = (m_A + m_B)^{-1} + m_C^{-1}$$

Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{\partial^2}{\partial R^2}R + \frac{\hat{\ell}^2}{2\mu R^2} + \hat{H}_{AB} + V(R, r, \chi)$$

Rovibrational molecular states

$$[\hat{H}_{AB} - \epsilon_{\nu j}]\frac{\phi_{\nu j}(r)}{r}Y_{jm_j}(\hat{r}) = 0, \quad \text{Dirac notation: } |\nu j m_j\rangle$$

Asymptotic kinetic energy relative motion: $\frac{\hbar^2 k_{\nu j}^2}{2\mu} = E - \epsilon_{\nu j}$

Wave vector $\boldsymbol{k}_{\nu j} = k_{\nu j}\hat{\boldsymbol{k}}$,

Flux normalized plane wave: $\Psi^{PW}_{\nu j m_j} = |\nu j m_j\rangle v_{\nu j}^{-\frac{1}{2}} e^{i\boldsymbol{k}_{\nu j}\cdot\boldsymbol{R}}$

Asympototic partial wave expansion flux normalized plane wave:

$$\Psi^{PW}_{\nu j m_j} \simeq |\nu j m_j\rangle \frac{2\pi}{ik_{\nu j}R} v_{\nu j}^{-\frac{1}{2}} \sum_{\ell m_\ell} Y_{\ell m_\ell}(\hat{\boldsymbol{R}})[-e^{-i(k_{\nu j}R-\ell\pi/2)}+e^{i(k_{\nu j}R-\ell\pi/2)}]i^\ell Y_{\ell m_\ell}(\hat{\boldsymbol{k}})^*$$

Switching on the potential $V(R, r, \chi)$ affects the outgoing part

$$\Psi^{\mathrm{SC}}_{\nu j m_j} \simeq \frac{2\pi}{ik_{vj}R} \sum_{\nu' j' m_j'} \sum_{\ell' m_\ell'} \sum_{\ell m_\ell} v_{\nu' j'}^{-\frac{1}{2}} |\nu' j' m_j'\rangle |\ell' m_\ell'\rangle i^\ell Y_{\ell m_\ell}(\hat{\boldsymbol{k}})^*$$

$$\times [-\delta_{\nu'\nu}\delta_{j'j}\delta_{m_j' m_j}\delta_{\ell'\ell}\delta_{m_\ell' m_\ell} e^{-i(k_{\nu j}R-\ell\pi/2)} + e^{i(k_{\nu' j'}R-\ell'\pi/2)} S_{\nu' j' m_j' \ell' m_\ell';\nu j m_j \ell m_\ell}]$$

Rewrite as incoming plane wave + outgoing spherical wave:

$$\Psi^{\mathrm{SC}}_{\nu j m_j} \simeq |\nu j m_j\rangle v_{\nu j}^{-\frac{1}{2}} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} + \sum_{\nu' j' m_j'} |v' j' m_j'\rangle v_{\nu' j'}^{-\frac{1}{2}} \frac{e^{ik_{\nu' j'}R}}{R} f_{\nu' j' m_k' \leftarrow \nu j m_j}(\hat{\boldsymbol{R}}; \hat{\boldsymbol{k}})$$

We can now find the expression for the scattering amplitude:

$$f_{\nu' j' m_j' \leftarrow \nu j m_j}(\hat{\boldsymbol{R}}; \hat{\boldsymbol{k}}) = \frac{2\pi}{ik_{\nu j}} \sum_{\ell' m_\ell' \ell m_l} i^{\ell-\ell'} Y_{\ell' m_\ell'}(\hat{\boldsymbol{R}}) T_{\nu' j' m_j' \ell' m_\ell';\nu j m_j \ell m_\ell} Y_{\ell m_\ell}(\hat{\boldsymbol{k}})^*$$

