Towards a Full Vibrationally-Specific Model for CO_2 Excitation and Dissociation

STELLAR-CO2 v.1

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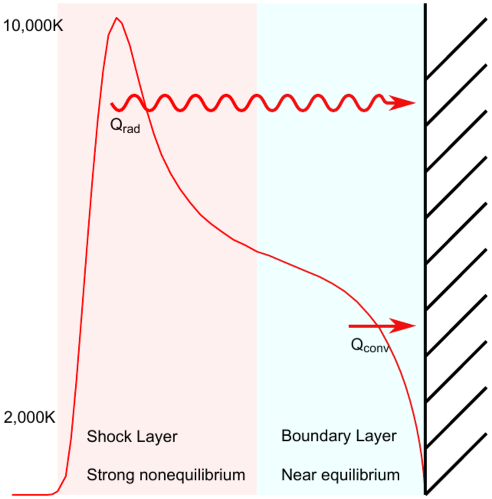
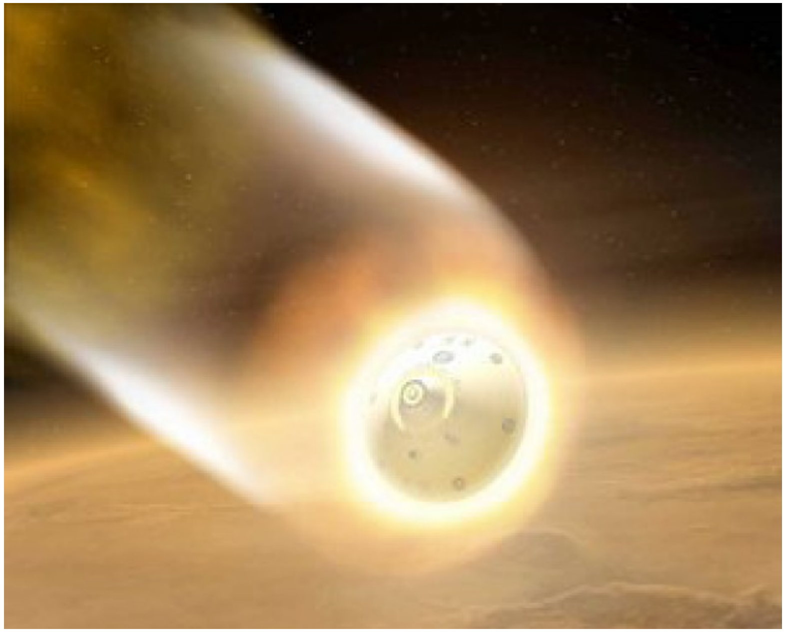
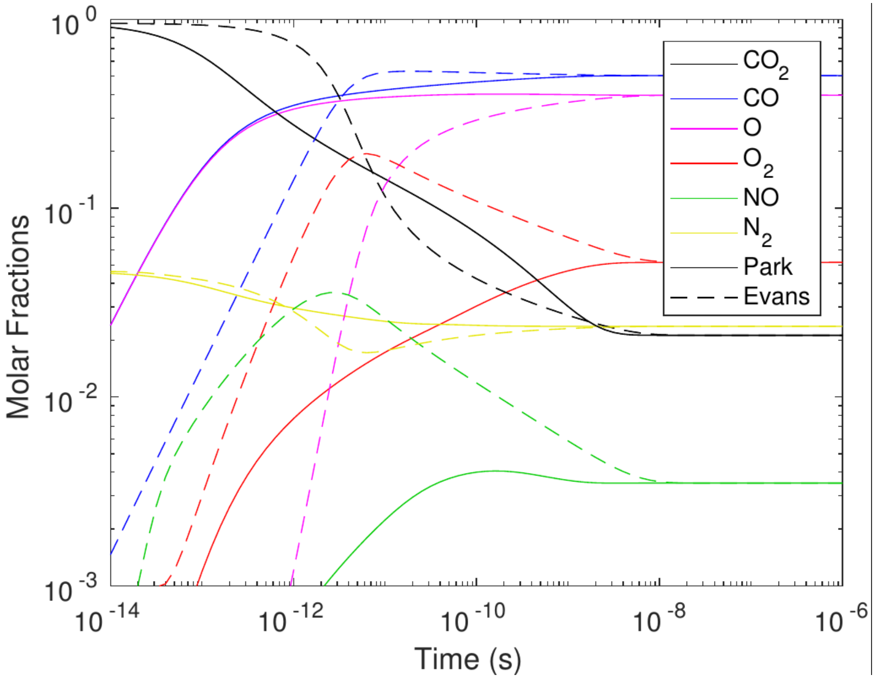
Context

Besides the well know interest in CO2 plasma reforming, technology demands from Mars and Venus exploration also drives the need for better physics and more precisely accurate kinetic databases for CO2 excitation, radiation, and dissociation at high temperatures





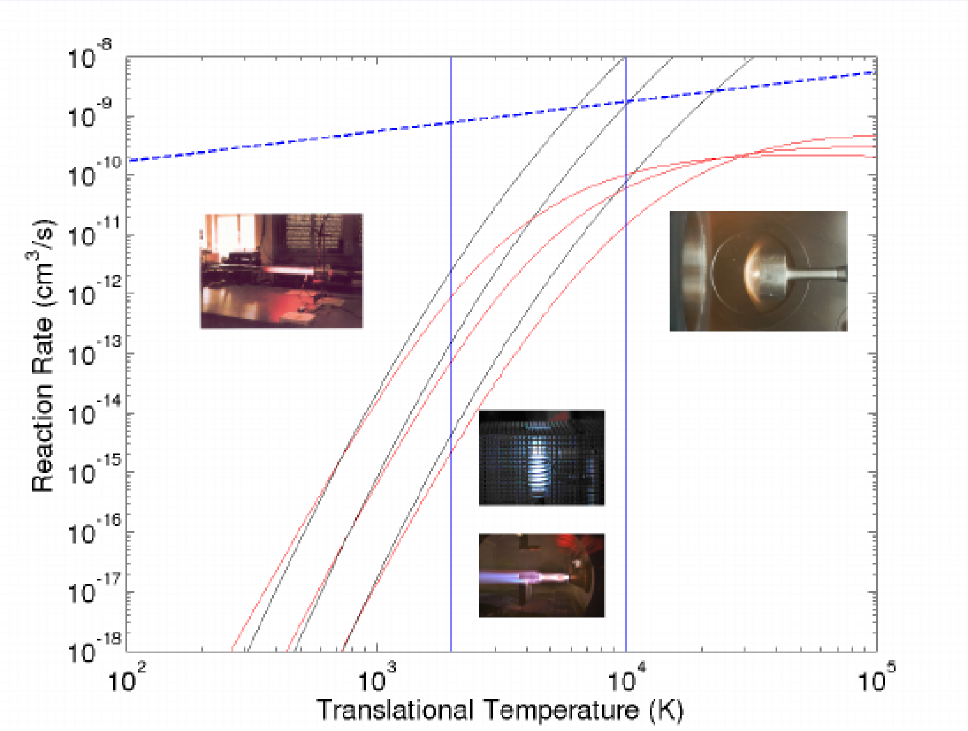


Our Goals

- Improving the fundamentals of CO2 vibrationally specific modeling, which have outdated and shaky physical foundations
- Apply advanced algorithmic techniques to reduce modeling complexity, without any “a-priori” assumption

First-Order SSH Model vs. FHO Model

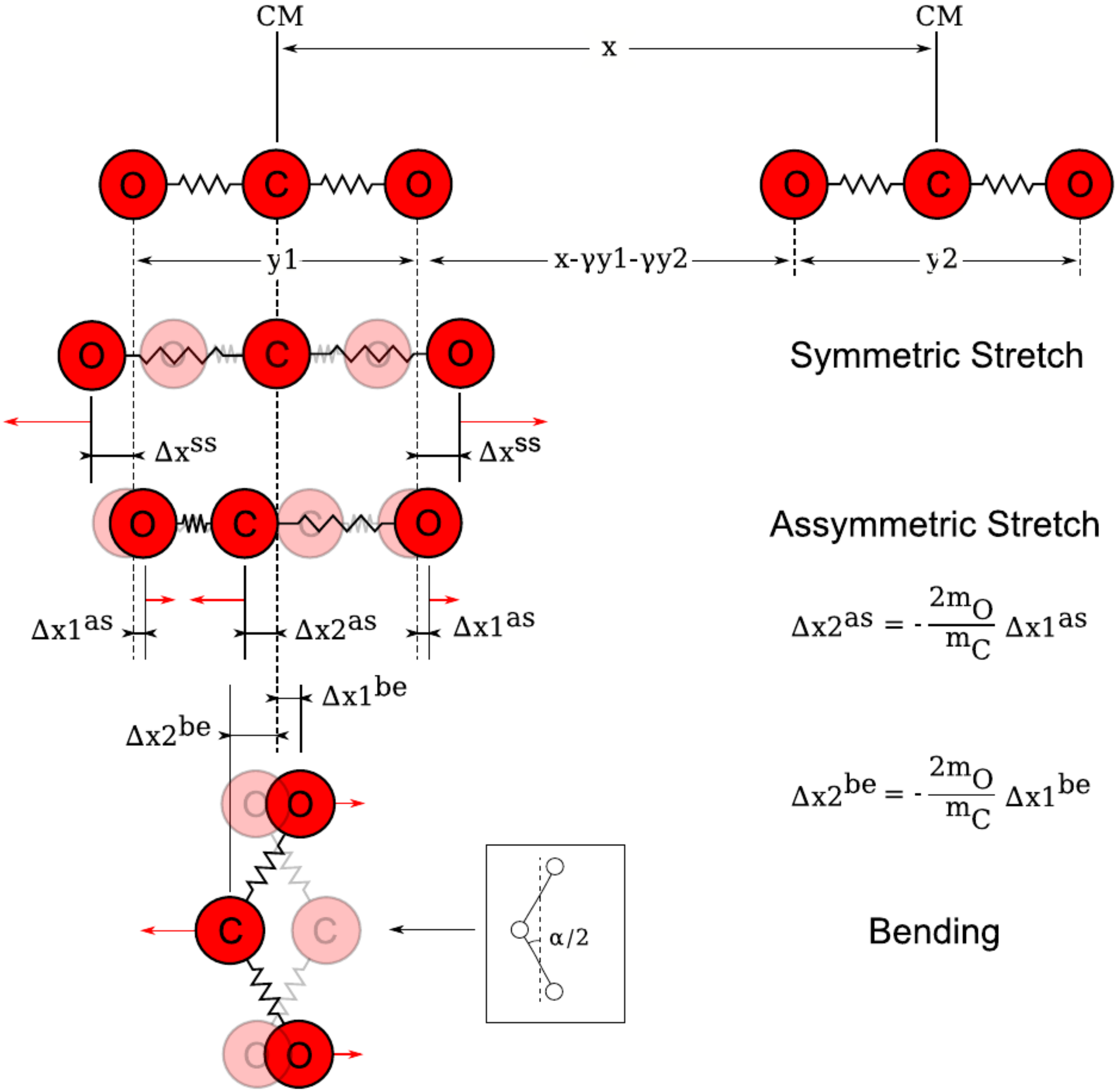
- FHO model nicely reproduces results from more sophisticated approaches (QCT methods, etc...), and is physically consistent at high T.
- SSH model also nicely scales at low T, but fails at high T.
- For a large range of plasma sources, VT and VD processes can only be properly simulated through the FHO model or sophisticated methods.



