NEAR-THRESHOLD STATES
IN OZONE ISOTOPE EFFECT

Sergy Yu. Grebenschikov
MPI für Dynamik und Selbstorganisation, Göttingen

Critical Stability, Eriche, Oct. 17 2008

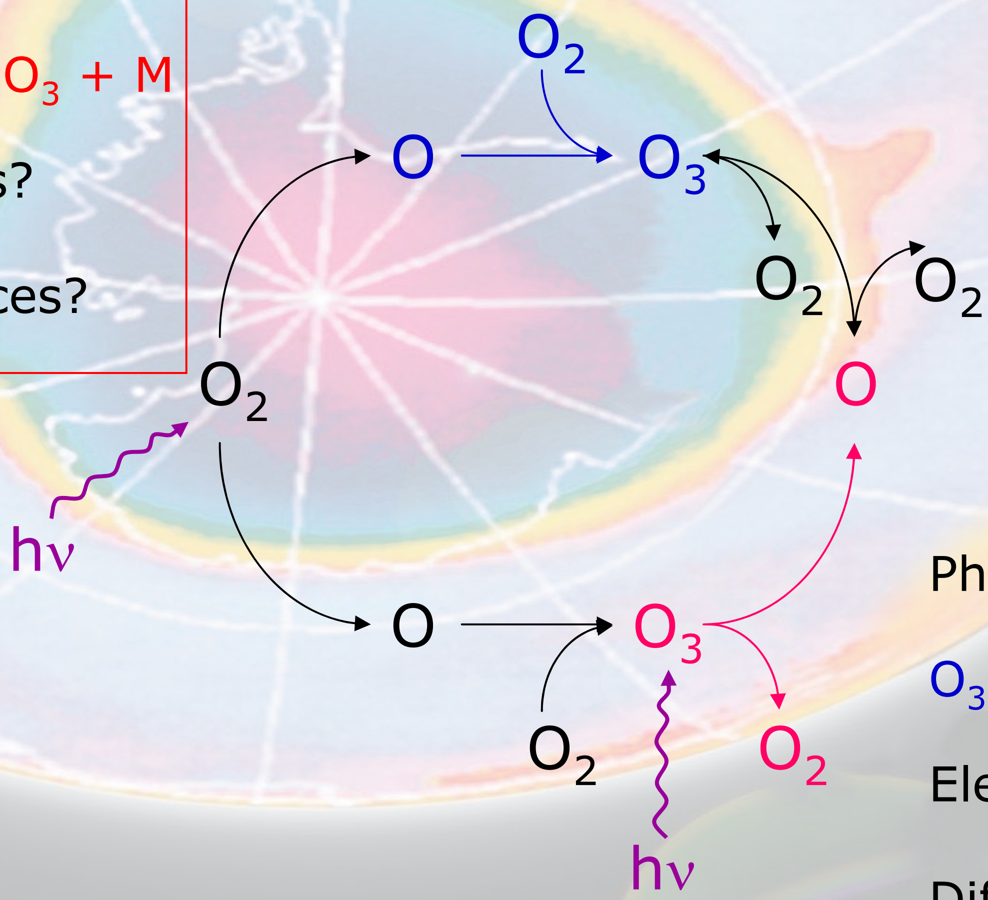
CHAPMAN CYCLE OF OZONE LIFE

Recombination:

$O_2 + O + M \rightarrow O_3 + M$

Isotope effects?

P,T-dependences?



Photodissociation:

$O_3 + h\nu \rightarrow O_2 + O$

Electronic states?

Diffuse structures?

OUTLINE OF THE TALK

I. BASIC PROPERTIES OF OZONE & THE ISOTOPE EFFECT

Isotopes & equilibrium forms

Elementary reactions and main experimental results

II. QUANTUM MECHANICS OF $O+O_2 \rightarrow O_3$ REACTION

Ozone at dissociation threshold (potential, spectrum, vdW states)

Resonance-driven recombination and isotope effect

III. COLLISIONAL DEACTIVATION NEAR THRESHOLD

Efficiency of stabilization in quantum O_3^*+Ar scattering

IV. CONCLUSIONS

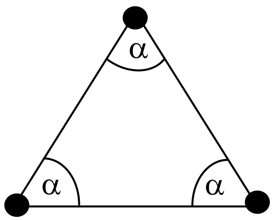
BASIC FACTS ABOUT OZONE

Oxygen isotopes:

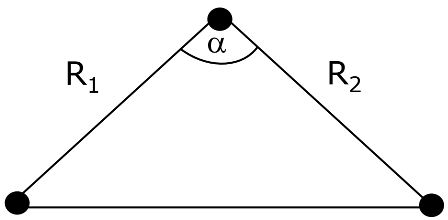
^{16}O (0.99763) ^{17}O (2.7×10^{-4}) ^{18}O (2.0×10^{-3})

6 **7** **8**

Equilibria of ozone:



D_{3h}, cyclic O_3



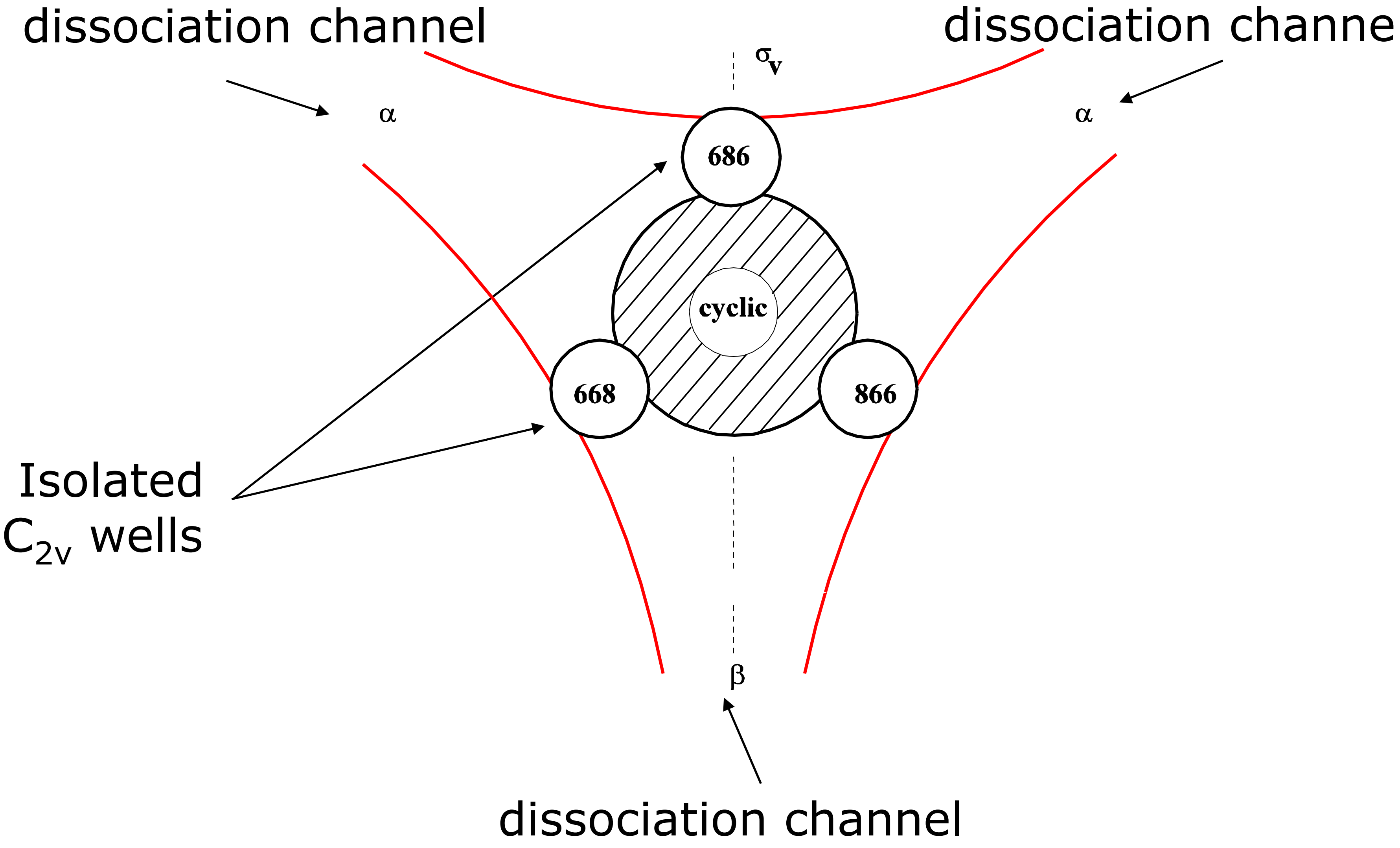
C_{2v}, open O_3

Three permutations of O atoms ⇔ three equivalent C_{2v} minima

868: Symmetric molecule; 688: Non-symmetric molecule

Central atom is special: 8**6**8 → **6** + 88 is **not** feasible.

