Collisional Rovibrational Molecular Excitation: Calculation and Scaling

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VAMDC-US

Collaborators

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Computation

- Collisional rovibrational excitation of molecules by atom/ion/molecule/electron
  - Astrophysical interest
  - Light colliders: H, H_2, He
  - Cross sections & rate coefficients
  - BASECOL format
- Better scaling predictions
  - Law/algorithm for approximations
  - Reliable molecular collisional data
  - Complete dataset of species

Calculations

- Codes
  - MOLSCAT – quantum mechanical nonreactive scattering program
  - TwoBC – not publicly available Bala/Krems
- Resources
  - GACRC – Georgia Advanced Computing Resource Center
    - 25.9 Tflops: linux cluster – Intel/AMD, large memory, infiniband, GPU
  - CSP cluster – 136 cores
  - Group Stancil – 64 cores
  - ORNL – soon

He Systems: Explicit Calculations

- He-CO
  - Low-lying rovibrational states (v = 0-3)
- In preparation:
  - HCl HF
- Explicit calculations already performed:
  - C_3 CO_2 H_2O NH_3 CH_4

H-CO System

Various PESs

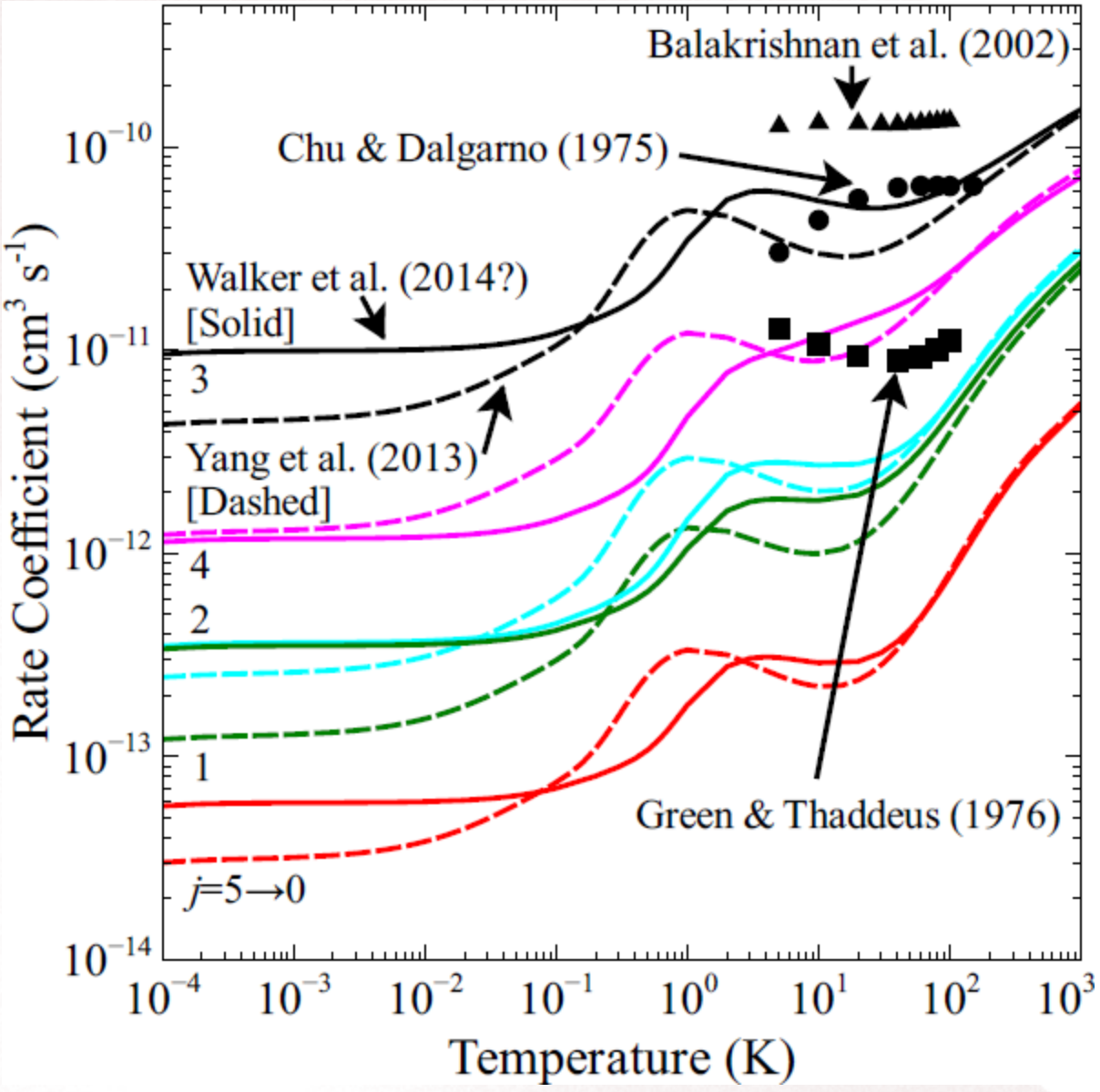
Song et al. (2013)