Differential cross section:

$$\sigma_{\nu' j' m_j' \leftarrow \nu j m_j}(\hat{\boldsymbol{R}}, \hat{\boldsymbol{k}}) = \frac{\text{outgoing flux in direction } \hat{\boldsymbol{R}}}{\text{incoming flux}} = |f_{\nu' j' m_j' \leftarrow \nu j m_j}(\hat{\boldsymbol{R}}, \hat{\boldsymbol{k}})|^2$$

Integral cross section:

$$\sigma_{\nu' j' m_j' \leftarrow \nu j m_j}(\hat{\boldsymbol{k}}) = \int\int \sigma_{\nu' j' m_j' \leftarrow \nu j m_j}(\hat{\boldsymbol{R}}, \hat{\boldsymbol{k}})\, d\hat{\boldsymbol{R}}$$

- Crossed beam experiment: fix direction $\hat{\boldsymbol{k}} = \boldsymbol{e}_z$ (find ICS expression!)
- No orientation, no alignment: average over initial m_j, sum over m_j'
- Bulk: average over all directions $\boldsymbol{k}$

$$\sigma_{\nu' j' m_j' \leftarrow \nu j m_j} = \frac{1}{4\pi}\int\int \sigma_{\nu' j' m_j' \leftarrow \nu j m_j}(\hat{\boldsymbol{k}}) = \frac{\pi}{k_{\nu j}^2} \sum_{\ell' m_\ell' \ell m_l} |T_{\nu' j' m_j' \ell' m_\ell'; \nu j m_j \ell m_\ell}|^2$$

Coupled channels = close coupling method

Channel: $|\boldsymbol{n}\rangle \equiv |\nu j m_j \ell m_l\rangle$
Coupled channel expansion $\Psi_{\boldsymbol{n}} = R^{-1} \sum_{\boldsymbol{n}'} |\boldsymbol{n}'\rangle U_{\boldsymbol{n}',\boldsymbol{n}}(R)$
Schrödinger equation: $[\hat{H} - E]\Psi_{\boldsymbol{n}} = 0$
Rewrite as:

$$\frac{1}{R}\frac{d^2}{dR^2} R\,\Psi_{\boldsymbol{n}} = \frac{2\mu}{\hbar^2}\left[\frac{\hat{\ell}^2}{2\mu R^2} + \hat{H}_{AB} + V(R,r,\chi) - E\right]\Psi_{\boldsymbol{n}}$$

Take matrix elements $\langle \boldsymbol{n}' | \Psi_{\boldsymbol{n}} \rangle$

$$U''_{\boldsymbol{n}',\boldsymbol{n}}(R) = \sum_{\boldsymbol{n}''} W_{\boldsymbol{n}',\boldsymbol{n}''}(R) U_{\boldsymbol{n}'',\boldsymbol{n}}(R)$$

or in matrix notation $\boldsymbol{U}''(R) = \boldsymbol{W}(R)\boldsymbol{U}(R)$

Boundary conditions

Boundary conditions:

$$\boldsymbol{U}(R = 0) = \mathbf{0}$$

and

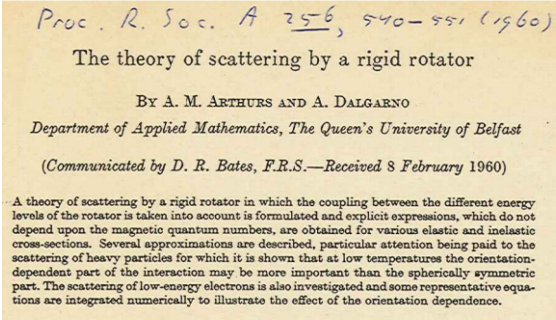
$$\boldsymbol{U}_{\boldsymbol{n}',\boldsymbol{n}}(R) \simeq -\delta_{\boldsymbol{n}',\boldsymbol{n}} v_{\boldsymbol{n}}^{-\frac{1}{2}} e^{-i(k_{\boldsymbol{n}} - \ell\pi/2)} + v_{\boldsymbol{n}'}^{-\frac{1}{2}} e^{i(k_{\boldsymbol{n}'} - \ell'\pi/2} S_{\boldsymbol{n}',\boldsymbol{n}}$$

