Computational future

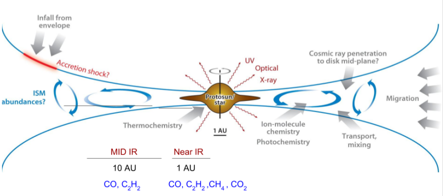
Gerrit C. Groenenboom

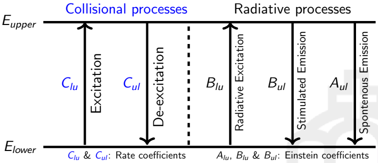
Theoretical Chemistry, Institute for Molecules and Materials,
Radboud University Nijmegen, The Netherlands

Groningen, 30 August 2024

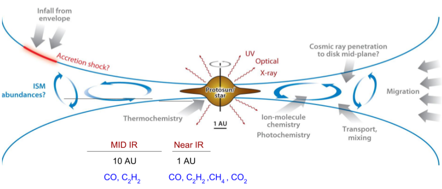
DAN Dutch Astrochemistry Network III

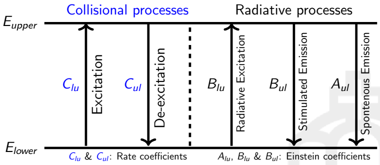
Radiative transfer modeling - molecular collisions





Radiative transfer modeling - molecular collisions





C_{lu} & C_{ul}: Rate coefficients

A_{lu}, B_{lu} & B_{ul}: Einstein coefficients

Databases with collisional rate constants and spectroscopic data:

LAMDA	Leiden Atomic and Molecular Database
Basecol	Ro-vibrational Collisional Excitation Database and Utilities
EMAA	Excitation of molecules and atoms for astrophysics

⇒ Data computed by theoretical chemists/molecular physicist . . .

Also: Reaction rates, photodissociation rates cross section, spectrocopy, CIA

Theoretical chemists/molecular physicists

Theoretical chemists/molecular physicists

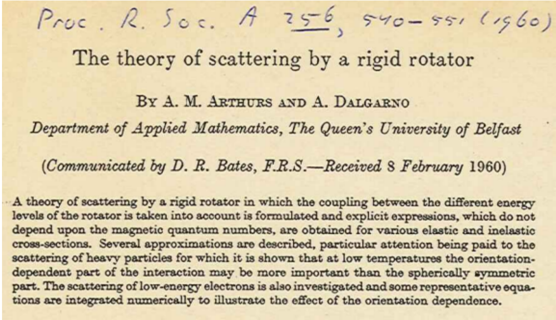
and what do they do . . .

- Compute potential energy surfaces - electronic Schrödinger equation
- Nuclear motion
  - Often: Molecular Dynamics - classical mechanics
  - Here: Quantum Dynamics/scattering - nuclear Schrödinger equation
- Which problems are hard, wich are easy? Will they do my molecule?

Typical rates: $10^{-7} - 10^{-8}$ s^{-1}

$\Rightarrow$ a little bit of history

Alex Dalgarno (1928-2015)



Proc. R. Soc. A 256, 540-551 (1960)

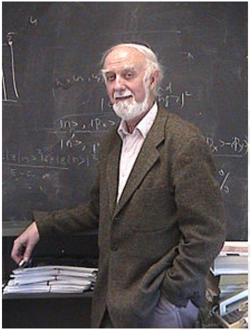
The theory of scattering by a rigid rotator

By A. M. Arthurs and A. Dalgarno

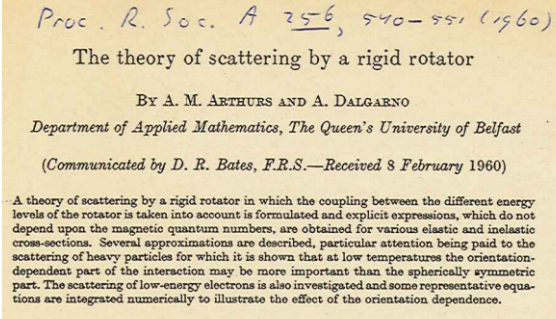
Department of Applied Mathematics, The Queen's University of Belfast

(*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.