1→0, 9→8, and 20→19 N_2–N_2 V–T rates. Comparison between Billing's QCT rates (×) and the FHO model (–). SSH rates are added

- The FHO model provides an interesting theory for the modeling of a wide range of plasma sources

Extension of the FHO model to linear triatomic transitions



Symmetric Stretch

Assymmetric Stretch

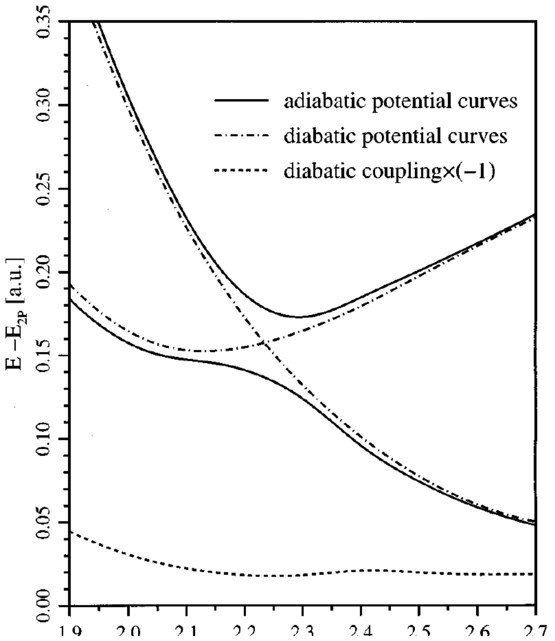
$$\Delta x2^{as} = -\frac{2m_O}{m_C}\Delta x1^{as}$$

$$\Delta x2^{be} = -\frac{2m_O}{m_C}\Delta x1^{be}$$

Bending

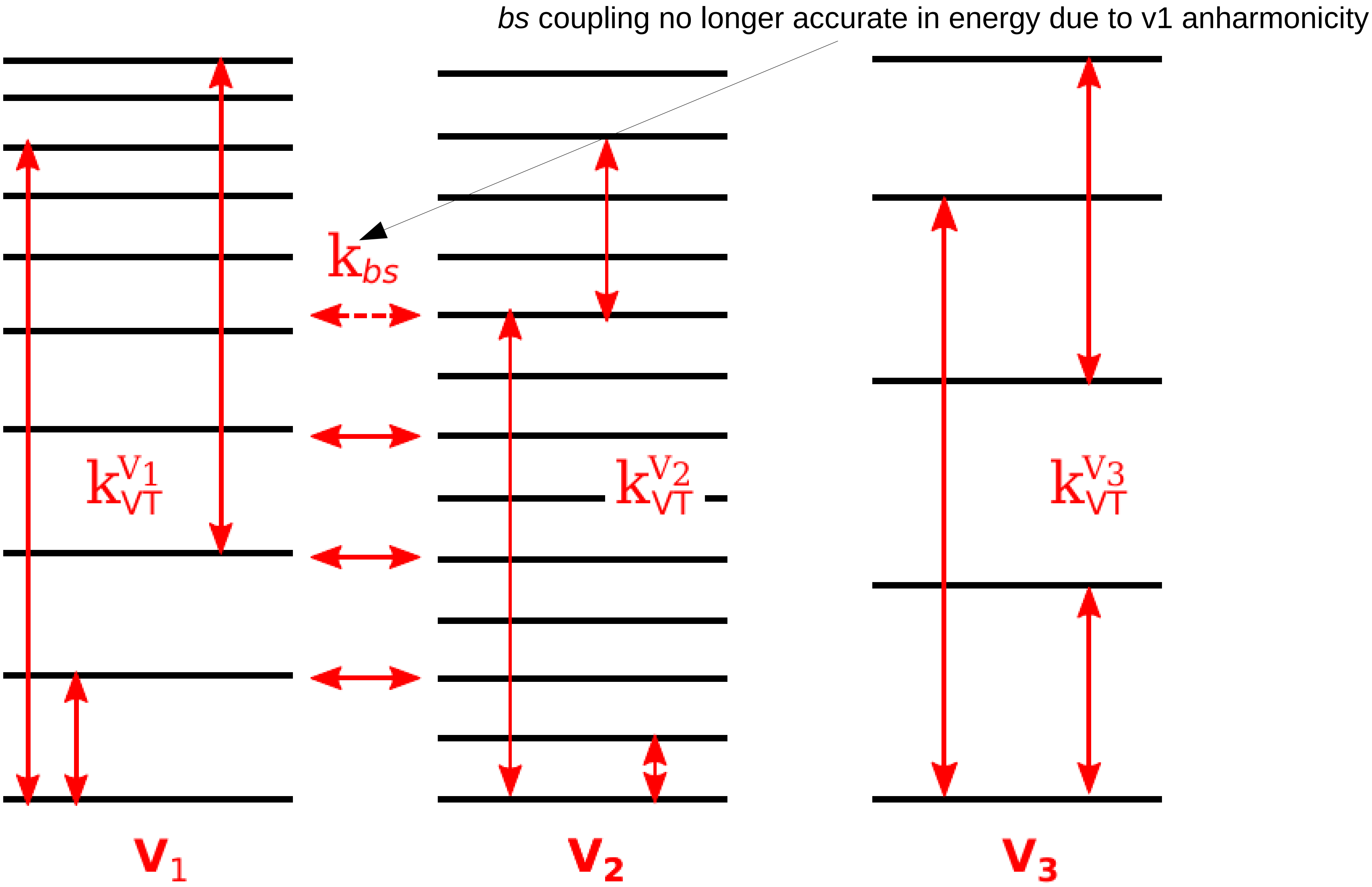
On the *bs* Fermi coupling approximation

- The coupling of v1 and v2 modes in a “lumped” mode with a characteristic T12 temperature is pervasive in current modeling approaches
- But there is enough evidence that the situations where this coupling may be valid are just a subset of all the possible gas conditions (mixture, p, T, etc..)
- The resonance is “accidental” and has no particular physical meaning. Similar to avoided crossings: You still need to consider diabatic potentials for partition functions calculations and thermodynamic properties
- Mostly approximation used as a convenient way to reduce complexity (the Human Mind hates complexity)...
- ...but this is why we invented computers anyway.
- Our approach: “*Calculate them All, The algorithm will sort them out** “



*Historical quote: *“kill them all, God will sort out the good from the wicked”* Sacking of Albi

STELLAR CO_2 v1

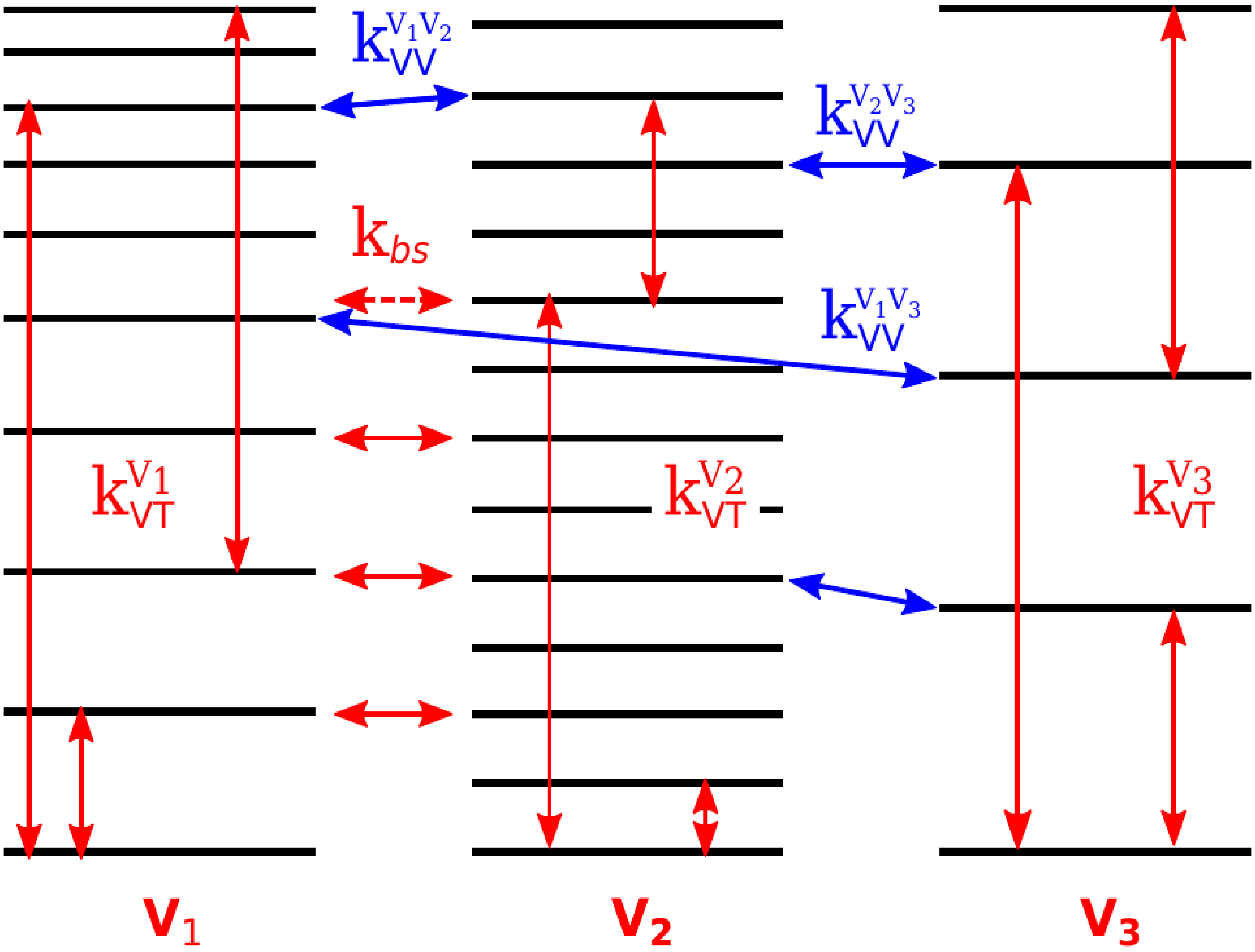


VT rates by FHO model, with P=0.12 rates for *bs* couplings
VT rates based on CO_2-CO_2 collisions only ($k_{VT}(CO_2\text{-}\{CO,O_2,C,O\})=k_{VT}(CO_2\text{-}CO_2)$)

How do we account for intermode transitions?