or in matrix notation

$$\boldsymbol{U}(R) = -\boldsymbol{I}(R) + \boldsymbol{O}(R)\boldsymbol{S}$$

where $\boldsymbol{I}$ is a diagonal matrix with flux normalized incoming waves on the diagonal and $\boldsymbol{O}(R) = \boldsymbol{I}(R)^*$

Total angular momentum representation



Proc. R. Soc. A 256, 540–551 (1960)

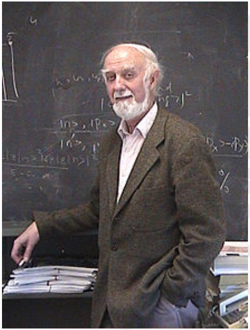
The theory of scattering by a rigid rotator

By A. M. Arthurs and A. Dalgarno

Department of Applied Mathematics, The Queen's University of Belfast

(Communicated by D. R. Bates, F.R.S.—Received 8 February 1960)

A theory of scattering by a rigid rotator in which the coupling between the different energy levels of the rotator is taken into account is formulated and explicit expressions, which do not depend upon the magnetic quantum numbers, are obtained for various elastic and inelastic cross-sections. Several approximations are described, particular attention being paid to the scattering of heavy particles for which it is shown that at low temperatures the orientation-dependent part of the interaction may be more important than the spherically symmetric part. The scattering of low-energy electrons is also investigated and some representative equations are integrated numerically to illustrate the effect of the orientation dependence.



Total angular momentum representation

Total angular momentum operators:

$$\hat{\boldsymbol{J}} \equiv \hat{\boldsymbol{j}} + \hat{\boldsymbol{\ell}}$$

Total angular momentum eigenstates:

$$|(j\ell)JM\rangle = \sum_{m_j=-j}^{j} \sum_{m_\ell=\ell}^{\ell} |jm_j\rangle|\ell m_\ell\rangle \underbrace{\langle jm_j\ell m_\ell|JM\rangle}_{\text{Clebsch-Gordan coefficients}}$$

$$\hat{J}^2|(j\ell)JM\rangle = \hbar^2 J(J+1)|(j\ell)JM\rangle$$
$$\hat{J}_z|(j\ell)JM\rangle = \hbar M|(j\ell)JM\rangle$$

Commutator: $[\hat{J}^2, \hat{J}_z] = 0$.
No external fields (isotropy of space) :

$$[\hat{H}, \hat{J}^2] = 0$$
$$[\hat{H}, \hat{J}_z] = 0$$

S-matrix in total angular momentum representation

Transformation of the S-matrix:

$$S^{J'M';JM}_{\nu'j'\ell';\nu j\ell} = \sum_{m_j' m_\ell' m_j m_\ell} \langle J'M'|j'm_j'\ell'm_\ell'\rangle S_{\nu'j'm_j'\ell m_\ell;\nu j\ell m_\ell} \langle jm_j\ell m_\ell|JM\rangle$$

Isotropy of space, J and M are good quantum numbers:

$$S^{J'M';JM}_{\nu'j'\ell';\nu j\ell} = \delta_{J'J}\delta_{M'M} S^{J}_{\nu'j'\ell';\nu j\ell}$$

Inverse relation:

$$S_{\nu'j'm_j'\ell m_\ell;\nu j m_j \ell m_\ell} = \sum_{JM} \langle j'm_j'\ell'm_\ell'|J'M'\rangle S^{J}_{\nu'j'\ell';\nu j\ell} \langle JM|jm_j\ell m_\ell\rangle$$