Alex Dalgarno (1928-2015)



Proc. R. Soc. A 256, 540-551 (1960)

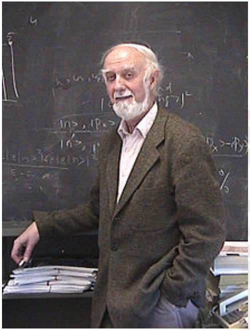
The theory of scattering by a rigid rotator

By A. M. Arthurs and A. Dalgarno

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

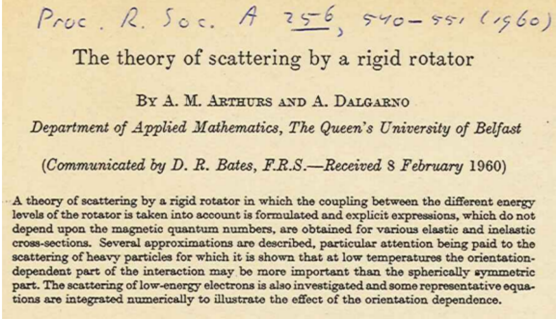
(*Communicated by D. R. Bates, F.R.S.—Received* 8 *February* 1960)

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.



- British mathematician, Harvard University/Center for Astrophysics/ITAMP
- Time-independent Schrödinger equation for collisional cross sections
- Key of 1960 paper: total angular momentum representation.

Alex Dalgarno (1928-2015)



Proc. R. Soc. A 256, 540–551 (1960)

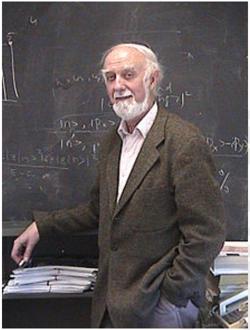
The theory of scattering by a rigid rotator

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.



- British mathematician, Harvard University/Center for Astrophysics/ITAMP
- Time-independent Schrödinger equation for collisional cross sections
- Key of 1960 paper: total angular momentum representation.

This turns computation of rates into many independent jobs:

- Total energies E, e.g., 100 values between 1 cm^{-1} and 1000 cm-1
- Total angular momentum: J, e.g., 0-100
- Parity odd/even inversion symmetry

⇒ Example: $100 \times 100 \times 2 = 20\,000$ jobs

Workshop NRCC 1979

Workshop participants. *Left to right:* L. Thomas, N. Harvey, J. Light, D. Secrest, G. Parker, A. Askar, D. Malik, R. Gordon, M. Alexander, R. Walker, M. Redmon, A. Allison, F. Krogh, H. Rabitz, B. Johnson, H. Shin, T. Schmalz, Y. Yung, D. Truhlar, W. Lester, Jr.

Workshop NRCC Proceedings No. 5, Argonne National Lab, 1979

- B. Robert Johnson, Log-derivative and renormalized numerov algorithm
- Millard H. Alexander, HIBRIDON

Hibridon: a program suite for time-independent non-reactive quantum scattering calculations
M.H. Alexander, P.J. Dagdigian, H.-J. Werner, J. Kłos, B. Desrousseaux, G. Raffy, and F. Lique
Comp. Phys. Commun., 289, 108761 (2023)
https://github.com/hibridon/hibridon

Not at this workshop: Sheldon Green - MOLSCAT code - now on Github by Jeremy Hutson

Collinear He+$H_2(v) \rightarrow$ He+$H_2(v')$, Secrest & Johnson

"Simplest coupled channels problem"

Hamiltonian for He+H_2

$$\hat{H} = \underbrace{\hat{H}_0}_{\text{H}_2\text{ Hamiltonian}} - \underbrace{\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2}}_{\text{kinetic energy}} + \underbrace{V(R,r)}_{\text{interaction potential}}$$

Time-independent Schrödinger equation, energy E

$$\hat{H}\Psi(R,r) = E\Psi(R,r)$$

Vibrational wave functions for H_2 — harmonic oscillator approximation

$$\hat{H}_0\phi_v(r) = \epsilon_v\phi_v(r), \quad v = 0, 1, 2$$

Coupled channel expansion

$$\Psi(R,r) = \sum_{v=0}^{2} \phi_v(r) \quad \underbrace{c_v(R)}_{\text{Need to solve}}$$

Johnson's Renormalized Numerov algorithm

Coupled channel expansion

$$\Psi(R, r) = \sum_{v=0}^{v_{\max}} \phi_v(r)\, c_v(R), \quad \text{expansion coefs: } \boldsymbol{c}(R) = \begin{pmatrix} c_0(R) \\ c_1(R) \\ c_2(R) \end{pmatrix}$$