- Not so much...
- Fermi resonance rate takes care of v1-v2 for the lower v’s...
- For v3-v1 and v3-v2 we might just look for “accidental resonance” levels (dE of the same order of magnitude than Fermi resonances) and then apply the rate for Fermi resonances
- STELLAR v2 updates will consider other intermode transitions/rates more in detail.

STELLAR CO_2 v2



VT & VV near-resonant intermode rates by FHO model, with P=0.12 rates for *bs* couplings
VT rates for each collision partner ($k_{VT}(CO_2\text{-}\{CO_2,CO,O_2,C,O\})$)

v_2/v_3 VT deactivation ratios

collisional partner dependence

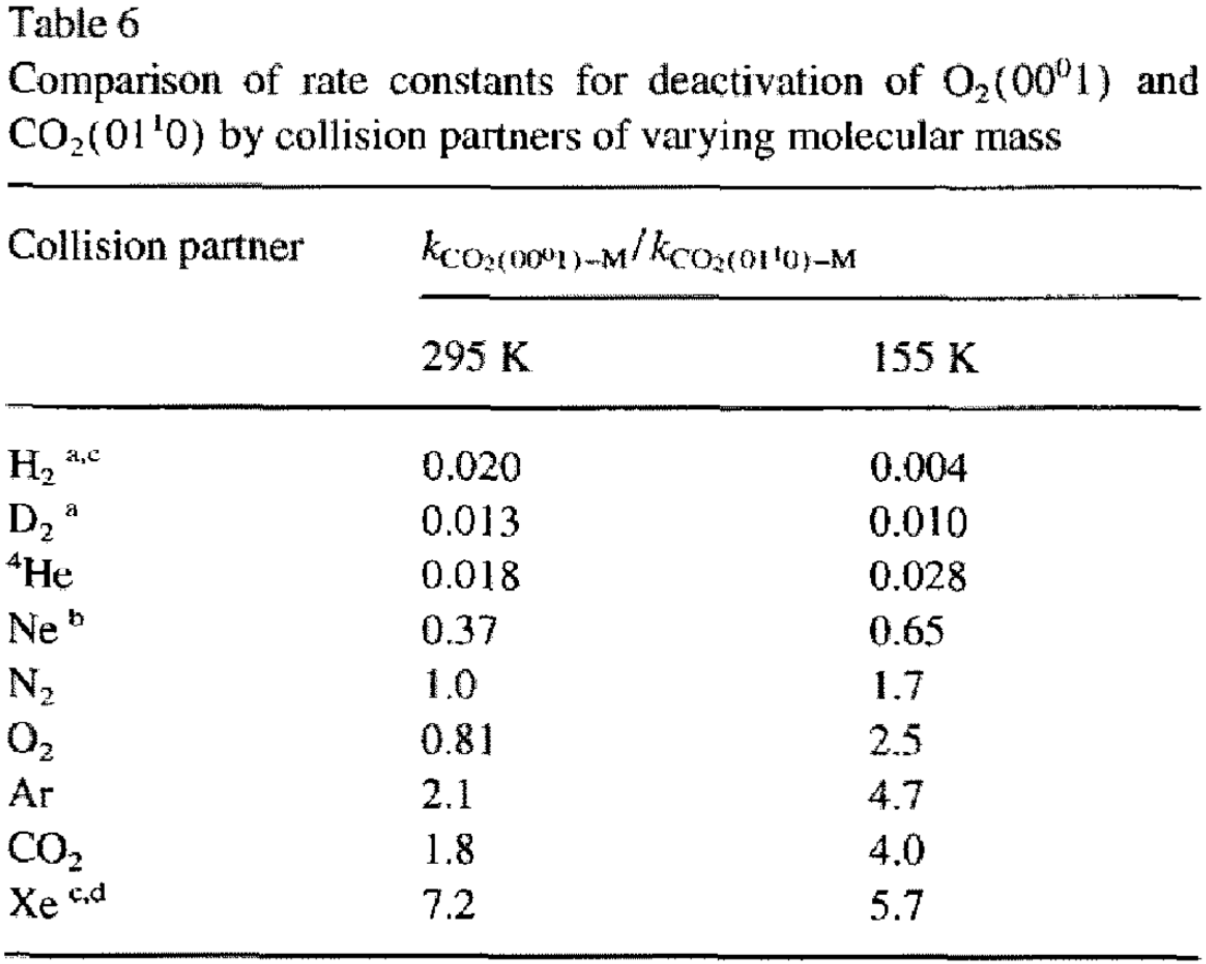


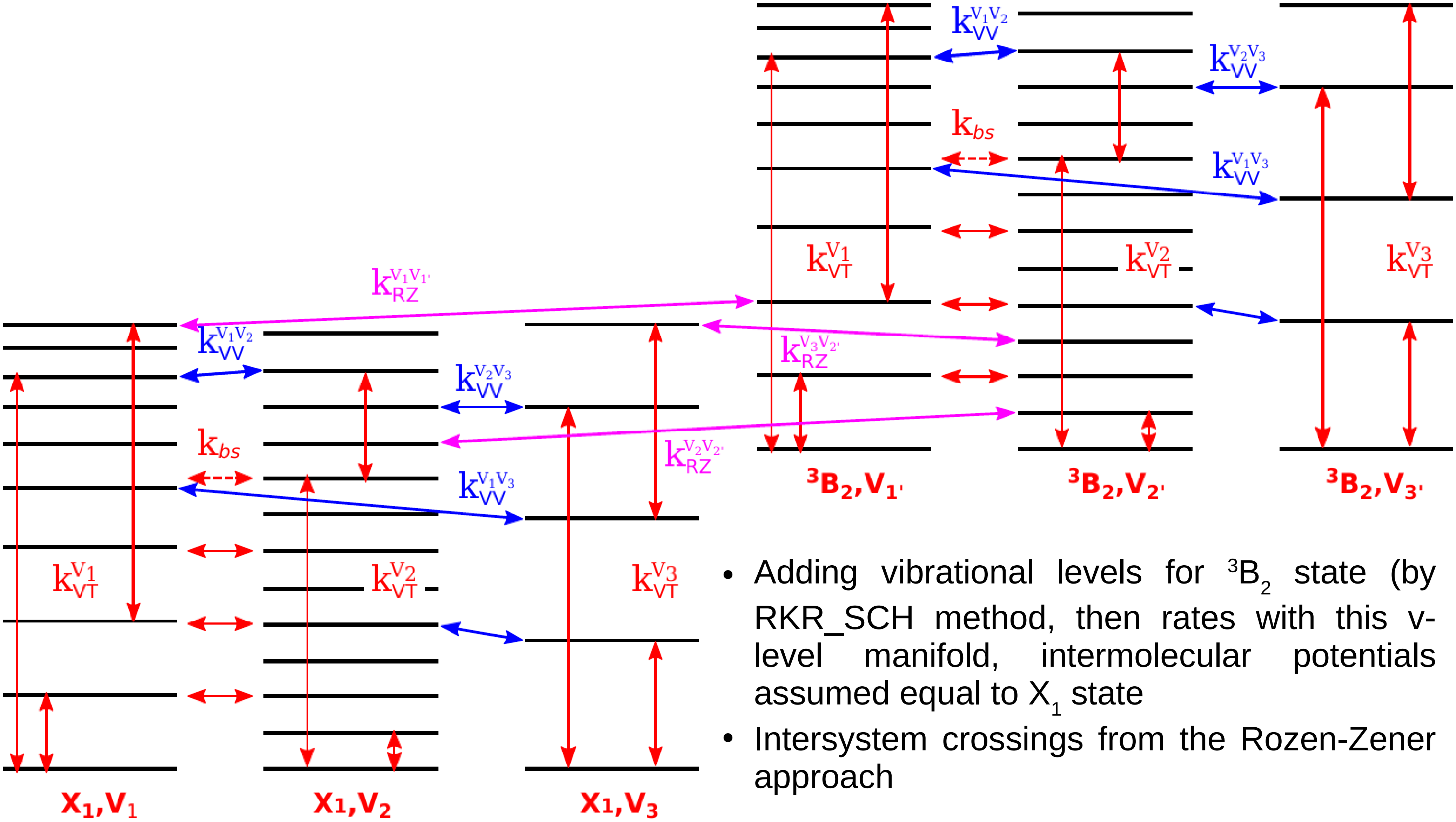
Table 6

Comparison of rate constants for deactivation of $O_2(00^01)$ and $CO_2(01^10)$ by collision partners of varying molecular mass

Collision partner	$k_{CO_2(00^01)-M}/k_{CO_2(01^10)-M}$	
	295 K	155 K
H_2 [a,c]	0.020	0.004
D_2 [a]	0.013	0.010
^4He	0.018	0.028
Ne [b]	0.37	0.65
N_2	1.0	1.7
O_2	0.81	2.5
Ar	2.1	4.7
CO_2	1.8	4.0
Xe [c,d]	7.2	5.7