Rate coefficients:

j = 0-70, v = 0-3

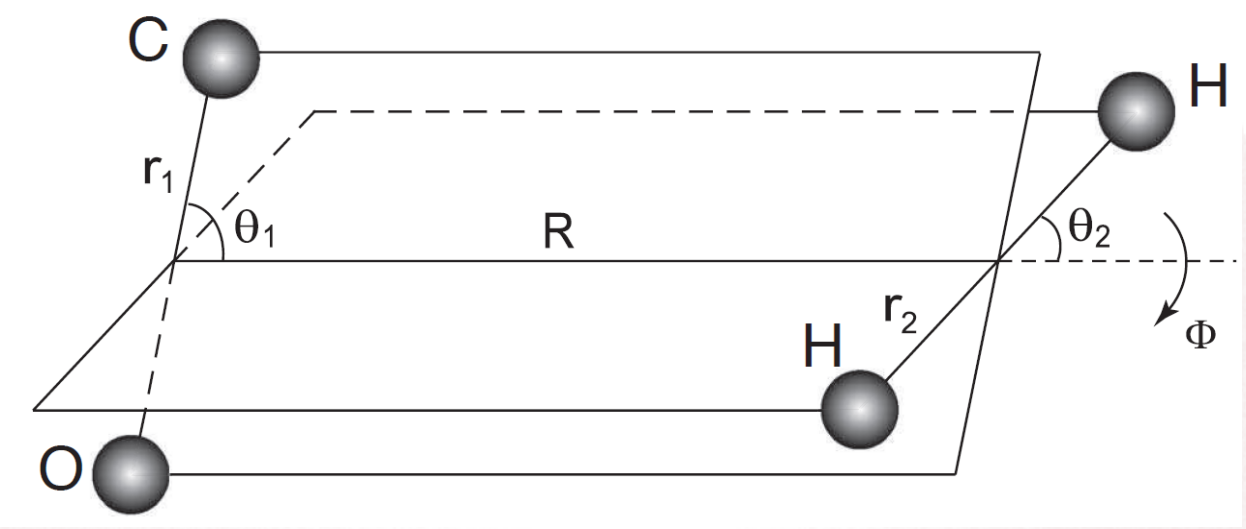
In preparation:

Walker et al. 2014?