Coupled channels equation

$$\frac{\partial^2}{\partial R^2} \boldsymbol{c}(R) = \boldsymbol{W}(R)\boldsymbol{c}(R)$$

Main steps in computation

1. Choose grid $\boldsymbol{c}(R_i)$ for $R_i = R_0 + i\Delta_R$ with $i = 1, 2, \ldots, n_R$.
2. Compute matrix elements of interaction potential

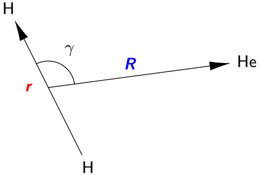
$$V_{v'v}(R_i) = \int_0^\infty \phi_{v'}^*(r)\, V(R_i, r)\phi_v(r)\, dr.$$

3. Solve CC Eq. with Johnson's Renormalized Numerov method

$$\boldsymbol{c}(R_{i-1}) = \boldsymbol{Q}_i \boldsymbol{c}(R_i)$$

$$\boldsymbol{Q}_{i+1} = \left[2 + \frac{10\Delta_R^2 \boldsymbol{W}_i}{12} - \left(1 - \frac{\Delta_R^2 \boldsymbol{W}_{i-1}}{12}\right) \boldsymbol{Q}_i\right]^{-1} \left(1 - \frac{\Delta_R^2 \boldsymbol{W}_{i+1}}{12}\right).$$

Atom-diatom rotationally inelastic scattering



$\mathrm{He} + \mathrm{H}_2(j) \rightarrow \mathrm{He} + \mathrm{H}_2(j')$

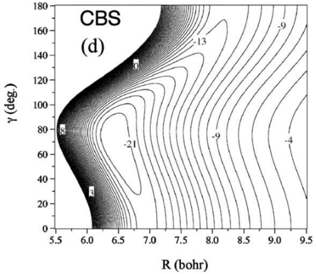
Rigid rotator: fix bondlength $r = |\boldsymbol{r}|$

Channel functions for rigid rotator approximation:

$$|(jl)JM_J\rangle = \sum_{m_j=-j}^{j} \sum_{m_l=l}^{l} Y_{j,m_j}(\hat{r}) Y_{j,m_l}(\hat{R}) \qquad \underbrace{\langle jm_j lm_l | JM_J\rangle}_{\text{Clebsch-Gordan coefficients}}$$

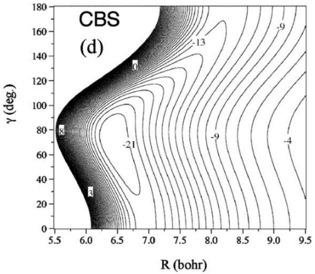
- j - rotational quantum number H_2 - we care about this one
- J - total angular momentum, good quantum number (great!)
- M_J - projection - results independent of this quantum number (great!)
- m_j and m_l - summed over (thanks Alex Dalgarno!)
- $p = (-1)^{j+l}$, parity good quantum number (great!)
- l - “end-over-end rotation” increases number of channels (bummer)

Example He+CO potential



- Peterson and McBane, J. Chem. Phys. **123**, 084314 (2005)
- One-electron basis: d-aug-cc-pVxZ, $x = D, T, Q \rightarrow$ extrapolate (CBS)
- CCSD(T) - treatment electron correlation
- $D_e = 22.34$ cm^{-1} $\quad$ (1 cm^{-1} = 1.4 kelvin)
- about 1000 geometries for 3D potential

Example He+CO potential

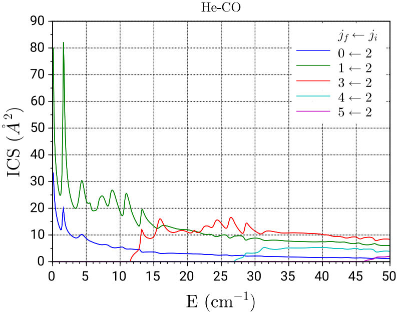


- Peterson and McBane, J. Chem. Phys. **123**, 084314 (2005)
- One-electron basis: d-aug-cc-pVxZ, $x = D, T, Q \rightarrow$ extrapolate (CBS)
- CCSD(T) - treatment electron correlation
- $D_e = 22.34 \text{ cm}^{-1} \quad (1 \text{ cm}^{-1} = 1.4 \text{ kelvin})$
- about 1000 geometries for 3D potential