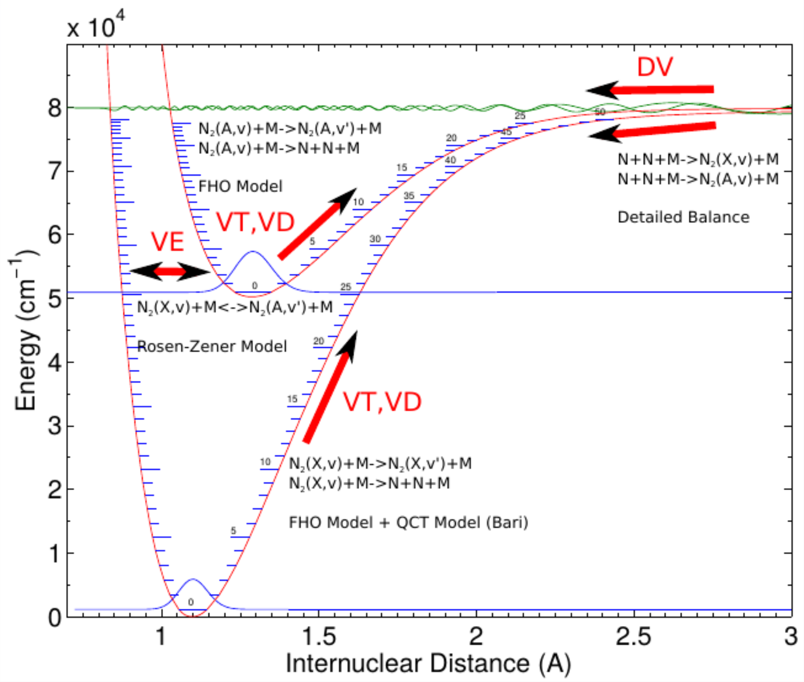
Siddles:1994, ChemPhys

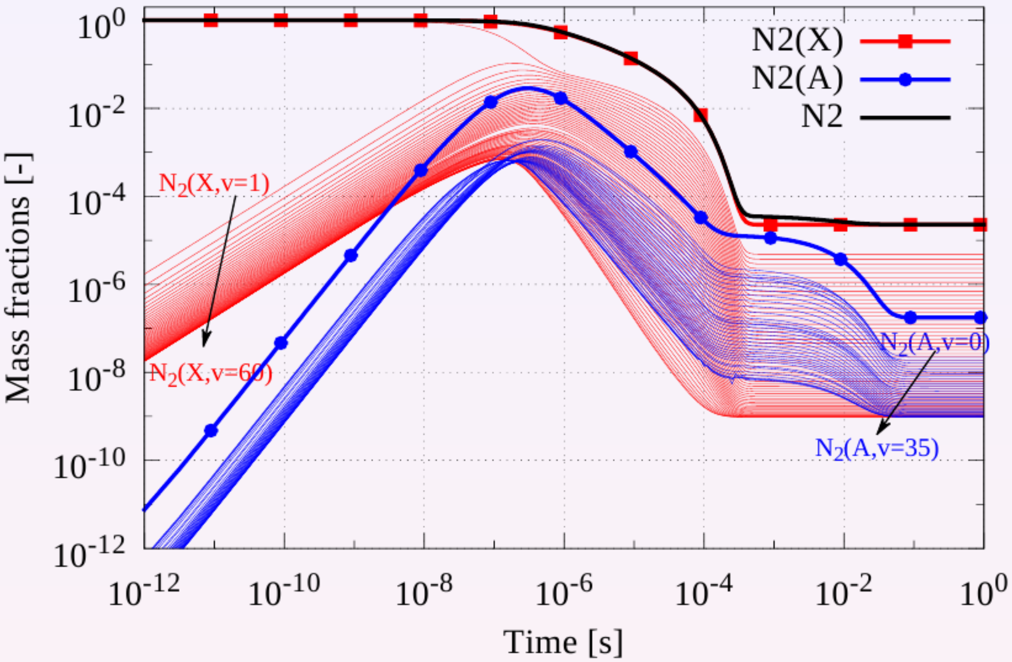
STELLAR CO_2 v3



- Adding vibrational levels for $^3B_2$ state (by RKR_SCH method, then rates with this v-level manifold, intermolecular potentials assumed equal to X_1 state
- Intersystem crossings from the Rozen-Zener approach

Sample Rosen-Zener VE model in N_2

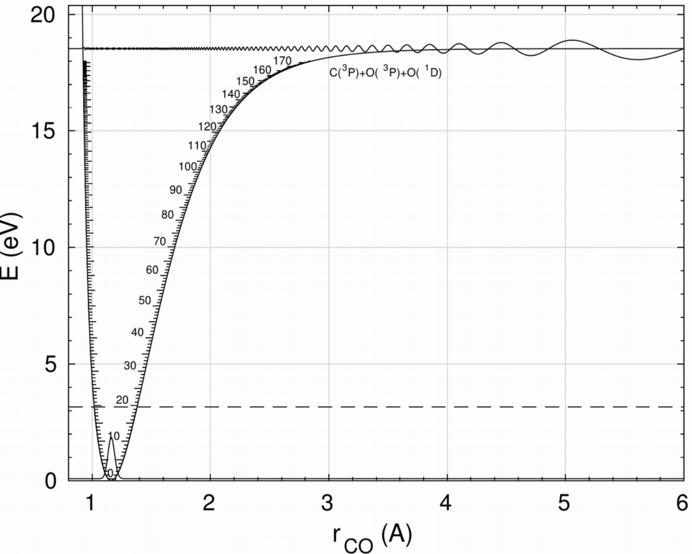


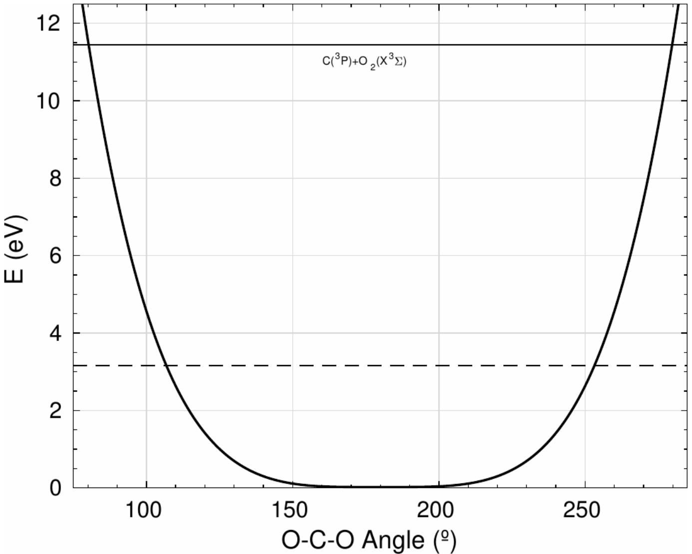


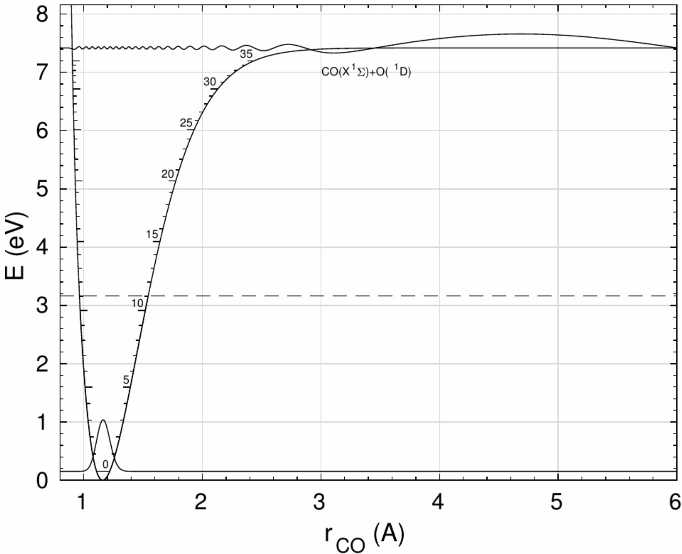
- $N_2(X)$, $N_2(A)$ Potential curves reconstruction using an extrapolated RKR method
- Calculation of all V-T, V-E and inverse processes using the FHO, Rosen–Zener and detailed balance models
- Further increases the complexity with about 10,000 rates just for N_2. Future more complete models for ionized air may well reach millions of rates

Definition of an adequate $v_{1,2,3}$ levels manifold

- Ames PES extrapolated by an Hulburth-Hirschfelder potential to the different dissociation limits
- Solving the radial Schrodinger equation to get the complete manifold of levels
- Lower levels are taken from the Chedin polynomial expansion





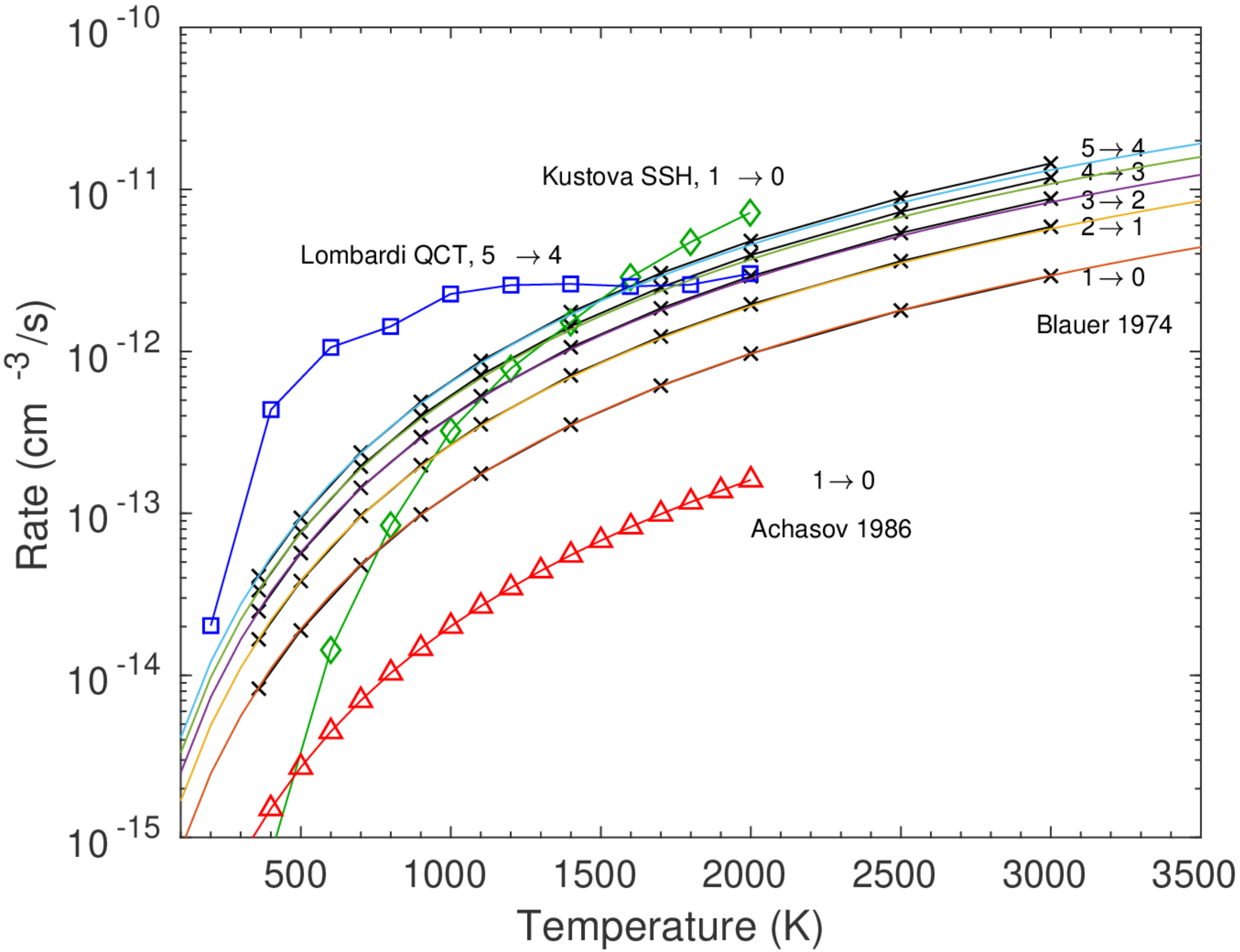


Applying the FHO model

- We select representative low-v rates from the literature and iterate a Morse intermolecular potential (+ S_{VT}, S_{VVT} steric factors) until a best-fit is achieved
- We then consider this intermolecular potential for all the higher v-levels rates
- We also consider all the possible multiquantum transitions