H_2 Systems

- H_2-CO (Yang et al., Nature Comm., submitted)
- H_2-CN (Yang et al., in prep.)
- H_2-H_2 (dos Santos et al. 2013)
- Computation in higher dimensions

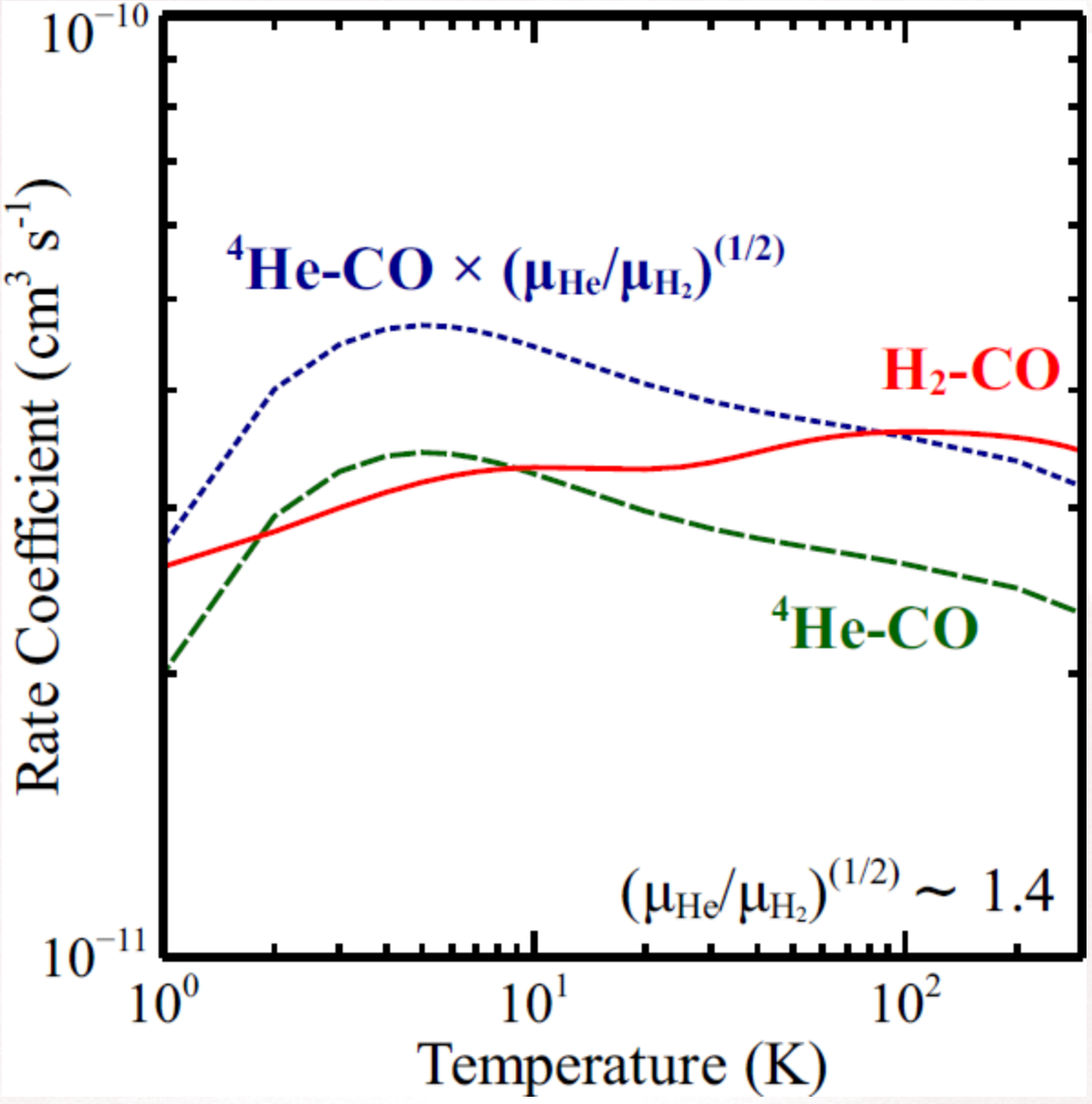


Jacobi Coordinates

Scaling Collisional Rate Coefficients