ICS, after averaging over initial m_j and summing over final m_j'

$$\sigma_{\nu'j'\leftarrow\nu j} = \frac{\pi}{k_{\nu j}^2}\frac{1}{2j+1}\sum_J (2J+1)\sum_{\ell\ell'} |T^J_{\nu'j'\ell';\nu jl}|^2$$

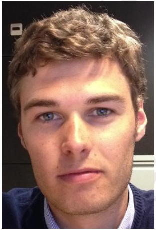
Applications of theoretical chemistry in astrochemistry

- Rovibrational inelastic collision rates for H+CO(v, j)

PhD project Lei Song

- Gauging magnetic field strengths with methanol masers

Boy Lankhaar (Now Onsola, Sweden)



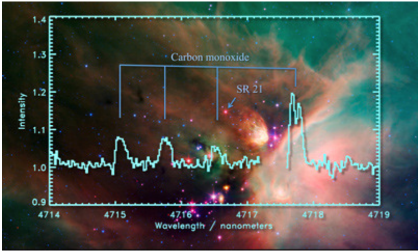
[2014]

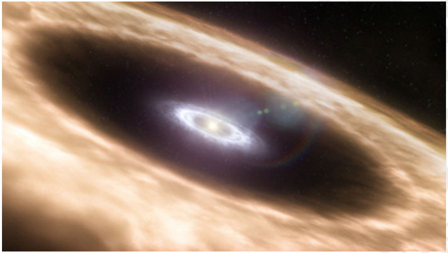
CO is observed in proto-planetary disks

- CO is **second most abundant** molecule in the universe
- Is is **coolant** essential for creating stars
- It is **probe** of temperature and density

Emission of CO from proto-planetary disk at 400 light years:

$$\mathrm{CO}(v = 1, j) \rightarrow \mathrm{CO}(v' = 0, j') + h\nu(\lambda = 4.7\mu\mathrm{m}, 2120\ \mathrm{cm}^{-1})$$





Pontoppidan, Blake, van Dishoeck *et al.*, Astrophys. J., 684, 1323 (2008)

Population of CO(v, j) levels

- Emmision of light - Einstein A coefficient

$$\mathrm{CO}(v,j) \stackrel{A}{\to} \mathrm{CO}(v',j') + h\nu$$

- Absorption of light - Einstein B coefficient

$$\mathrm{CO}(v,j) + h\nu \stackrel{B}{\to} \mathrm{CO}(v',j')$$

- Collision rates $r_{vj\to v'j'}(T)$ $\Leftarrow$ Missing

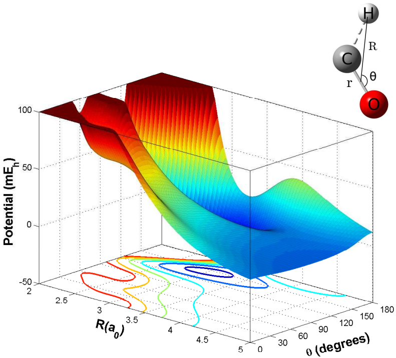
$$\mathrm{CO}(v,j) + \mathrm{H}/\mathrm{H_2}/\mathrm{He} \stackrel{r(T)}{\to} \mathrm{CO}(v',j') + \mathrm{H}/\mathrm{H_2}/\mathrm{He}$$

- Local thermal equilibrium

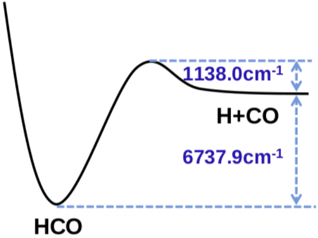
$$n_{\mathrm{H_2}} > \frac{A}{r}$$

$\Rightarrow$ Often no equilibrium

H+CO(v,j)



- 3-D potential, with MOLPRO
- 4400 *ab initio* points
- UCCSD(T), d-aug-cc-pVnZ
- extrapolated from $n = 3, 4, 5$
- $D_e = 0.8$ eV ~ 6500 cm^{-1}