FHO modeling of CO2 v_2 VT transitions

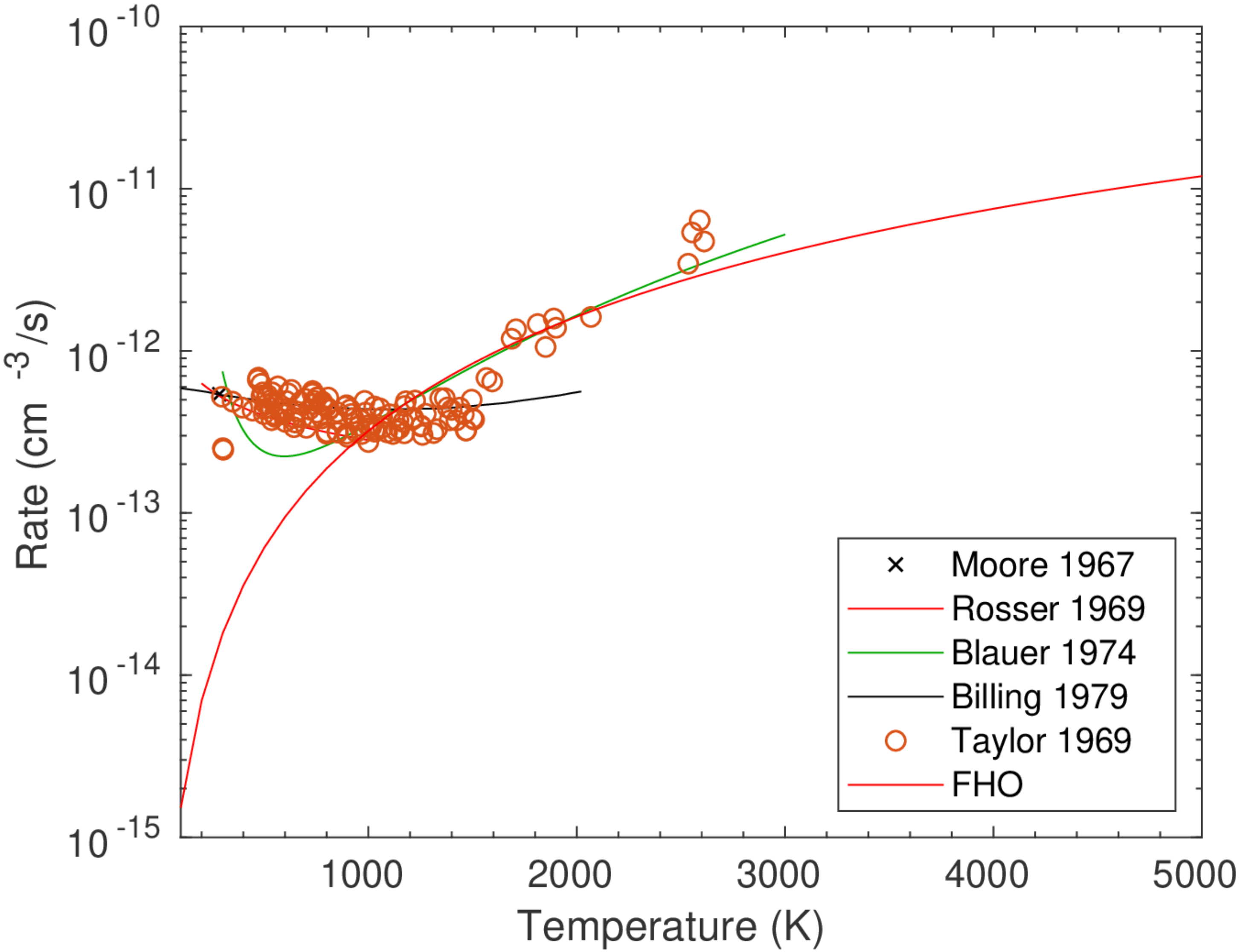
(the easy part)



Remarkably good fit with all the 5 Blauer V-T relaxation rates

FHO modeling of $CO_2(v_3=1)$-$N_2(v=0)$ resonant VV transitions

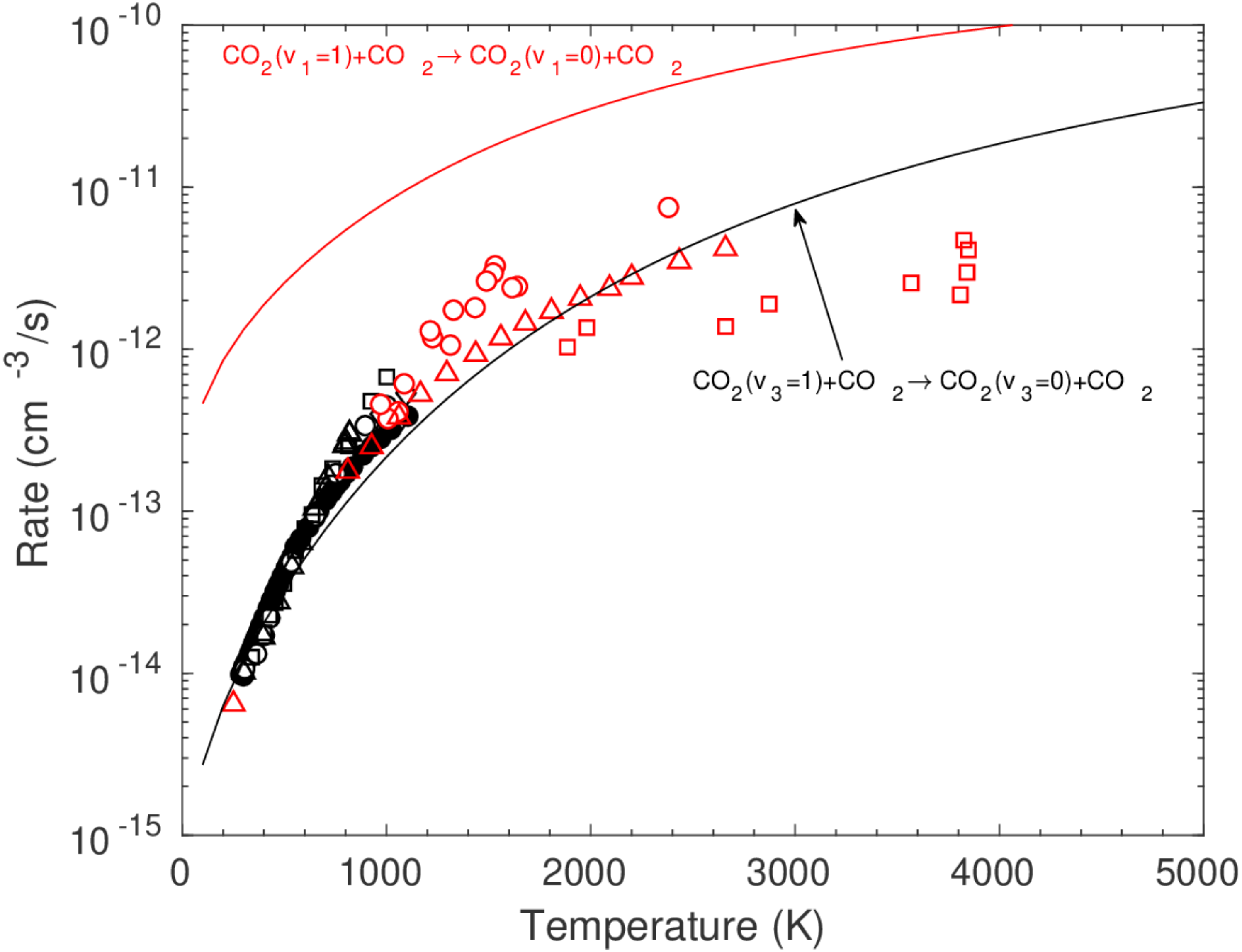
(the not-so easy part)



We made a semi-empirical correction to the FHO theory for better accounting VV resonant transitions. Need to use Sharma-Brau theory for low-T rates caculations

FHO modeling of $CO_2(v_3)$ VT transitions

(the difficult part)



Only data for global quenching of v3 mode exists. We make an FHO fit of this

FHO modeling of $CO_2(v_3)$ VT transitions

(the difficult part)

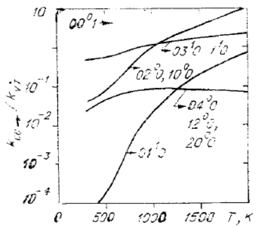


Fig. 6

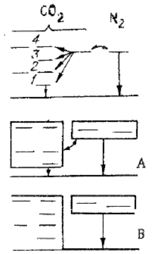
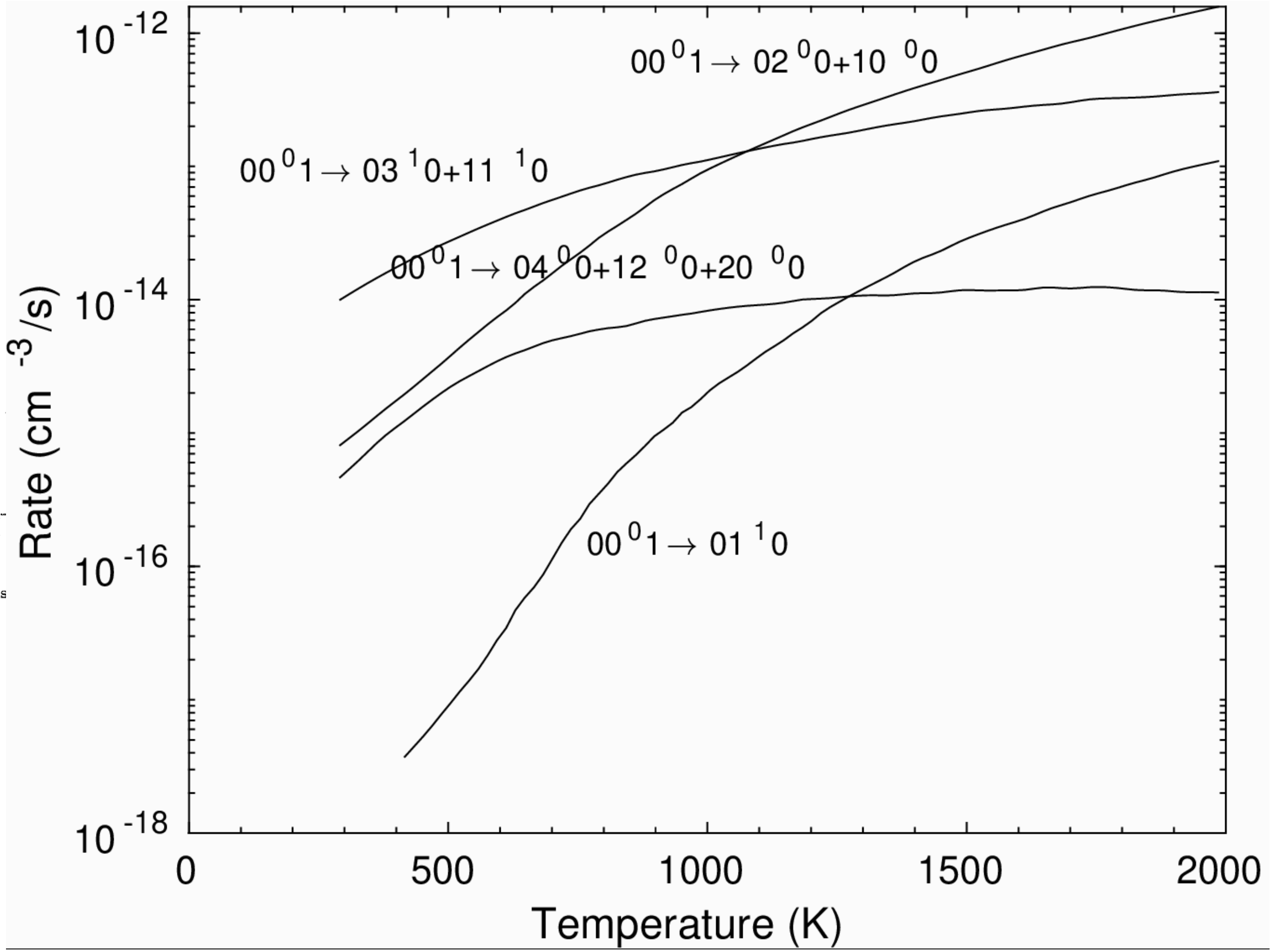


Fig. 7

Fig. 6. Relative values of the probability of the deactivation of the state 00^01 as a function of the temperature of the gas.