SCHEMATIC REPRESENTATION OF O_3 POTENTIAL



ISOTOPE EFFECT IN ELEMENTARY REACTIONS

Exchange: $$O + O_2 \xrightarrow{k^{EX}} O_2 + O$$ fast

Formation:

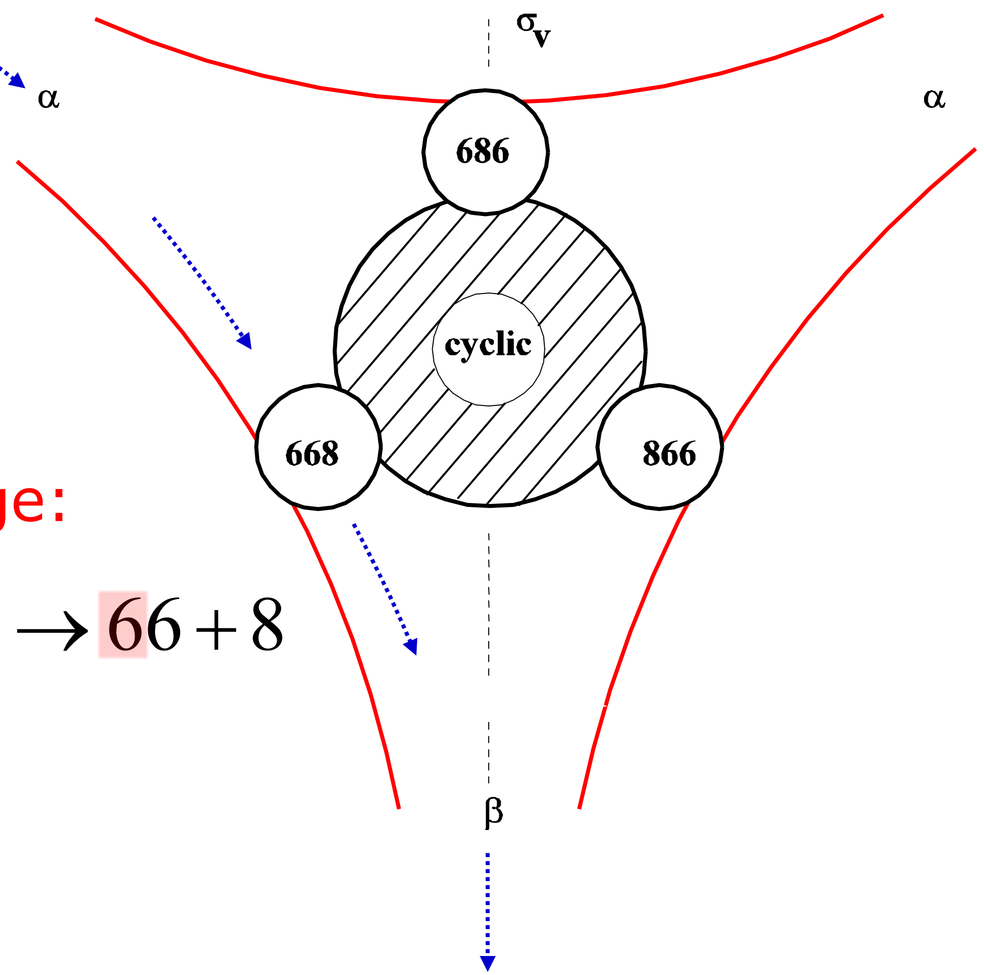
Association: $$O + O_2 \xrightarrow{k^{A}} O_3^*$$

Stabilization: $$O_3^* + M \xrightarrow{k^{ST}} O_3 + M$$ slow

Strong isotope sensitivity!
(Mauersberger & co-workers, 1981-1997)

ISOTOPE EFFECT IN ELEMENTARY REACTIONS

6 + 68



Exchange:

$$6 + 68 \rightarrow 668^{*} \rightarrow 66 + 8$$

(fast)

8 + 66

ISOTOPE EFFECT IN ELEMENTARY REACTIONS

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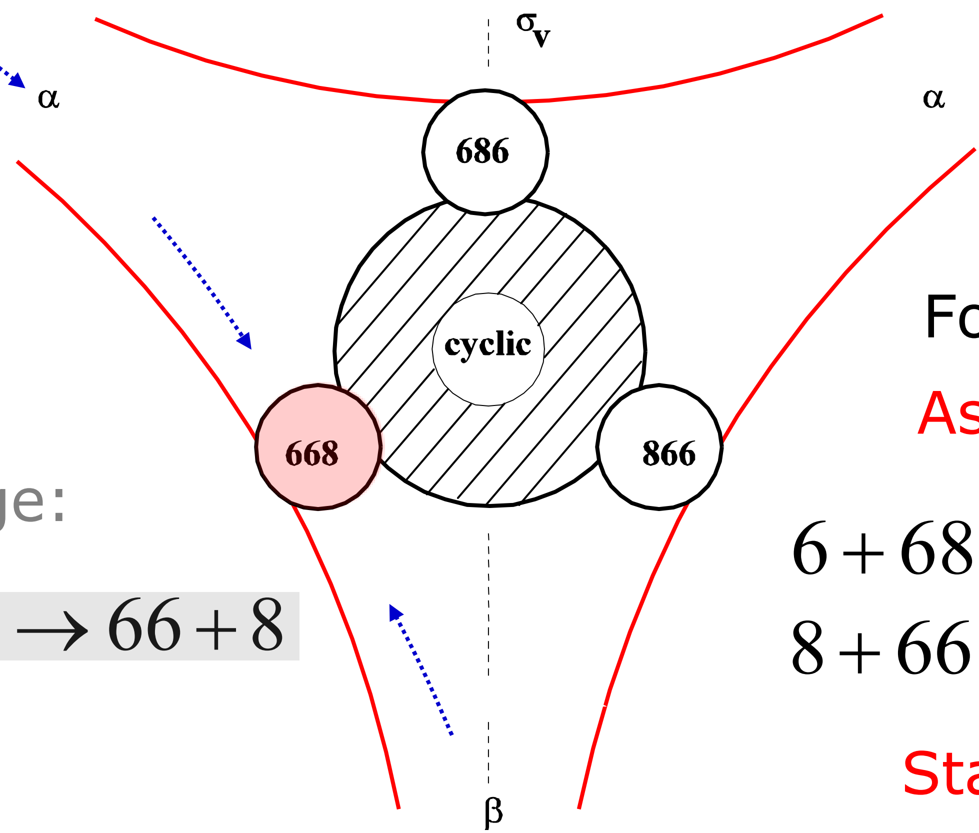

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$$6 + 68 \rightarrow 668^{*} \rightarrow 66 + 8$$

(fast)

Formation:

Association

$$6 + 68 \xrightarrow{k^{A}_{6+68}} 668^{*}$$

$$8 + 66 \xrightarrow{k^{A}_{8+66}} 668^{*}$$

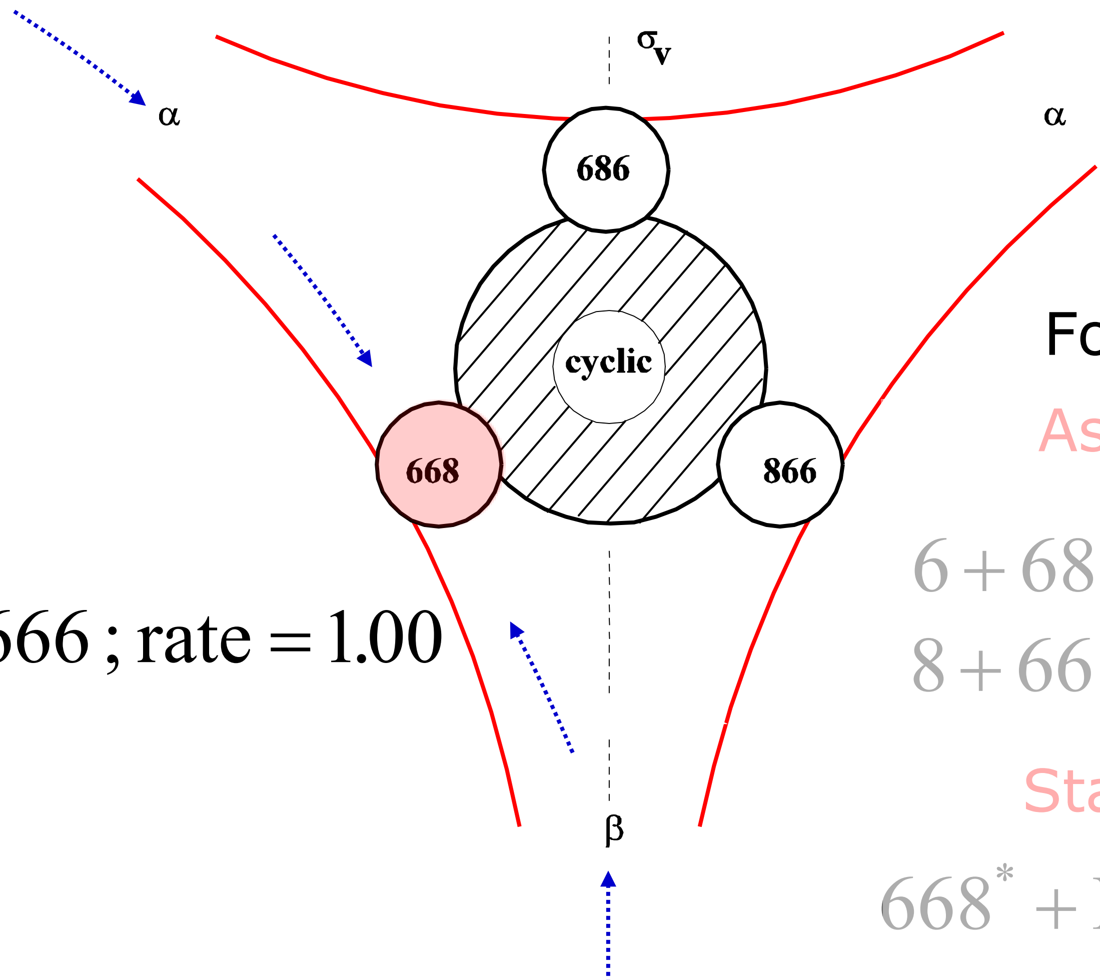
Stabilization

$$668^{*} + \mathrm{M} \rightarrow 668 + \mathrm{M}$$

(slow)

ISOTOPE EFFECT IN RECOMBINATION REACTION

6 + 68



$$6 + 66 \rightarrow 666\,;\ \text{rate} = 1.00$$

8 + 66

Formation:

Association

$$6 + 68 \xrightarrow{k^A_{6+68}} 668^*$$

$$8 + 66 \xrightarrow{k^A_{8+66}} 668^*$$

Stabilization

$$668^* + \mathrm{M} \rightarrow 668 + \mathrm{M}$$

(slow)

Mauersberger (1997-2001)

ISOTOPE EFFECT IN RECOMBINATION REACTION

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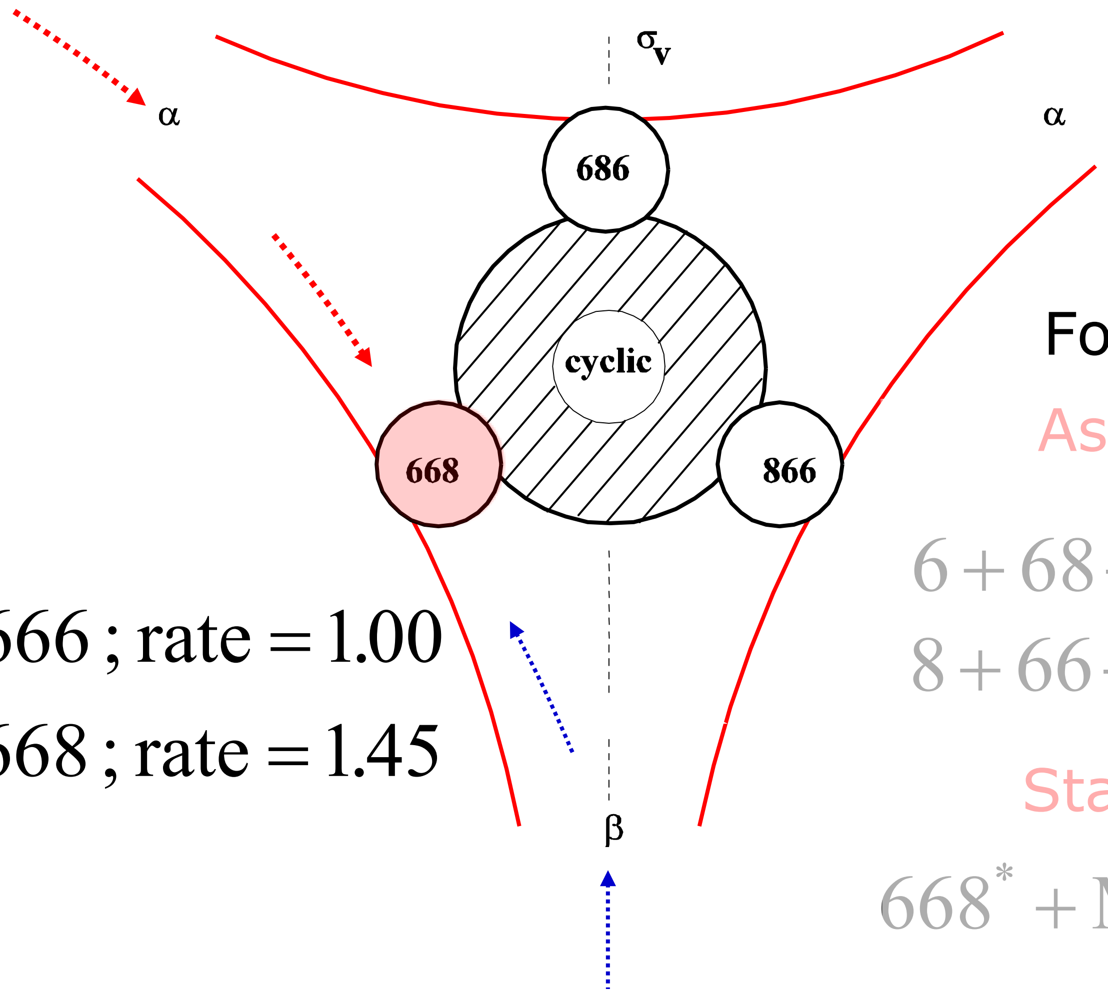

8 + 66

$$6+66 \rightarrow 666\,;\ \text{rate}=1.00$$

$$6+68 \rightarrow 668\,;\ \text{rate}=1.45$$

Formation:

Association

$$6+68 \xrightarrow{k^{A}_{6+68}} 668^{*}$$

$$8+66 \xrightarrow{k^{A}_{8+66}} 668^{*}$$

Stabilization

$$668^{*}+\mathrm{M} \rightarrow 668+\mathrm{M}$$

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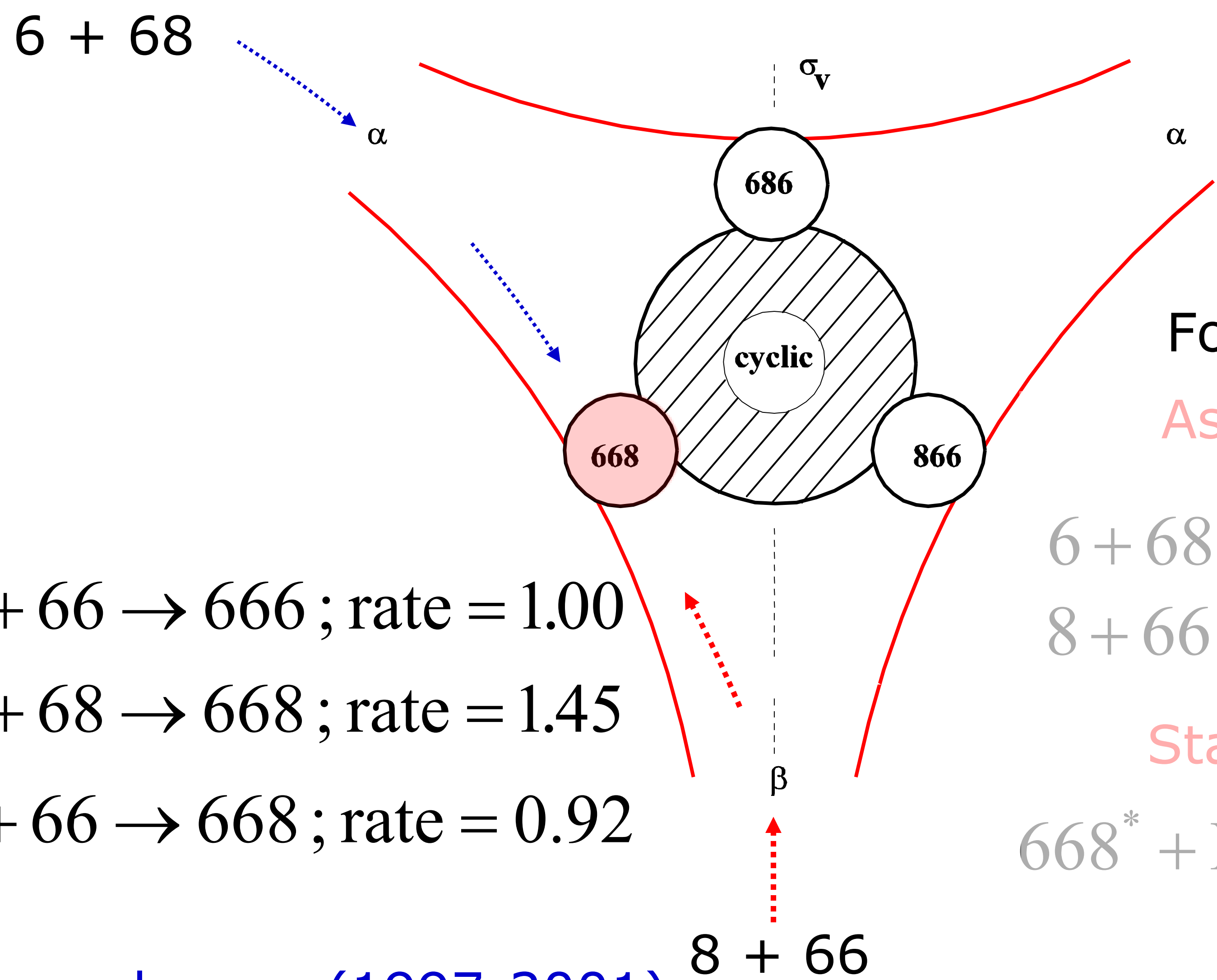

$$6+66 \rightarrow 666\,;\,\text{rate} = 1.00$$

$$6+68 \rightarrow 668\,;\,\text{rate} = 1.45$$

$$8+66 \rightarrow 668\,;\,\text{rate} = 0.92$$

Formation:

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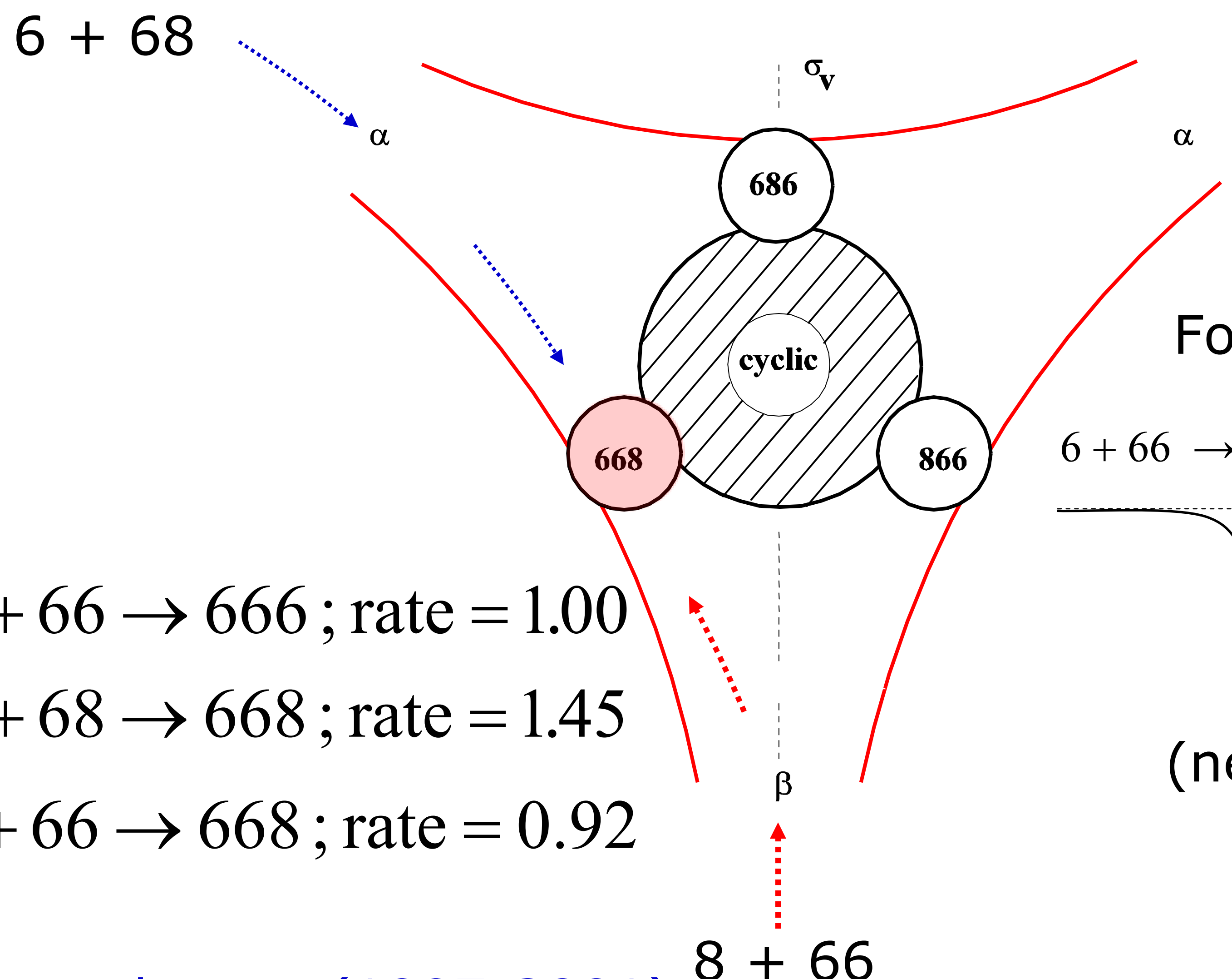