Lei Song, A. van der Avoird, G. C. Groenenboom,
J. Phys. Chem. A, **117**, 7571 (2013)

Good news: HCO bound states ($J = 0$)

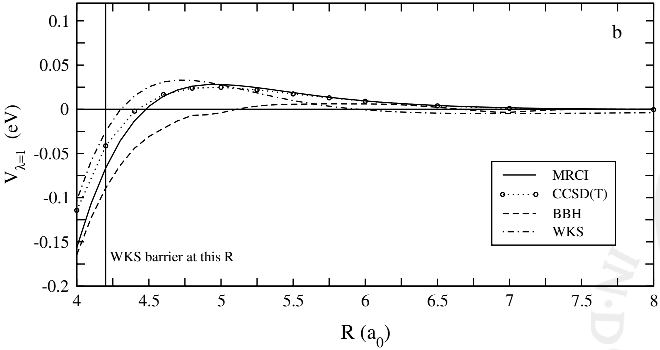
(ν_1, ν_2, ν_3)	Experimental	Calculated	Deviation
(0,0,1)	1080.76	1079.6	−0.11%
(0,1,0)	1868.17	1871.6	0.18%
(0,0,2)	2142	2145.2	0.15%
(1,0,0)	2434.48	2428.5	−0.25%
(0,1,1)	2942	2950.0	0.27%
(0,0,3)	3171	3186.2	0.48%
(1,0,1)	3476	3464.1	−0.34%
(0,2,0)	3709	3719.0	0.27%
(0,1,2)	3997	4013.1	0.40%
(0,0,4)	4209[a]	4195.7	−0.32%
(1,1,0)	4302	4301.5	−0.01%
(1,0,2)	4501[a]	4478.7	−0.50%
(2,0,0)	4570[a]	4546.0	−0.53%
(0,2,1)	4783.2	4797.2	0.29%

	D_e (cm^{-1})	Dissociation barrier	
$He + CO$	23	0	van der Waals
H_2+CO	94	0	van der Waals
$H + CO$	6840	1140	chemical bond

Cost of scattering calculation $\sim \mathrm{channels}^3$

- He+NO: 700 channels, [Vogels *et al.*, Science, **350**, 787 (2015)]
- OH+NO: 4 400 channels, [Kirste *et al.*, Science, **338**, 1060 (2012)]
- H+CO: 11 000 channels, [Song *et al.*, JCP **142**, 204 303 (2015)]

H+CO long range potential



B. C. Shepler, **B. H. Yang**, T. J. Dhilip Kumar, **P. C. Stancil**, J. M. Bowman, **N. Balakrishnan**, P. Zhang, E. Bodo, and A. Dalgarno Astron. Astrophys., 475, L15 (2007)

- Barrier our 3-D potential: 1138 cm^{-1} = 3.25 kcal/mol = 1637 K

Scattering calculation

Coupled Channels (CC)

- Partial waves $J = 0, \ldots, 100$
- CO(v, j) states:, all $v < n$, B$n(j_1, j_2, \ldots, j_n)$
- **Big:** B9(79,70,59,45,45,30,30,25,25) $\sim$ **11,000** channels
- **Small:** B3(61,52,40,22) $\sim$ **4,300** channels
- R-grid: : 3 - 40 a_0
- Variable channel basis
- Code optimized/memory use/parallel code

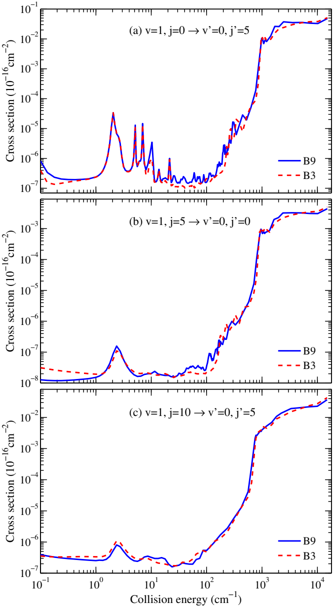
Coupled States (CS)