Fig. 7. Different mechanisms of the mechanism of vibrational energy exchange in a molecule of carbon dioxide gas and in a mixture of CO_2—N_2.

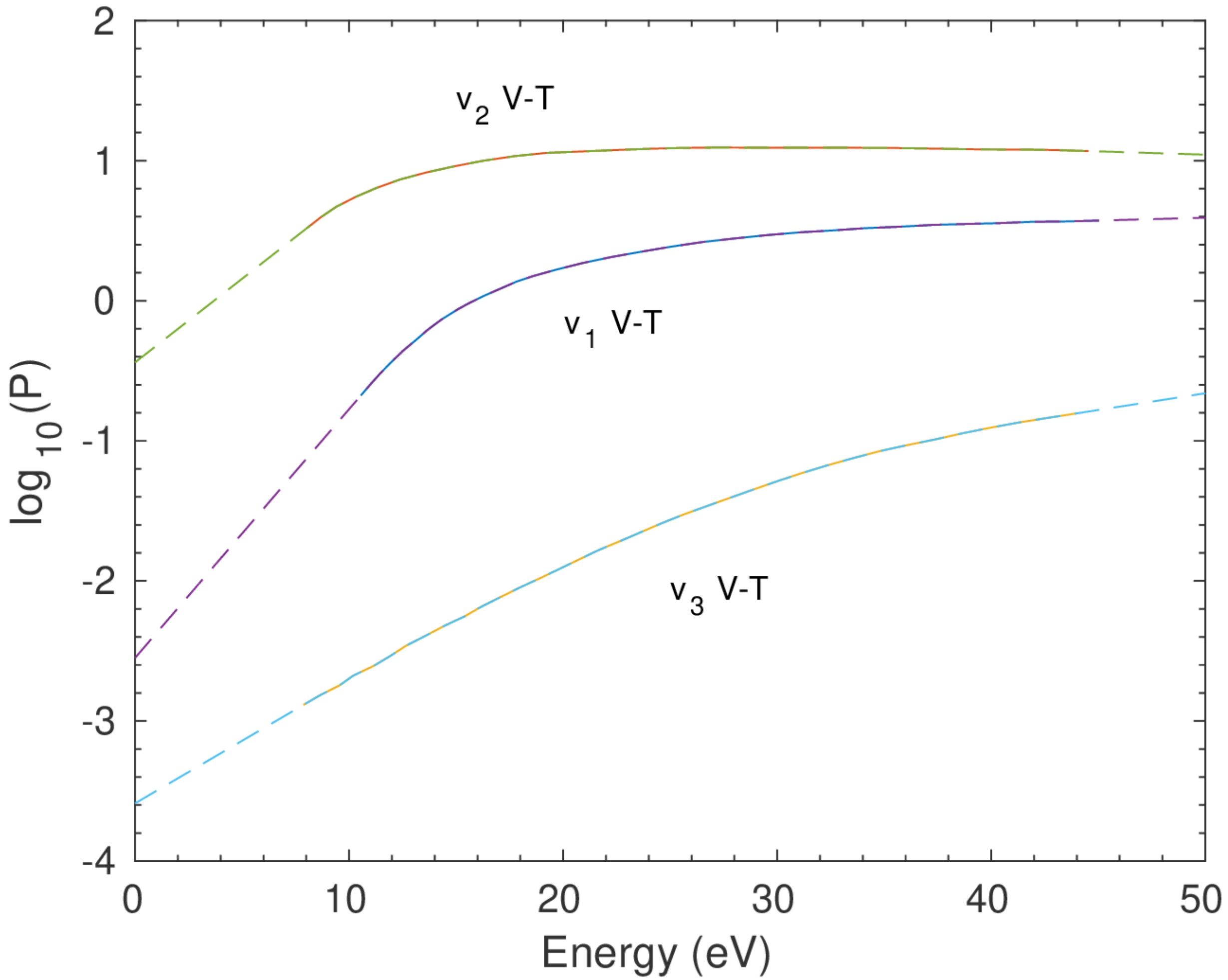


Losev (1976) made a review of the T-dependent branching ratios for v_3 quenching.

We can get 4 new rates out of the previous FHO one, but not the real v_3 VT rate!

FHO modeling of $CO_2(v_3)$ VT transitions

(the difficult part)

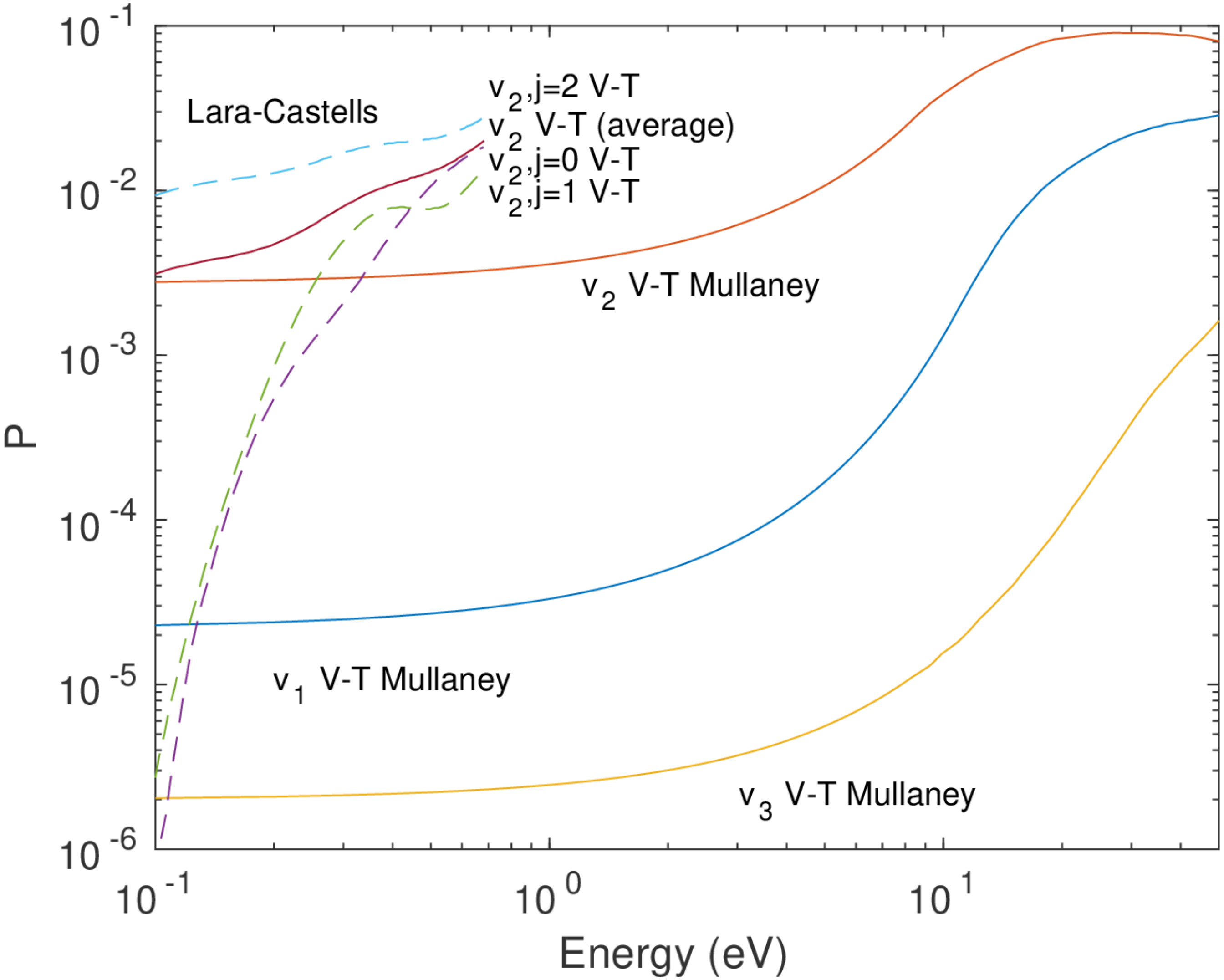


We make a careful extrapolation of the cross-sections to low energies, with the help of my imaginary friend Dimitri

Mullaney (1982) made a quantum-chemistry calculation of v1,v2, v3 VT excitation rates for CO2-O collisions. We get the quenching rates by detailed balance