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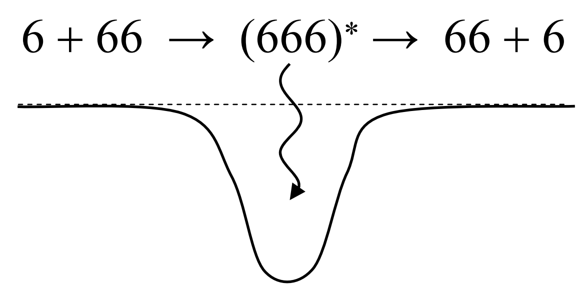
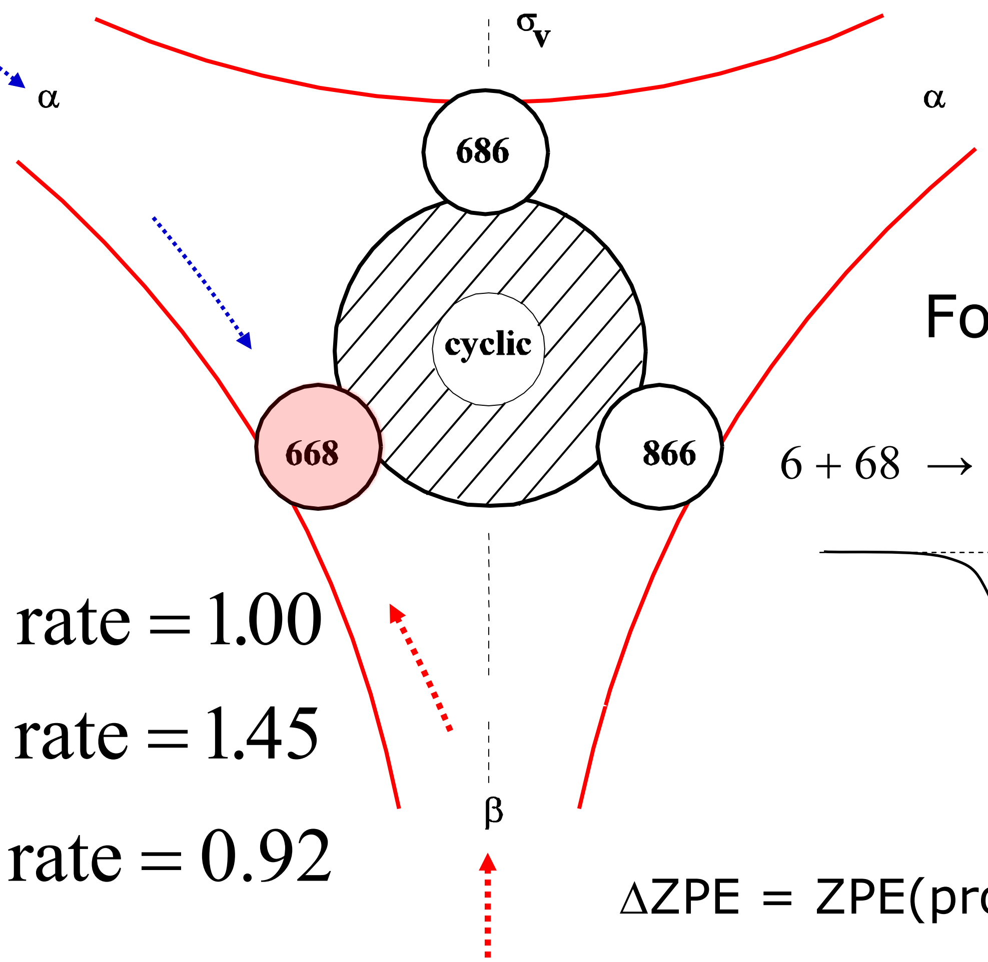


(neutral)

Mauersberger (1997-2001)

ISOTOPE EFFECT IN RECOMBINATION REACTION

6 + 68



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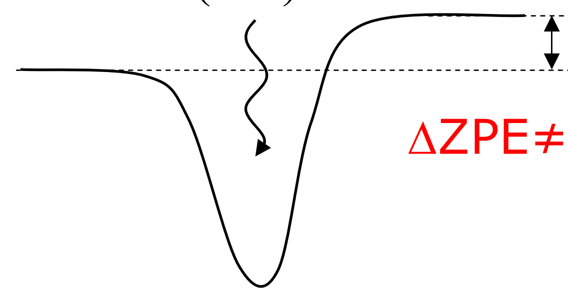
Formation:

$$6 + 68 \longrightarrow (668)^{*} \longleftarrow 66 + 8$$



ΔZPE≠0

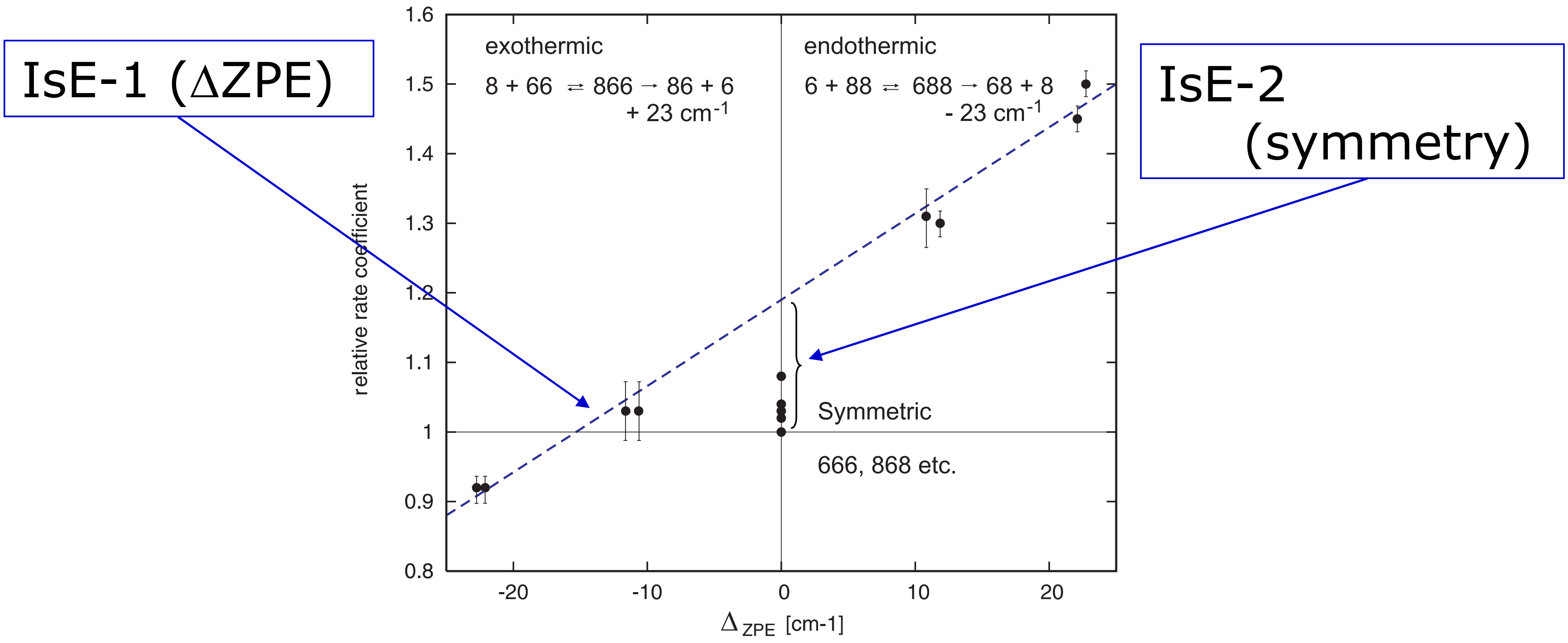
ΔZPE = ZPE(prod.) – ZPE(react.)

[ZPE(66)–ZPE(68)=23 cm^{-1}]

Mauersberger (1997-2001)

ISOTOPE EFFECT IN RECOMBINATION REACTION

Isotope dependence of k_{rel}: systematic if plotted against ΔZPE



Atmospheric conditions: enrichments are only due to IsE-2!