- Take K as good quantum number
- Order magnitude faster

Infinite order sudden (IOS)

- Average over fixed orientations
- Vibrational transitions

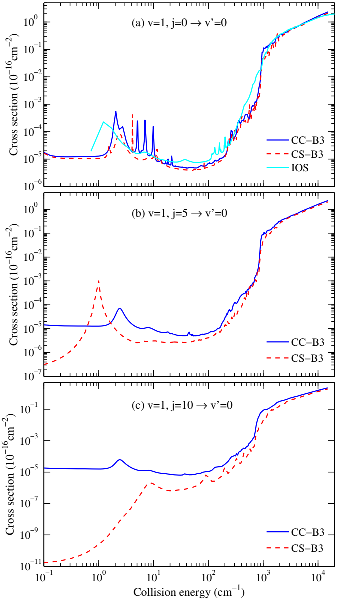
State-to-state H+CO cross sections: basis convergence



- Big basis (B9): error 10%
- Small basis (B3): error 25%

$\Rightarrow$ B3 good enough

Coupled channels vs coupled states - quenching

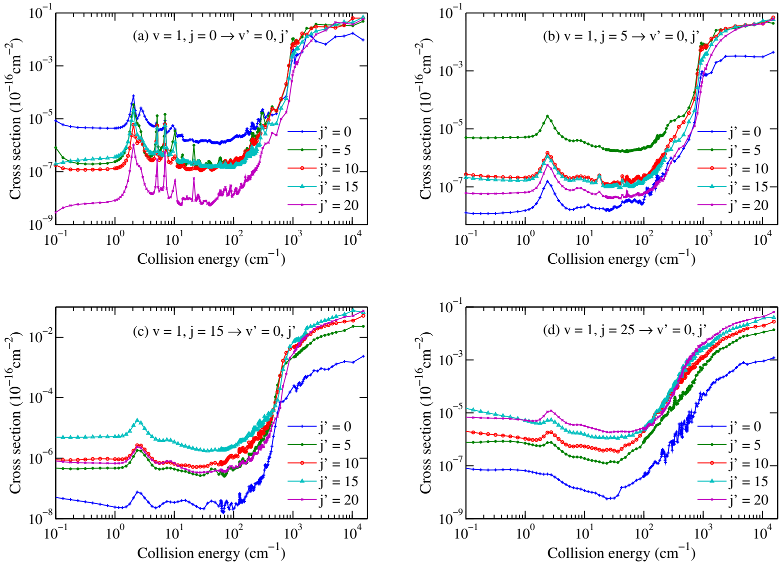


Coupled states fails $E < 1000$ cm^{-1}

$\Rightarrow$ Must use coupled channels

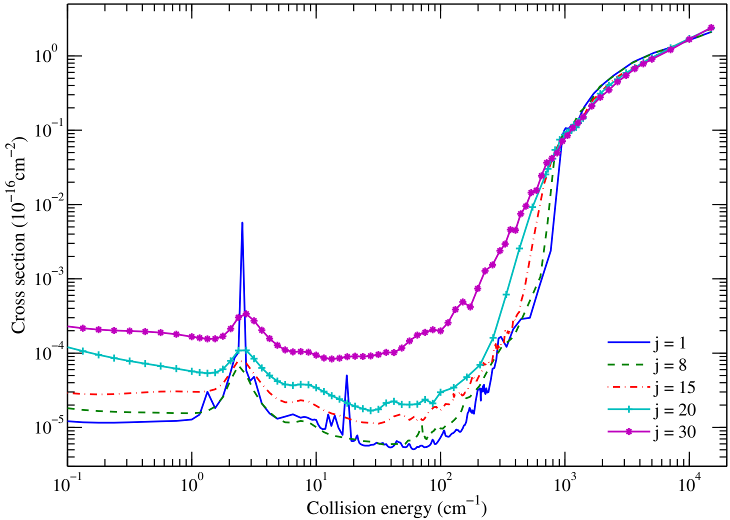
Classical mechanics also fails
(Marc C. van Hemert, Leiden)