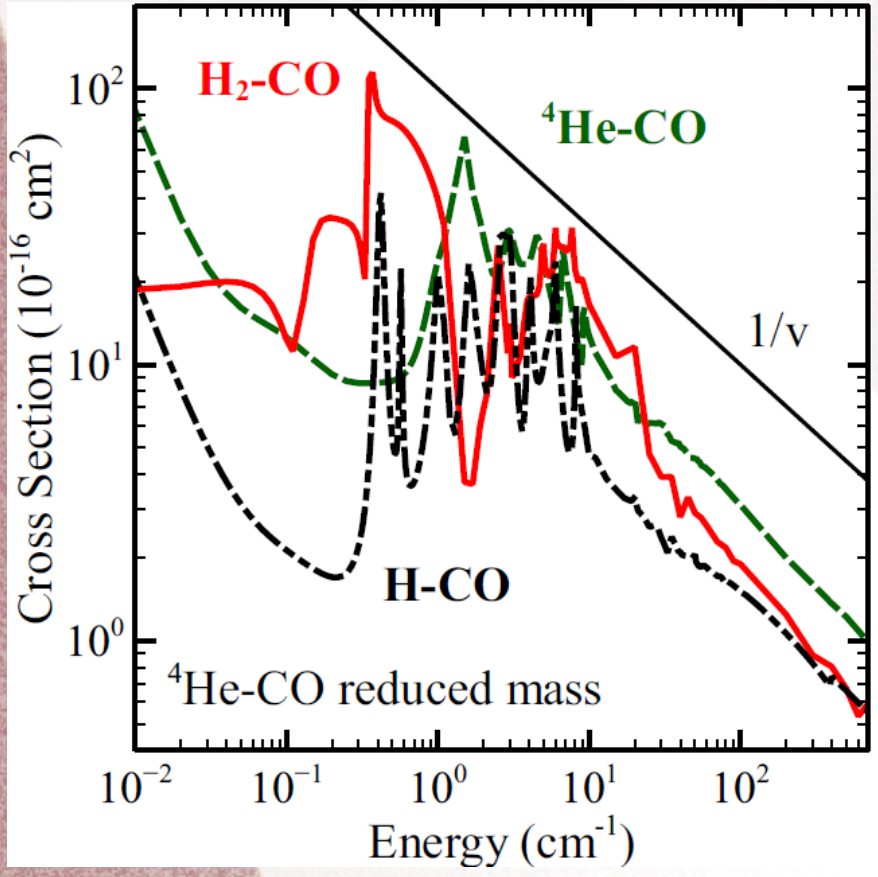
- Standard reduced-mass scaling
  - Widely adopted from Green et al. (1978)
- Recently tested, not approved
  - SiS (Lique et al. 2008)
  - H_2O (Daniel et al. 2010)
  - SO_2 (Cernicharo et al. 2011)
  - CO, H_2O (Walker et al. 2014)
  - HF (Yang et al., in prep.)