"Rotational excitation of CO by He impact", Thomas, Kraemer, Diercksen, Chem. Phys. **51**, 131 (1980)

- CISD/TZ (configuration interaction)
- 50% uncertainty in well depth
- Coupled channels and IOS (infinite order sudden) with MOLSCAT

Cross section He+CO($j_i = 2$) $\rightarrow$ He+CO(j_f)



Calculation in 2024 (by me)

- 500 energies, E step of 0.02 cm^{-1}
- CO rotational states: $j_{\max} = 10$
- Partial waves: $J_{\max} = 10$
- Radial propagation steps: $n_R = 80$
- Number of coupled channels: 10-120
- (5-60 in parity adapted basis)

- CPU time: about one minute on PC (6 cores) [Scilab script]
- Experimental observation of $j = 0 \rightarrow 1$, five resonances for $E = 0 - 25$ cm^{-1}, A. Bergeat *et al.*, Nature Chemistry 2015

Scaling of CPU time with # coupled channels (n)

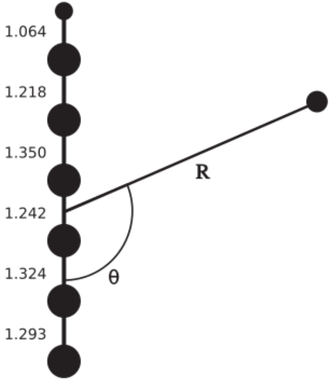
- Matrix multiplication/inversion: CPU time: $t \propto n^3$
- CPU time on PC (single core) for $n = 1000$: $t \approx 0.1$ sec.
- Main frame year 1980: same operation about one hour!

Rotational energy

$$E_j = Bj(j+1) - \ldots$$

	B (cm^{-1})	#($E_j < 1000$)
$H_2(^1\Sigma_g^+)$	61	4/2=2
$CO(^1\Sigma^+)$	1.7	24
$C_6H(^2\Pi)$	0.046	147×2=294

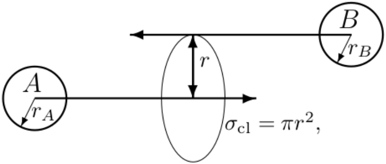
How about l?



Walker, Lique, Dawes, MNRAS **473**, 1407 (2018)

Estimating l, impact parameter

If molecules where hard spheres



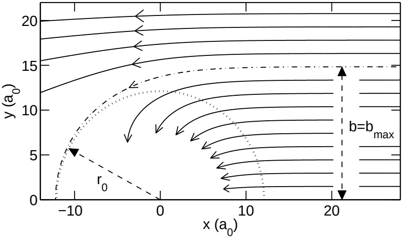
"End-over-end" angular momentum of complex:

$$l = \mu v r$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$E = \frac{1}{2}\mu v^2$$

With long range interactions



Example:

- $\mu = m_{\mathrm{He}}$
- $E = 1000\ \mathrm{cm}^{-1}$
- $b = 10\ \mathrm{a}_0$
- $\Rightarrow l = 80$

Coupled states approximation

- Introduce body-fixed angular momentum projection quantum number: Ω
- Unitary transformation from l to Ω:

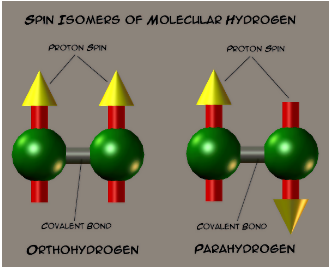
$$|(jl)JM_J\rangle = \sum_{\Omega} |j\Omega)JM_J\rangle\, U^{(j,J)}_{\Omega,l}$$

- Potential matrix elements independent of Ω
- Kinetic energy coupling $T_{\Omega,\Omega\pm1}$ (Coriolis coupling)
- Coupled States Approximation: neglect $T_{\Omega,\Omega\pm}$ coupling
- ⇒ often good approximation at high collision energy

Many papers in the 1970's, Sheldon Green, Don Kouri, R. T Pack

What about collisions with H_2 and HD instead of He?