FHO modeling of $CO_2(v_3)$ VT transitions

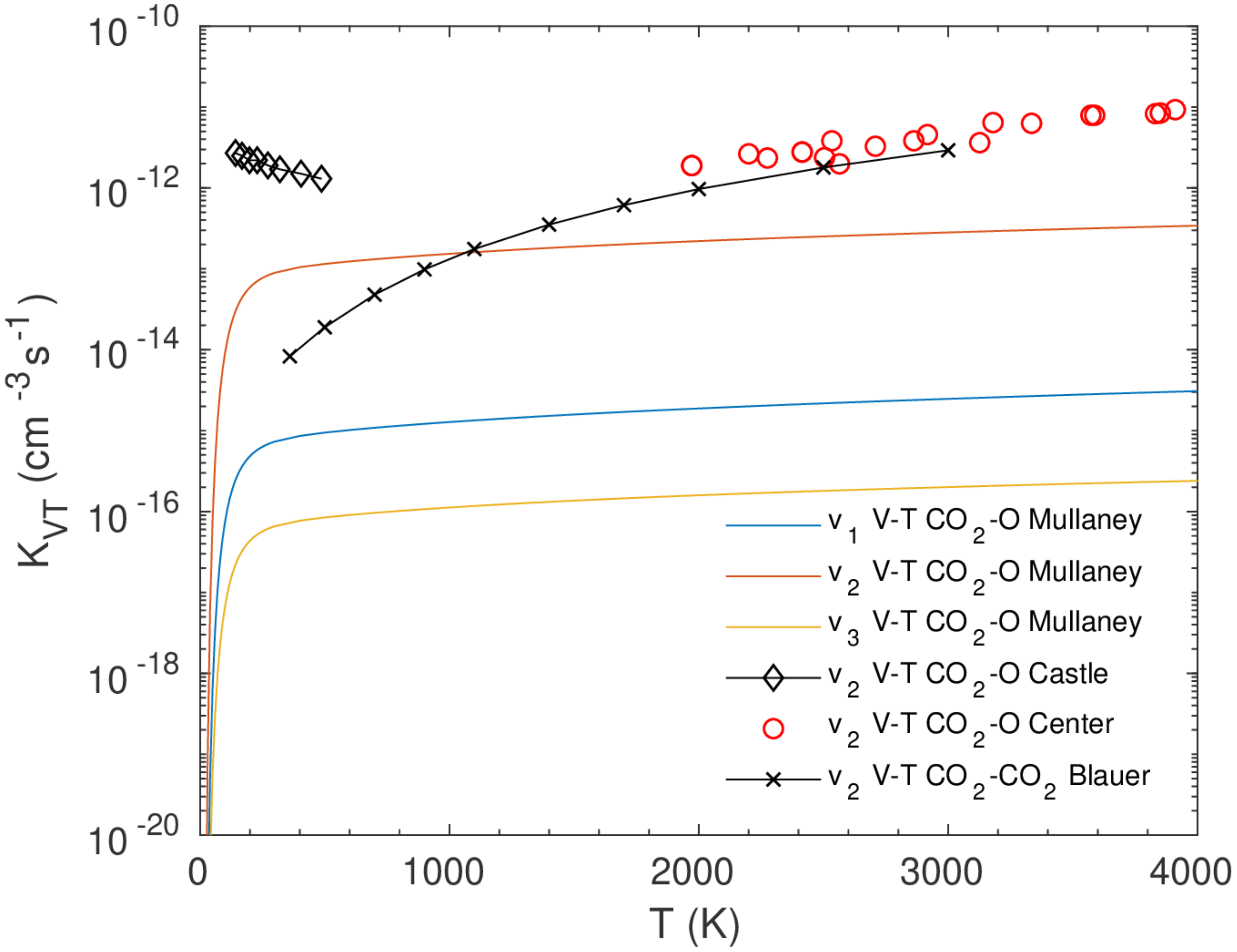
(the difficult part)



Comparison with more recent results from Lara-Castells (2006) for the v2 VT quanching probability show that the Mullaney Cross-sections appear to have correct orders of magnitude

FHO modeling of $CO_2(v_3)$ VT transitions

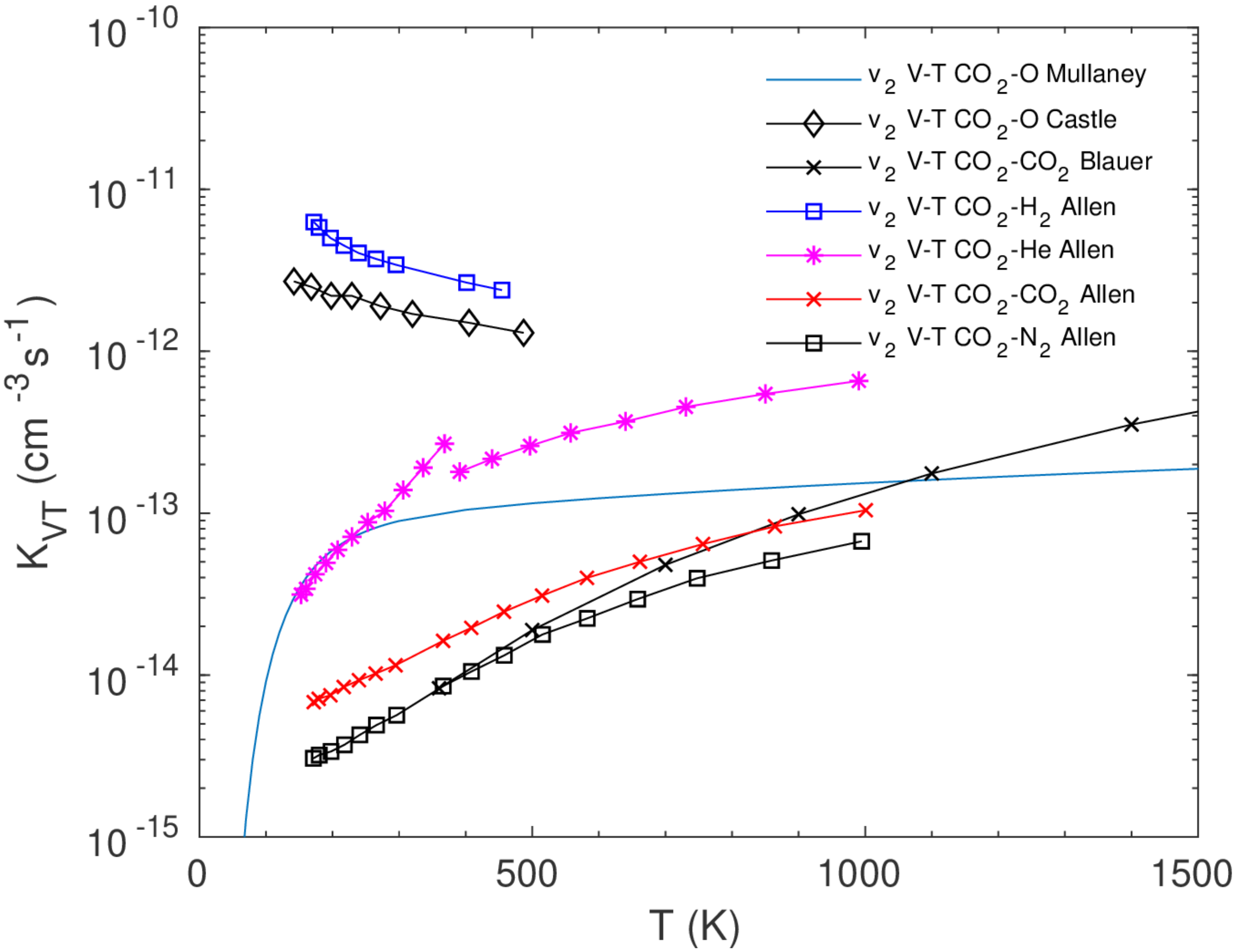
(the difficult part)



We integrate cross-sections with the a Maxwellian vdf and get the corresponding rates. The v_2 VT rate has the correct order of magnitude and compares “decently” to experimental data (for CO_2-CO_2 collisions since for CO_2-O collisions there are spin-orbit coupling resonances

FHO modeling of $CO_2(v_3)$ VT transitions

(the difficult part)

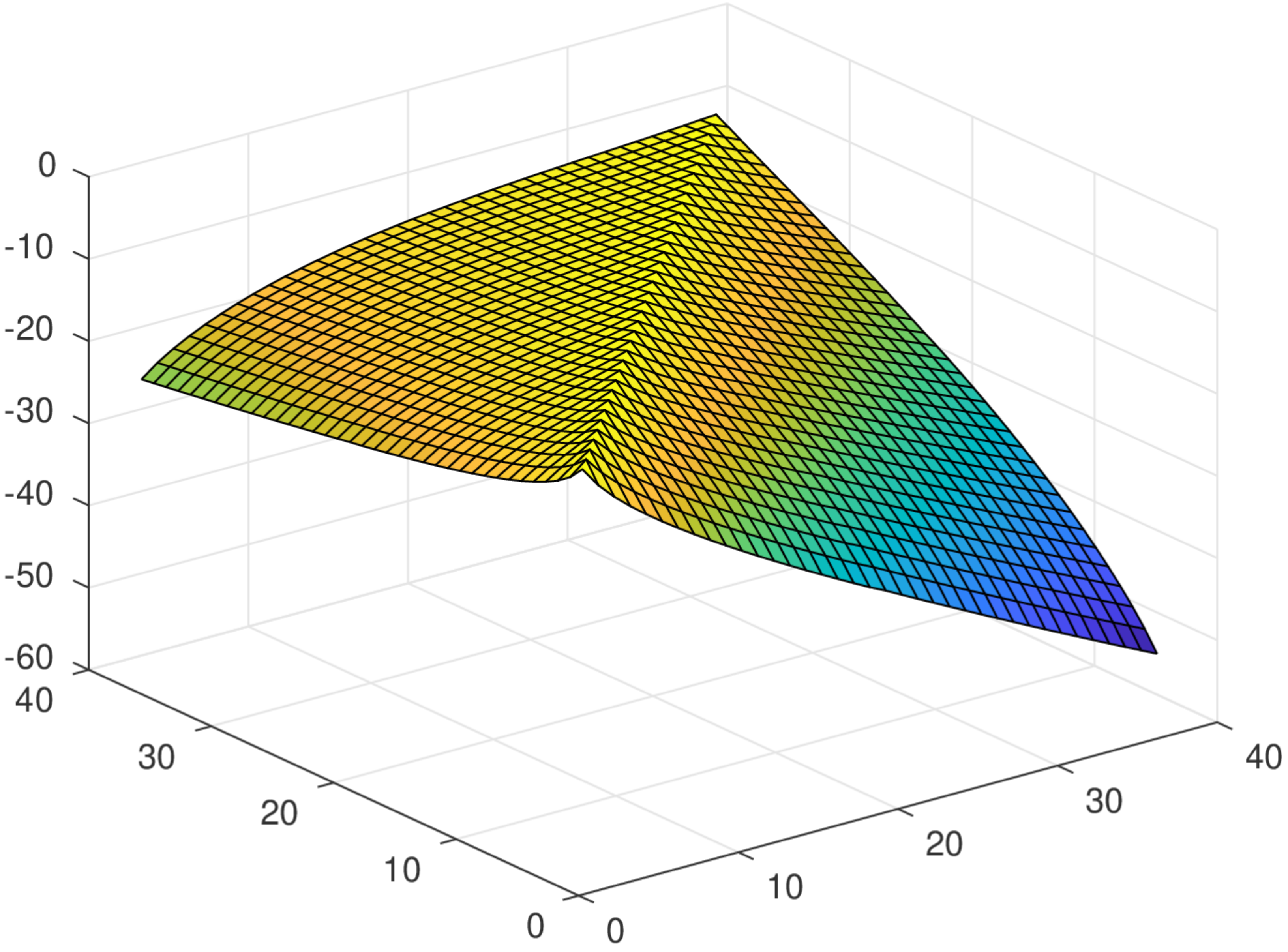


More comparisons

Finalizing calculations

- Results give the correct orders of magnitude differences
- v1/v3 has a one order of magnitude difference, same as with the FHO simulation considering same intermolecular potential and different energy spacings
- v2/v3 has a 3 order of magnitude difference, same as quoted in the literature
- Now we can apply the FHO model to reproduce the same v3 VT quenching data, but with a 1e-3 factor