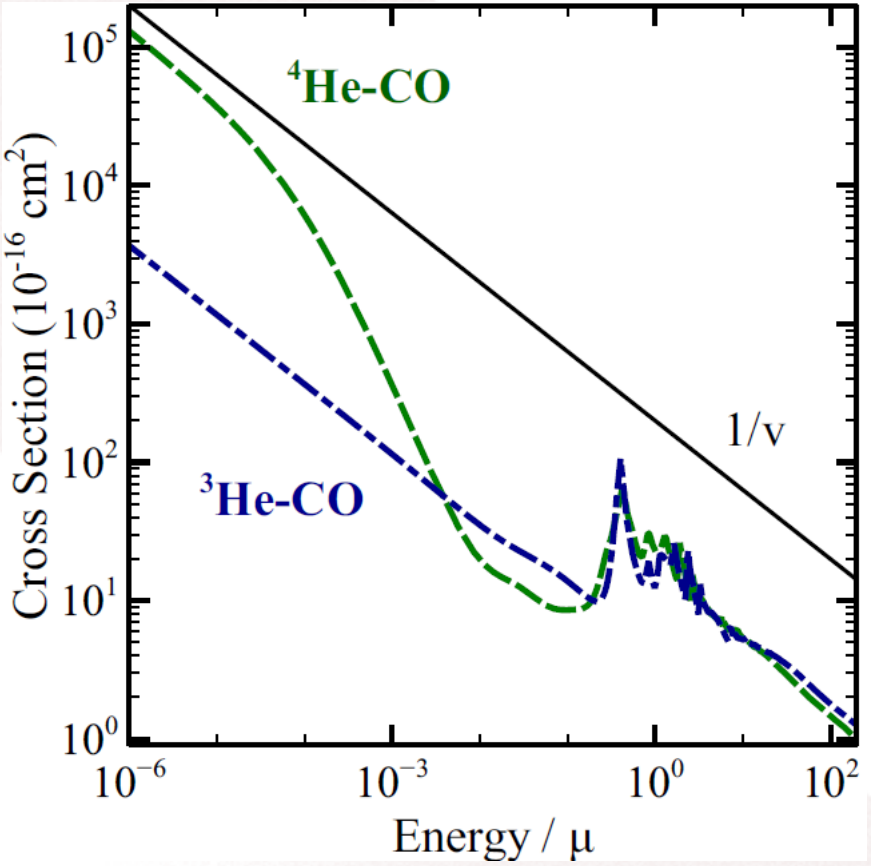
Reduced-Mass Scaling ^{4}He and H_2 with CO($j = 1 \rightarrow 0$)



Invalid Assumptions

- Cross section depends on
  - Interaction potential
  - Kinetic energy, which depends on reduced mass





Rate Coefficients

- Rewrite rate equation with cross section as a function of velocity

$$k_{j\to j'}(T) = \frac{4}{\pi^{1/2}}\left(\frac{\mu}{2k_BT}\right)^{3/2}\int_0^\infty \sigma_{j\to j'}(v)\exp(-\mu v^2/2k_BT)v^3dv$$

- Find σ as an analytic function of υ, then...