Ortho- and para- H_2



`https://en.wikipedia.org/wiki/Spin_isomers_of_hydrogen`

- Para-H_2: channels: $j = 0, 2, 4, \ldots$
- Ortho-H_2: channels: $j = 1, 3, \ldots$
- For $j = 0$, quadrupole moment $= 0$
- $m_{\mathrm{H}_2}/m_{\mathrm{He}} = 1/2 \Rightarrow$ de Broglie wavelength $\times\sqrt{2}$

Switching to HD?

- No more symmetry: $j = 0, 1, 2, \ldots$
- Rotational constant: $B = 46\ \mathrm{cm}^{-1}$ (vs $61\ \mathrm{cm}^{-1}$ for H_2)

Including vibrations: He+CO(v, j)

C. Cecchi-Pestellini, E. Bodo, N. Balakrishnan, A. Dalgarno, ApJ, **571**, 1015 (2002)

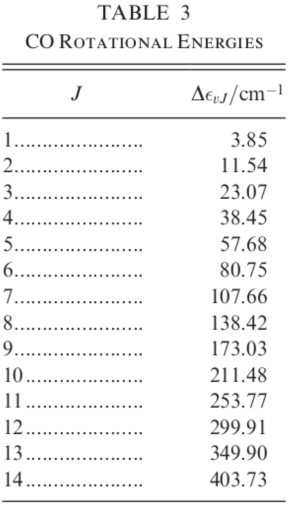


TABLE 3

CO Rotational Energies

J	$\Delta\epsilon_{vJ}/\mathrm{cm}^{-1}$
1	3.85
2	11.54
3	23.07
4	38.45
5	57.68
6	80.75
7	107.66
8	138.42
9	173.03
10	211.48
11	253.77
12	299.91
13	349.90
14	403.73

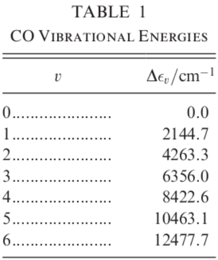


TABLE 1

CO Vibrational Energies

v	$\Delta\epsilon_v/\mathrm{cm}^{-1}$
0	0.0
1	2144.7
2	4263.3
3	6356.0
4	8422.6
5	10463.1
6	12477.7

How did they handle this?

- 4 CPU Compaq Digital Alpha
- Adapted MOLSCAT code
- Collision energies: 5 to 600 cm^{-1}
- Rotational transitions: coupled channels
- Vibrational transitions: infinite-order sudden (IOS)

H+CO(v, j)

Similar to He+CO(v, j)?

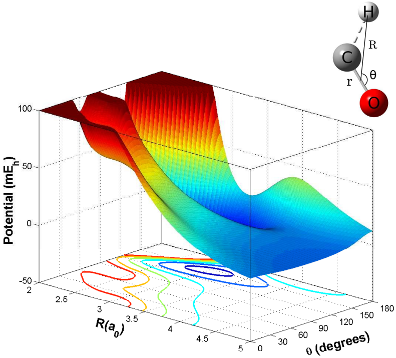
H+CO(v, j)

Similar to He+CO(v, j)?

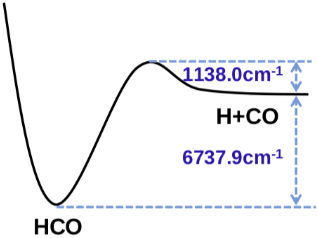
- Sensitivity anaysis: H+CO(v, j) key - Ewine van Dishoeck (Leiden)
- Dutch Astrochemistry Network I - funding for laboratory astrochemistry