REDUCTION OF THE RECOMBINATION DYNAMICS

Full scattering problem: $$O + O_2 + M \rightarrow O_3 + M$$

State-specific "Lindemann mechanism":

...Association: $$O + O_2 \rightarrow O_3^*(n)$$

...Stabilization: $$O_3^*(n) + M \xrightarrow{P(n,n')} O_3 + M$$

Strong Collisions: Stabilization in ONE STEP

$$P(n) = \omega / (\omega + \Gamma_n)$$

RECOMBINATION VIA AN ISOLATED RESONANCE

$$O(\alpha) + O_2(\alpha; j'; v' = 0) \xrightarrow{\text{capture}} O_3^*(n) \xrightarrow{\text{stabilization}} O_3\,(+M)$$

Recombination cross-section (incoming channel α):

$$\sigma_{\text{rec}}(\alpha;n) = \sigma_{\text{cap}}(\alpha;n)\,\frac{\omega}{\omega + \Gamma_n^{\text{J}}}$$

σ_{rec} (α;n) gives thermal recombination rate from channel α:

$$k_{\text{rec}}(T;\alpha;n;\text{J}) = \frac{1}{Q}(2\text{J}+1)\,\frac{\omega\,\Gamma_n^{\text{J}}(\alpha)}{\omega + \Gamma_n^{\text{J}}}\exp\left(-E_n^{\text{J}}/k_B T\right)$$

partial width

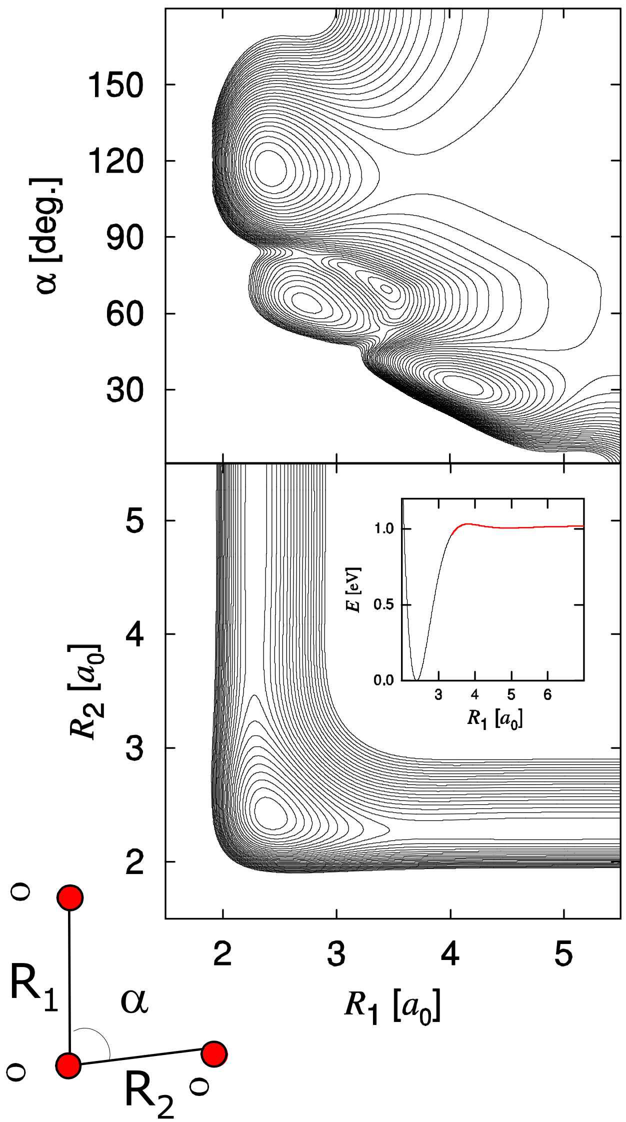
QUANTUM MECHANICAL CALCUATIONS OF O_3

- Global full-dimensional accurate Potential Energy Surface
- (Numerical) solution of the Schrödinger equation for nuclei:

  at dissociation threshold

  for large (and many!) angular momenta J

PES OF THE GROUND ELECTRONIC STATE OF O_3



Three equivalent C_{2v} wells (+cyclic)

~ 1eV (9000 cm^{-1}) deep potential

250 bound states in each C_{2v} well:

Good agreement with experiment

Submerged dissociation barrier

Shallow vdW wells in entrance channels

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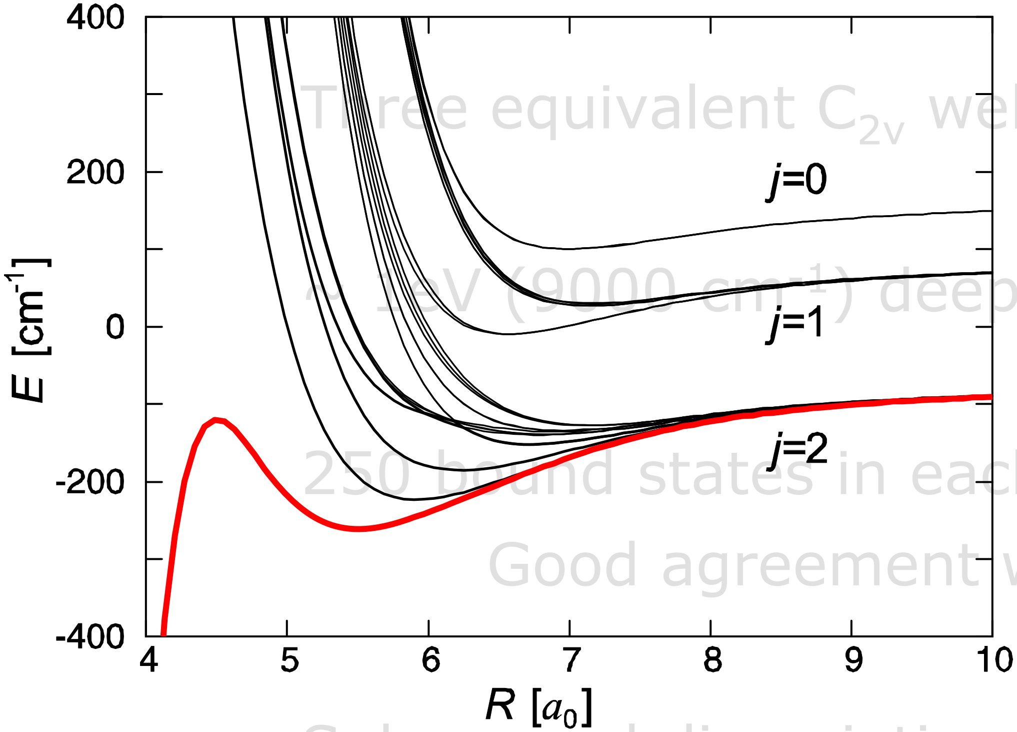

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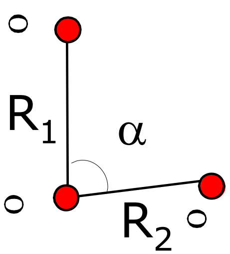