H+CO(v, j) $\rightarrow$ H+CO(v', j') - several months later

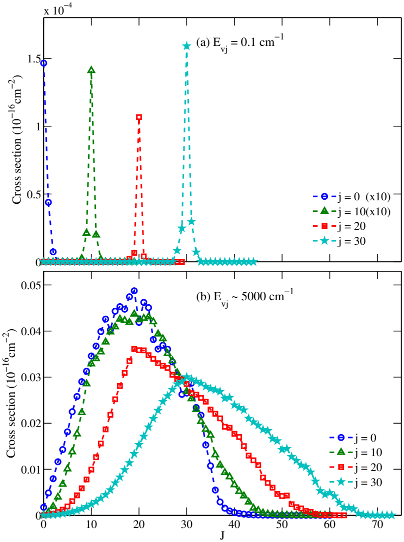


Rotation-translation coupling helps to cross barrier

$v = 1, j \to v = 0$

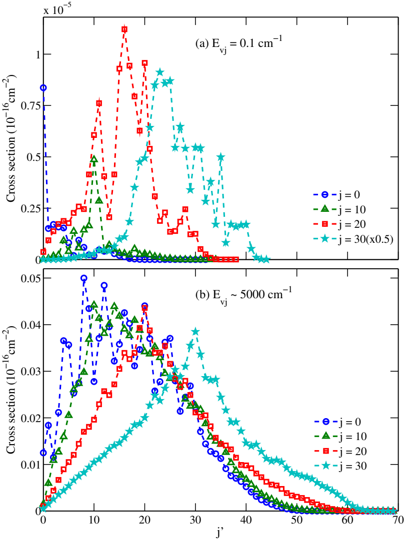


Partial wave (J) contributions



- Low energy: *s*-wave
- High energy: many partial waves

CO(v, J') product distributions



Collision rates

Boltzmann average of cross section

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

Vibrational quenching

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

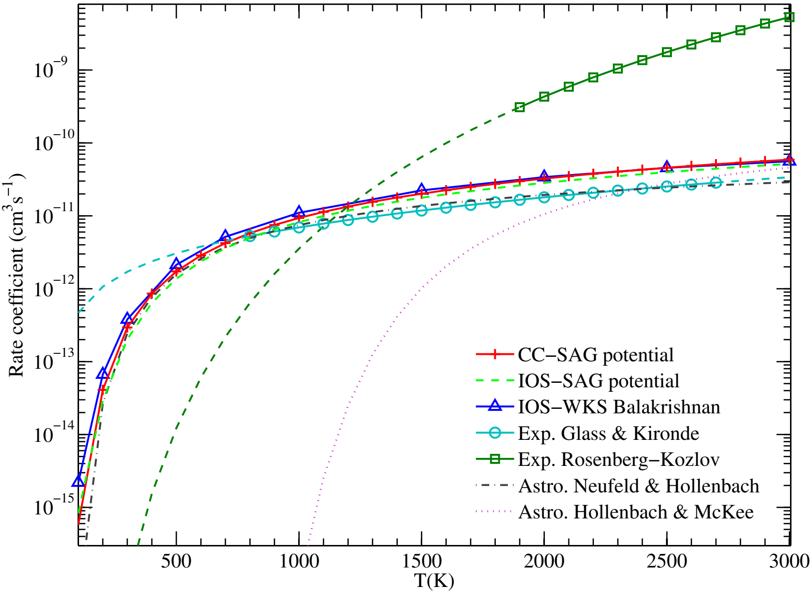
Extrapolation used in astrochemical applications