, Ph project Lei Song on H+CO(v, j), 2012-2016

H+CO potential, 3D



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



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

Quality of potential: 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%

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

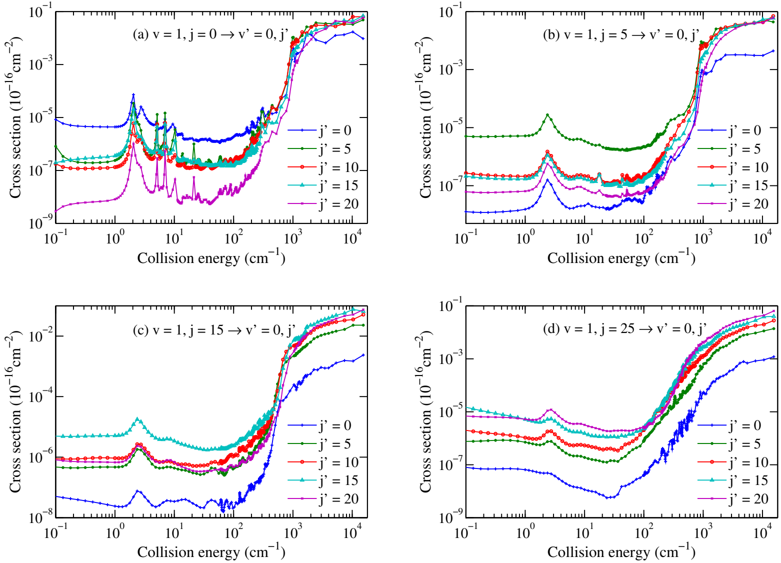
Coupled channels scattering calculation H+CO(v, j)

	Big basis	**small basis**
v	j_{max}	j_{max}
0	79	61
1	70	52
2	59	42
3	45	22
4	45	
5	30	
6	30	
7	25	
8	25	

- **Big basis** $\sim$ **11,000** channels
- **Small basis** $\sim$ **4,300** channels
- Partial waves $J = 0, \ldots, 100$
- R-grid: : 3 - 40 a_0

Lei Song, N. Balakrishnan, A. vd Avoird, T. Karman, and GCG, J. Chem. Phys., **142**, 204303 (2015)

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



Lei Song, N. Balakrishnan, A. vd Avoird, T. Karman, and GCG, J. Chem. Phys., **142**, 204303 (2015)

Collision rates, vibrational quenching, extrapolation

Boltzmann average of cross section

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

Vibrational quenching

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

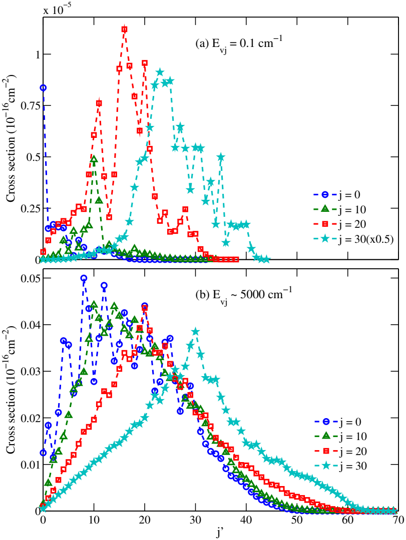
Extrapolation used in astrochemical applications

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

with

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

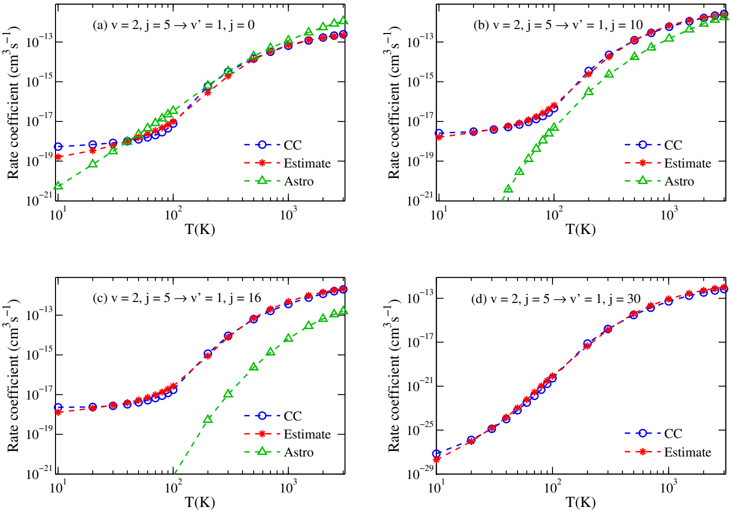
CO(v, J') product distributions



Competition between:

- Energy gap law: minimize energy transfer from CO to H
- Angular momentum constraint: minimize angular momentum transfer from CO to H

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

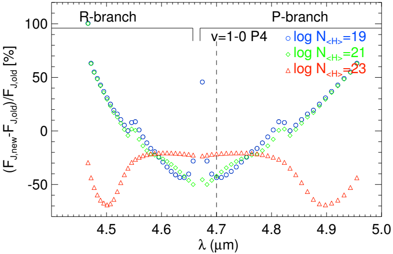


- Song, Balakrishnan, Walker, Stancil, Thi, Kamp, vd Avoird, and GCG, *Astrophys. J.*, 2015
- Astro: W. F. Thi, Inga Kamp, *et al.*, A&A, **551**, A49 (2013)
- Extrapolation formula works well starting with $(v = 1, j) \rightarrow (v' = 0, j')$ data.