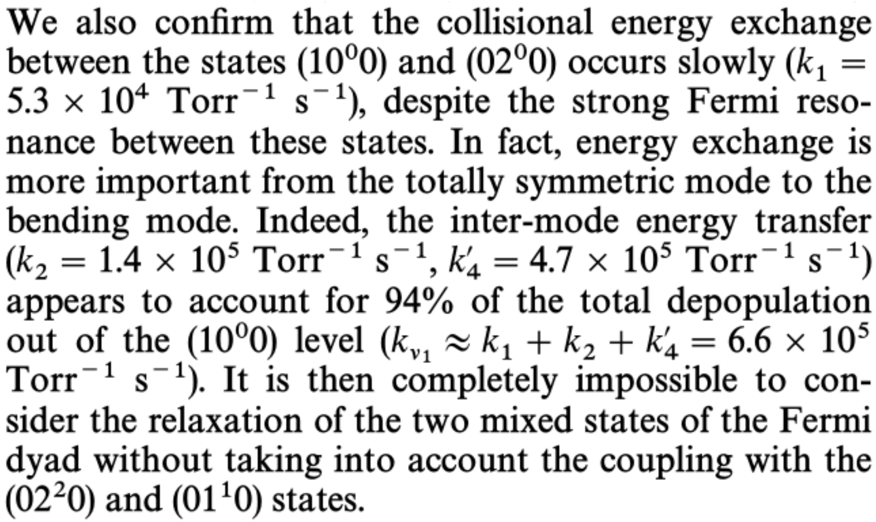
Final v2 VT database (1000K)



Conclusions

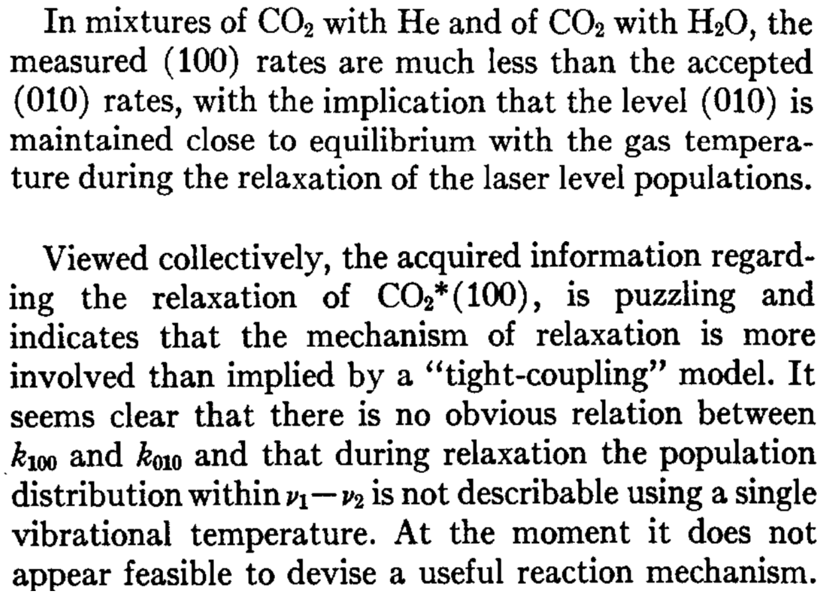
- Lots of experimental data on kinetics for low CO_2 v levels (T=150- 4000K)
- Quantum chemistry data more scarce, recent works mostly focused on the $CO_2(v_2)$+O rate at very low-T (atmospheric physics applications). We need accurate data over a large T range for the other transitions (v_1 & v_3)
- CO_2 plasma reforming kinetic models based on the SSH approach. Absolutely no reason to keep using this legacy model
- You musn't use the *bs* coupling approximation, or if you really must, at least verify the applicability of this condition
- In the absence of good quantum chemistry rates (they will come eventually!), the FHO model is a very good bridging approach that should be seriously considered by the kinetic modeling community
- FHO computer routine for diatomic and triatomic (new) collisions with a few example scripts, plus STELLAR-CO2 v1 database available (soon!) at http://esther.ist.utl.pt/stellar.html

Selected litterature comments on *bs* coupling approximation



We also confirm that the collisional energy exchange between the states (10^00) and (02^00) occurs slowly ($k_1 = 5.3 \times 10^4$ Torr^{-1} s^{-1}), despite the strong Fermi resonance between these states. In fact, energy exchange is more important from the totally symmetric mode to the bending mode. Indeed, the inter-mode energy transfer ($k_2 = 1.4 \times 10^5$ Torr^{-1} s^{-1}, $k_4' = 4.7 \times 10^5$ Torr^{-1} s^{-1}) appears to account for 94% of the total depopulation out of the (10^00) level ($k_{\nu_1} \approx k_1 + k_2 + k_4' = 6.6 \times 10^5$ Torr^{-1} s^{-1}). It is then completely impossible to consider the relaxation of the two mixed states of the Fermi dyad without taking into account the coupling with the (02^20) and (01^10) states.

Millot:1998 JRamanSpectrosc



In mixtures of CO_2 with He and of CO_2 with H_2O, the measured (100) rates are much less than the accepted (010) rates, with the implication that the level (010) is maintained close to equilibrium with the gas temperature during the relaxation of the laser level populations.

Viewed collectively, the acquired information regarding the relaxation of $CO_2^*(100)$, is puzzling and indicates that the mechanism of relaxation is more involved than implied by a "tight-coupling" model. It seems clear that there is no obvious relation between k_{100} and k_{010} and that during relaxation the population distribution within $\nu_1-\nu_2$ is not describable using a single vibrational temperature. At the moment it does not appear feasible to devise a useful reaction mechanism.

Rosser:1972 JChemPhys

Nice discussion on the conditions where bs levels equilibrate

Allen:1980 Chem Phys

don't build on shaky foundations!

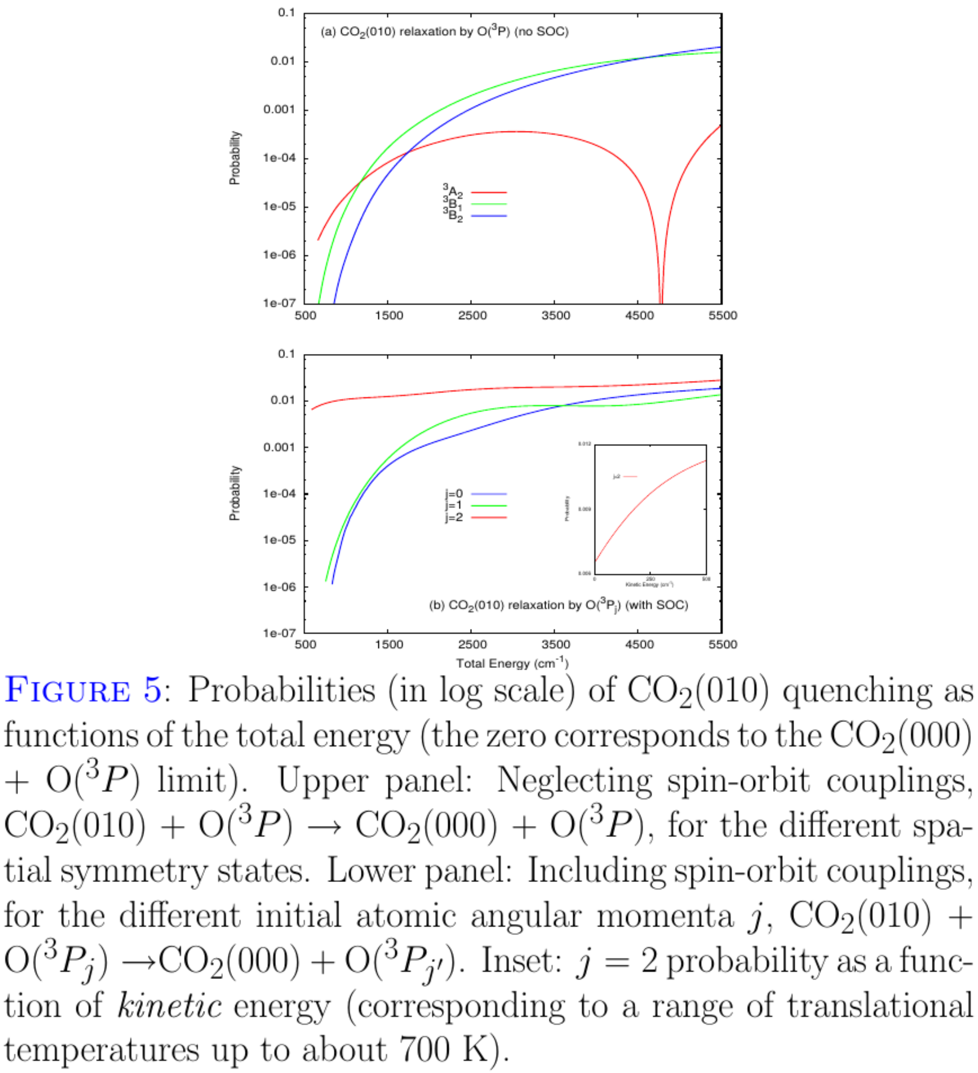
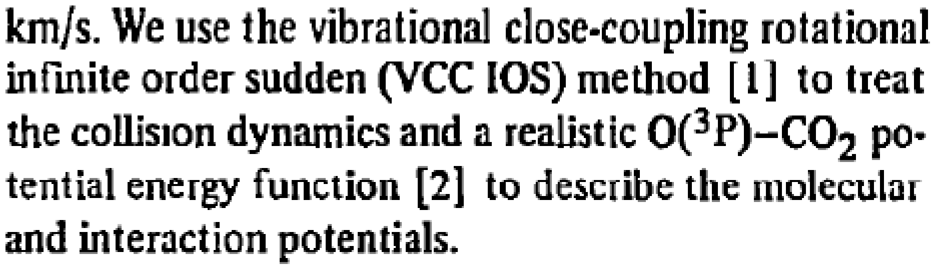


FIGURE 5: Probabilities (in log scale) of $CO_2(010)$ quenching as functions of the total energy (the zero corresponds to the $CO_2(000)$ + $O(^3P)$ limit). Upper panel: Neglecting spin-orbit couplings, $CO_2(010) + O(^3P) \rightarrow CO_2(000) + O(^3P)$, for the different spatial symmetry states. Lower panel: Including spin-orbit couplings, for the different initial atomic angular momenta j, $CO_2(010)$ + $O(^3P_j) \rightarrow CO_2(000) + O(^3P_{j'})$. Inset: $j = 2$ probability as a function of *kinetic* energy (corresponding to a range of translational temperatures up to about 700 K).



km/s. We use the vibrational close-coupling rotational infinite order sudden (VCC IOS) method [1] to treat the collision dynamics and a realistic $O(^3P)-CO_2$ potential energy function [2] to describe the molecular and interaction potentials.

Mullaney-Harvey:1982

Lara-Castells:2006