$$r_{vj\to v'j'}(T) = P_{vv'}(T) r_{0,j\to 0,j'}(T)$$

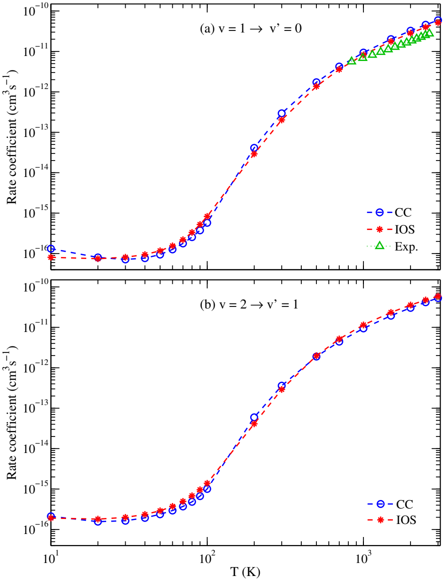
with

$$P_{vv'}(T) = \frac{r_{v\to v'}(T) \sum_j g_j e^{-E_{vj}/k_B T}}{\sum_j g_j e^{-E_{vj}/k_B T} \sum_{j'} r_{0,j\to 0,j'}(T)}$$

Vibrational quenching $r_{1\to0}(T)$

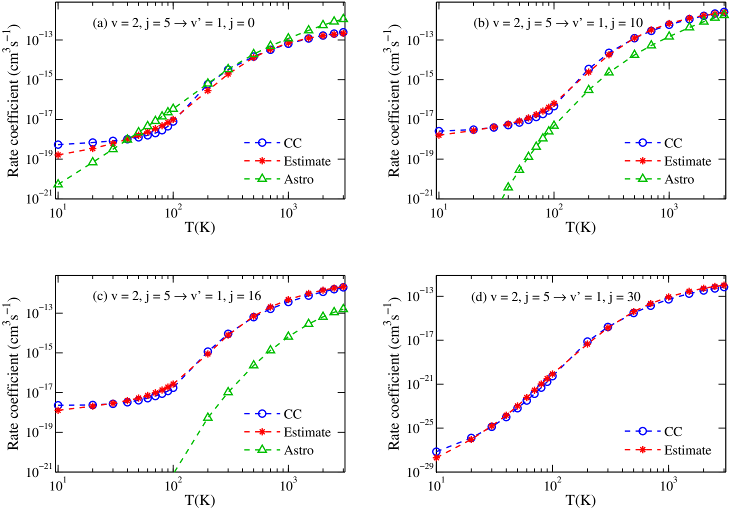


Vibrational quenching: compare IOS with CC



⇒ IOS works well

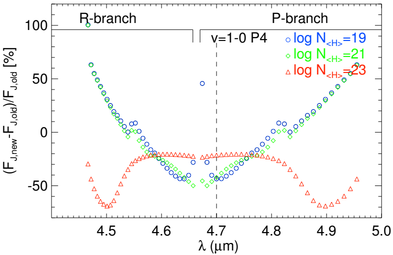
Collisions rates H+CO: $r_{v=2,j\to v'=1,j'}(T)$



- Astro: W. F. Thi, I. Kamp, *et al.*, A&A, **551**, A49 (2013)
- Extrapolation formula works well with good input data

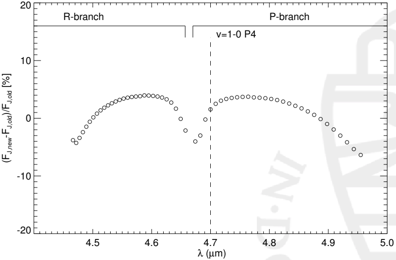
Slab model

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



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, GCG, *Astrophys. J.*, **813**, 96 (2015)