H+CO: application to astrophysical models

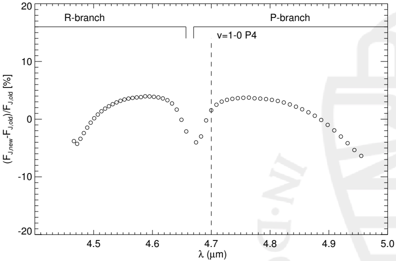
Slab model

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



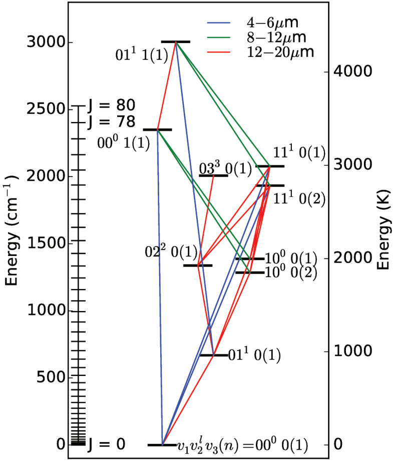
Disk model

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)

CO_2 vibrational transitions



CO_2 vibrations

	(cm^{-1})	mode
ν_1	1333	symmetric stretch
ν_2	667	bend
ν_3	2349	asymmetric stretch

States: (v_1, v_2^l, v_3)
Vibrational angular momentum:

$$l = v_2, v_2 - 2, \dots, -v_2$$

Symmetric stretch not IR active,
but: $2 \times 667 = 1334$

Fermi resonance: $(10^0 0)$-$(02^0 0)$

“CO_2 infrared emission as a diagnostic of plantet-forming regions od disks”,

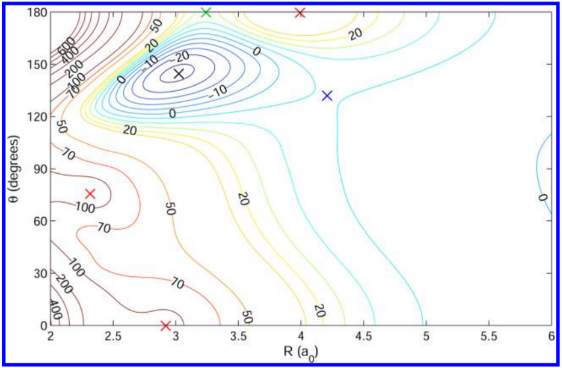
A. D. Bosman, S. Bruderen, E. F. van Dishoeck, A&A 601, A36 (2017)

He+CO$_2(v_1, v_2, v_3)$

Taha Selim, DAN II)
Chemical Physics part of the problem
PhD defense October, 2024

Jelena Boskovic (DAN III)
with Floris van der Tak, RUG
Astrochemical applications
Started March 2024

Conical intersections and Renner-Teller coupling in HCO



- Red crosses - conical intersections (Lowest ∼ 11 000 cm^{-1}
- Green cross - Renner Teller coupling at linear geometry, 1747 cm^{-1}

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

Ongoing project Kim Steenbakkers, Sandra Brünken:

Spectroscopy of CCH^+ - Renner Teller coupling, ground state $^3\Pi$, low lying $^3\Sigma^-$

Conclusion - computational future

- Steady progress electronic structure methods
  - electron correlation: CCSD(T), CCSDT(Q), . . .
  - basis set: aug-cc-pVTZ, aug-cc-pVQZ, . . .
  - Open-shell systems, conical intersections ⇐ hard
- Fitting higher dimensional potentials: machine learning, AI methods
  ⇒ not always the biggest problem, but lots of interest
- Dynamics: rotation-vibration, larger molecules ⇐ ongoing efforts
- Nonadiabatic dynamics ⇐ hard
- Software advances - data science techniques ⇐ many opportunities
- Price/flop keeps going down, great - but: power usage is concern
- Theoretical advances, bonus - similar to hardware improvements

Thank you! Questions?