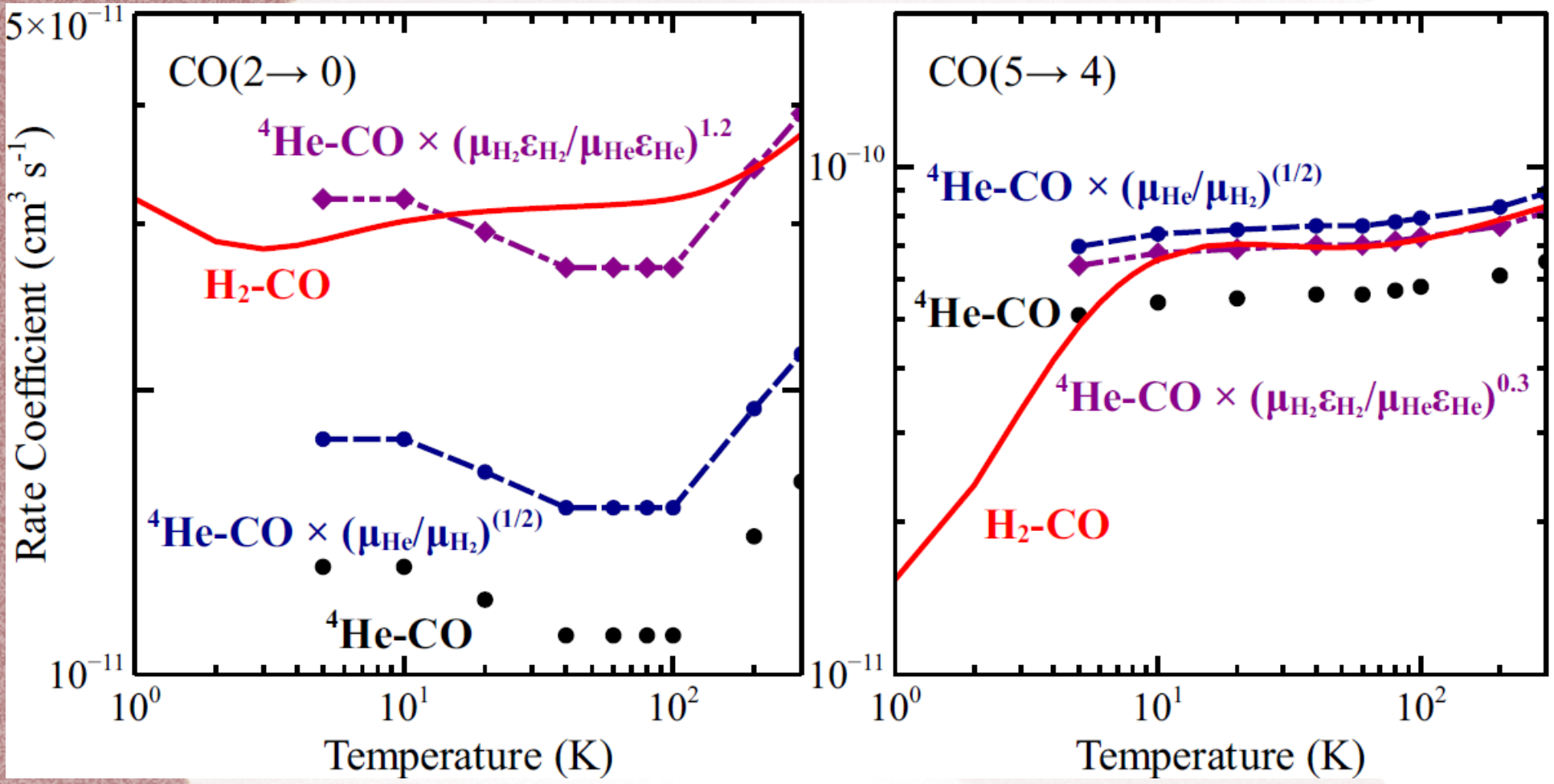
$$\sigma_{j\to j'}(v) = Cv^a \qquad k = k(T^b, \mu^{-b})$$

$$b = (1/2)(a+1)$$

Best Scaling Options

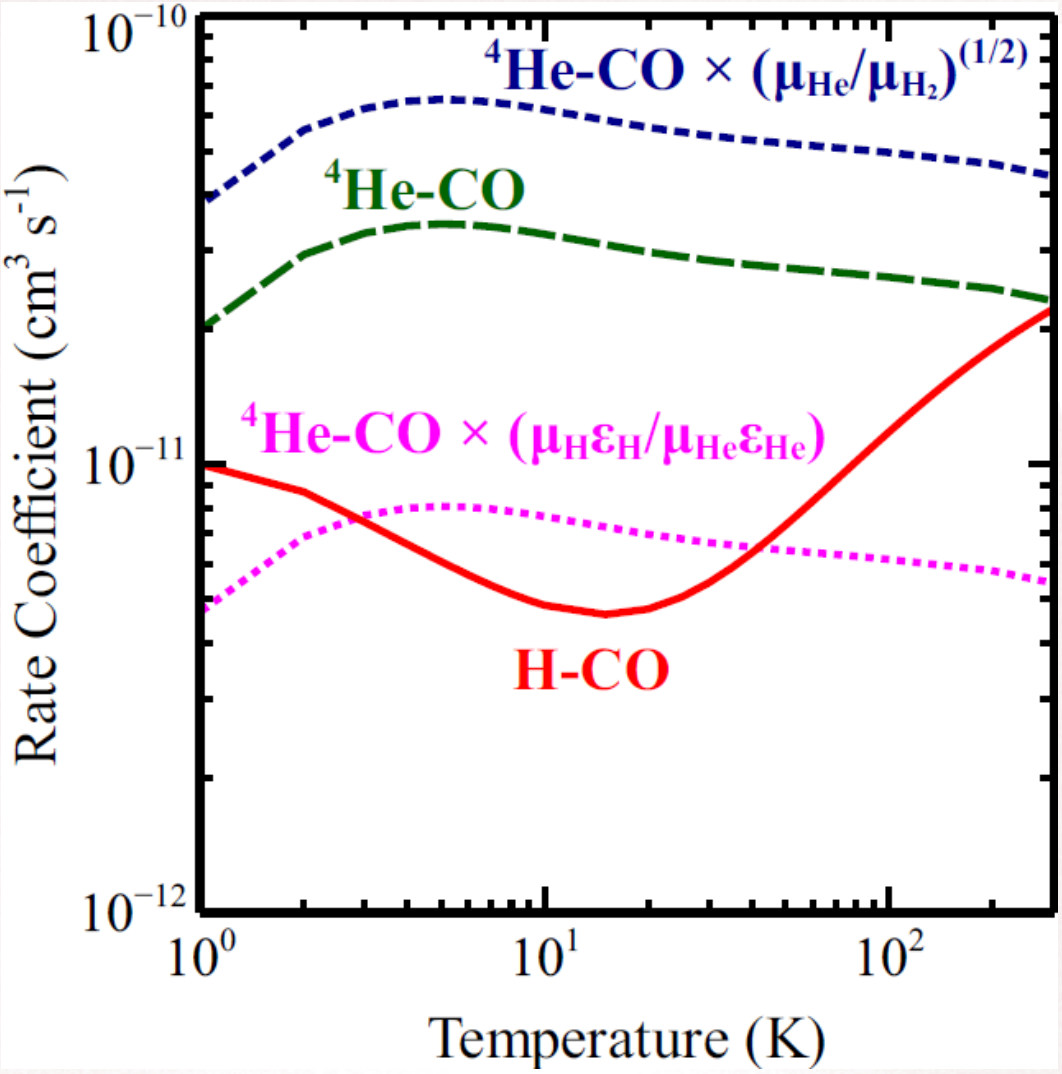
- Analytic Reduced-Mass Scaling (ARMS)
  - Assume cross section is function of velocity
  - Analytic form dependent on power 'a'
  - 'a' not necessarily 1/2
- Reduced-Potential (RP)
  - Dynamics of reduced mass and potential surface
  - Well depth from quantum chemistry

Better Scaling – Reduced-Potential



H2: Yang et al. (2010) He: Cecchi-Pestellini et al. (2002)

Scaling
^{4}He–CO(j = 1→0) to H-CO



Universal Scaling Relation

- Energy Gap Law(s)
  - Nearest levels
  - Minimize ΔJ
- Competing processes
  - Selection, propensity rules

Final Scaling Goals

- Optimize scaling relations
- Generate rate coefficients
- BASECOL format
- Database of astrophysically important diatomic molecules

Other database work at UGA:

- Charge Exchange Database

Support: NASA grant NNX12AF42G

Thank You!

Cross Sections

- Total cross sections, σ, a function of collision energy
- Initial (v,j) to final (v',j')

$$\sigma_{vj\to v'j'}(E_{vj}) = \frac{\pi}{(2j+1)k_{vj}^2}\sum_{J=0}(2J+1)\sum_{l=|J-j|}^{J+j}\sum_{l'=|J-j'|}^{J+j'}|\delta_{jj'}\delta_{ll'}\delta_{vv'} - S^J_{jj'll'vv'}|^2,$$

$$k_{vj} = \sqrt{2\mu(E-\epsilon_{vj})}/\hbar$$

Rate Coefficients

- Integrate state-to-state cross sections with a Maxwell-Boltzmann distribution of velocities of the collider
- State-to-state rate coefficients

$$k_{j\to j'}(T) = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \frac{1}{(k_BT)^2} \int_0^\infty \sigma_{j\to j'}(E_k)\exp(-E_k/k_BT)E_k dE_k$$

E_k - kinetic energy

k_B - Boltzmann's constant

μ - reduced mass of the system

T – temperature