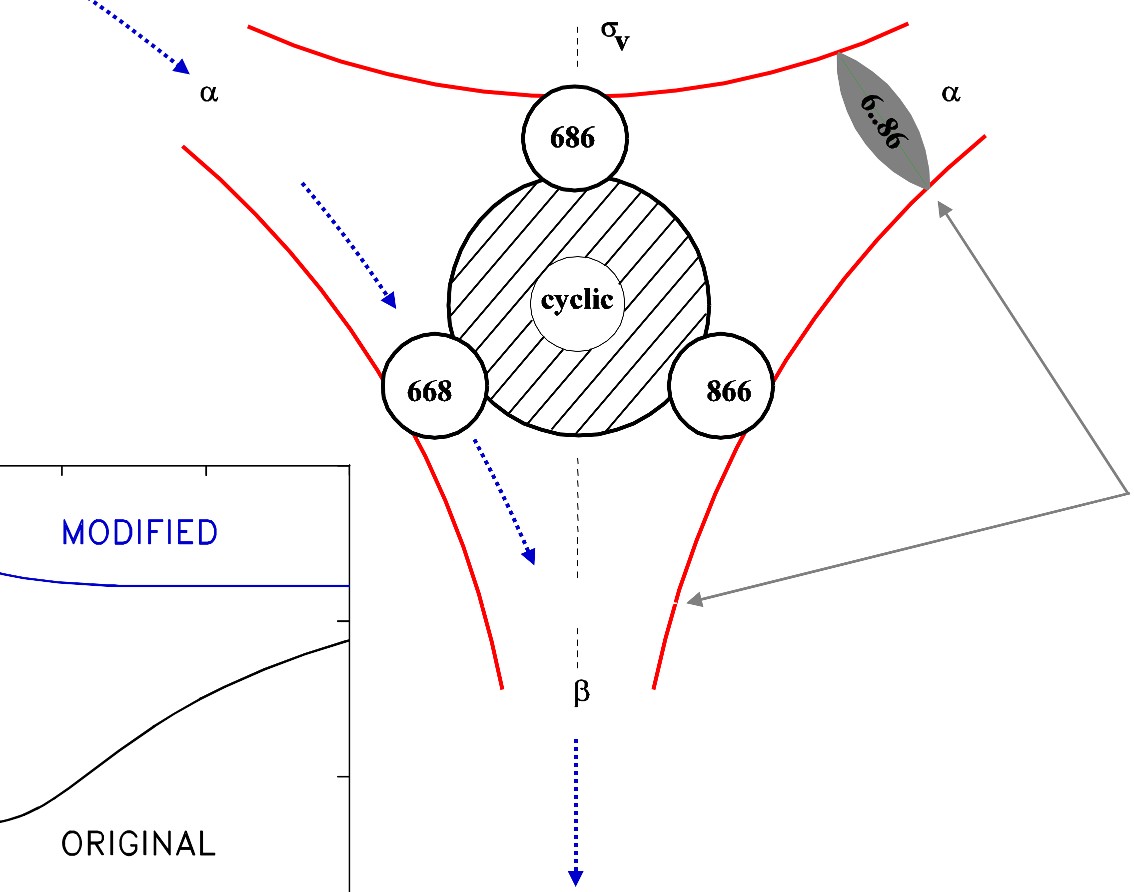
Shallow vdW wells in entrance channels

… with many weakly bound and

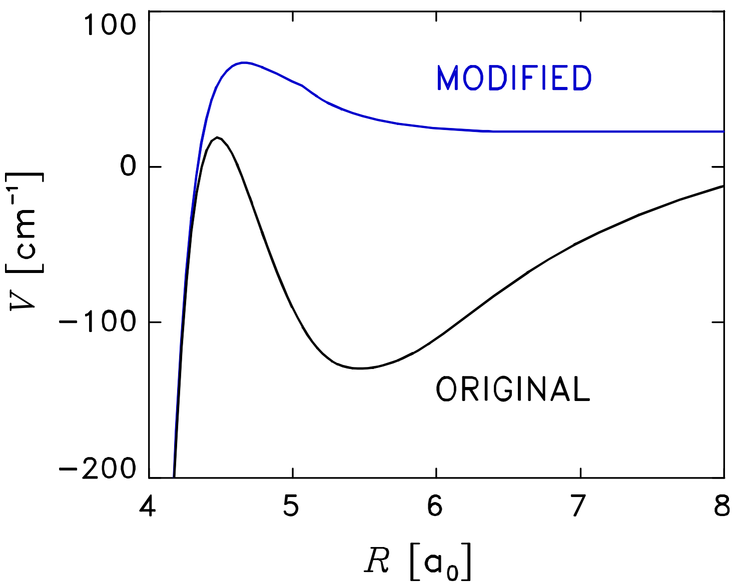
strongly delocalized states

MODEL FOR IsE-1: MINUS vdW…

6 + 86

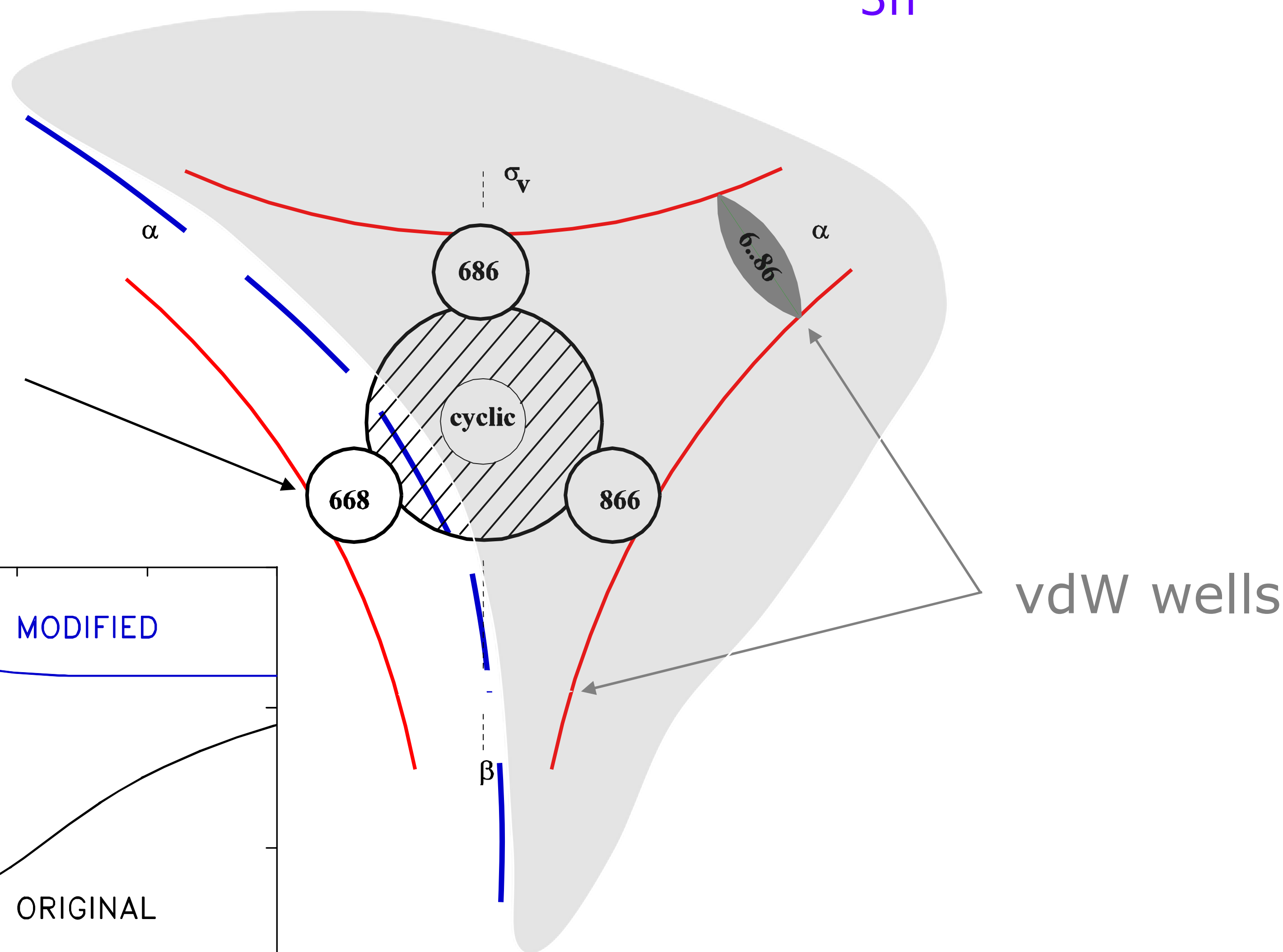


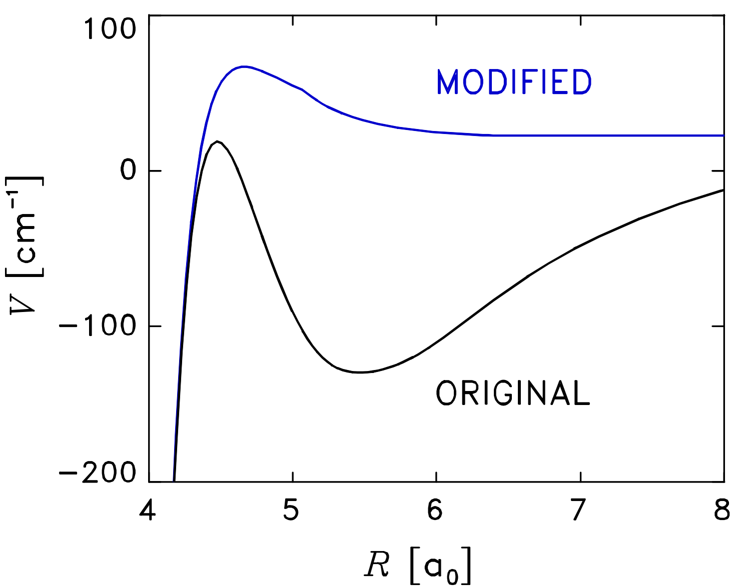
vdW wells



8 + 66

MODEL FOR IsE-1: MINUS vdW & D_{3h} SYMMETRY





CALCULATIONS OF RESONANCE SPECTRUM

Hamiltonian for a rotating molecule + absorbing potential

$$\hat{H}^{DVR} = \hat{H}_J^{DVR} - i\hat{W}^{DVR}$$

(Modified) Chebyshev expansion for the Green's function:

$$G^+(E) = \sum_{n=0}^{N_{ITER}} b_n(E)\, Q_n(\hat{H})$$

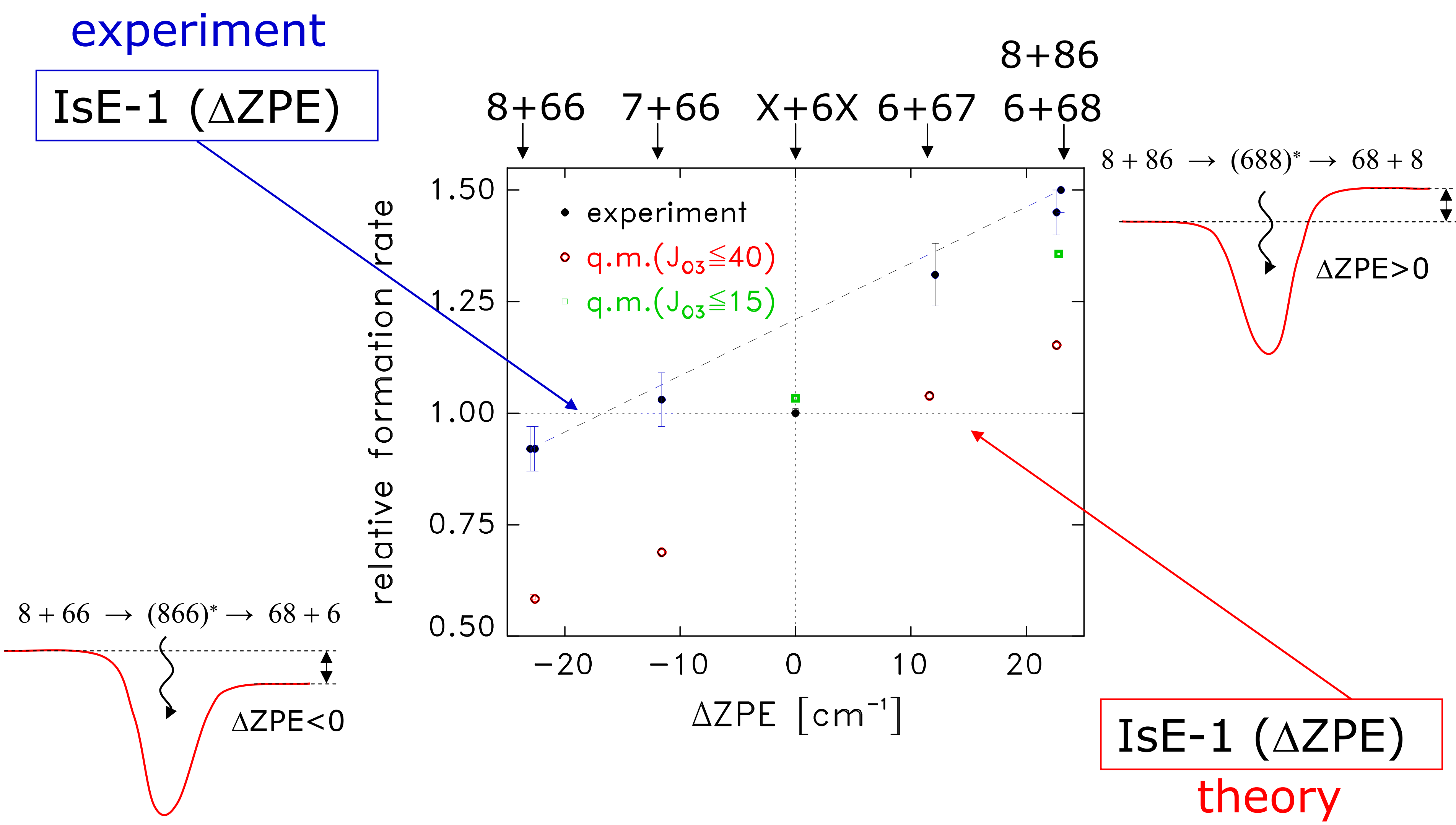
Filter diagonalization: A basis adapted for one energy window

$$\varphi_j \cong \boldsymbol{\delta}(\hat{H} - E_j)\Phi(0) \qquad E_{\min} \le E_j \le E_{\max}$$

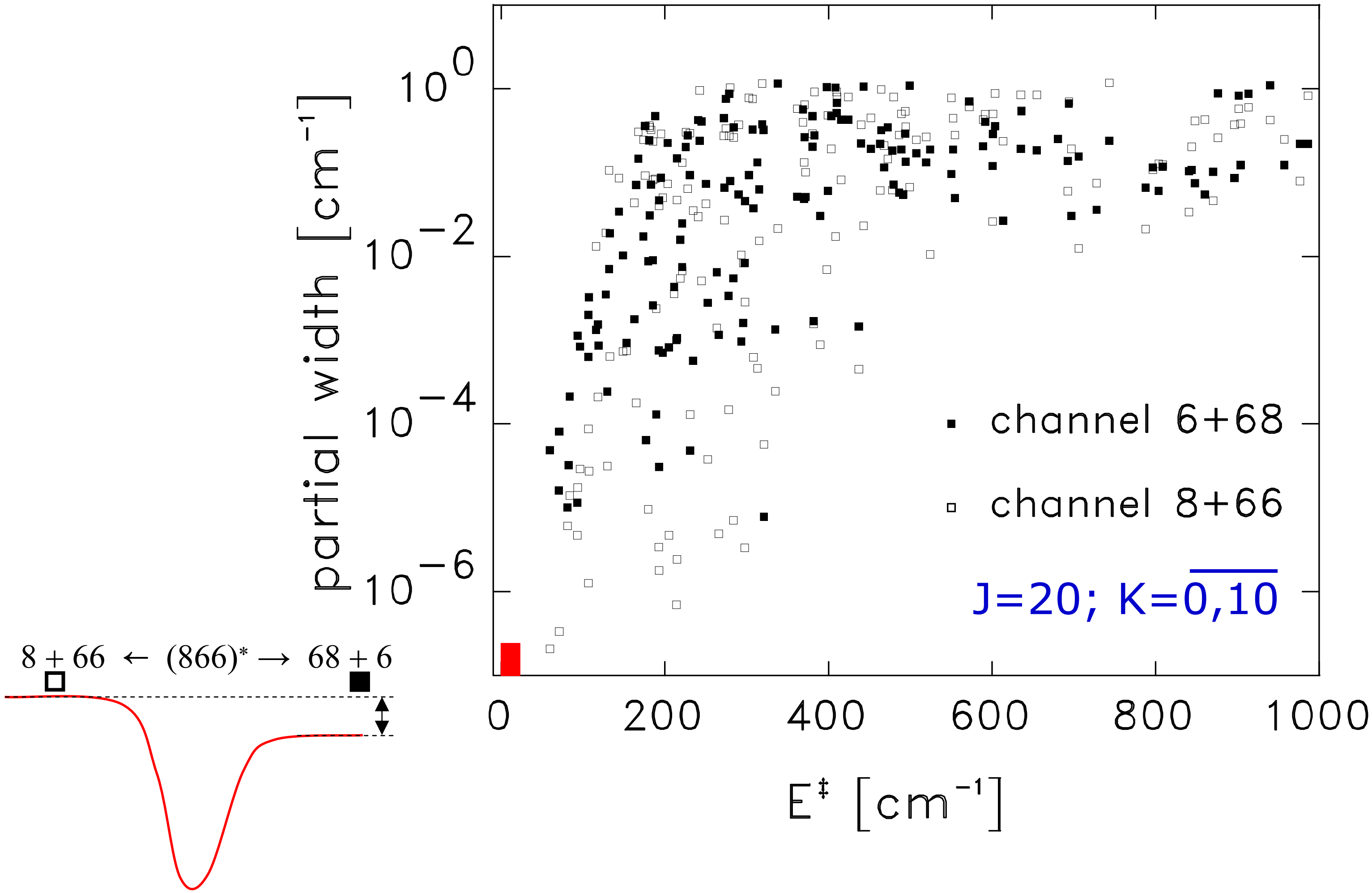
Partial widths $\Gamma(\alpha)$: Perturbation theory in asymptotic channels

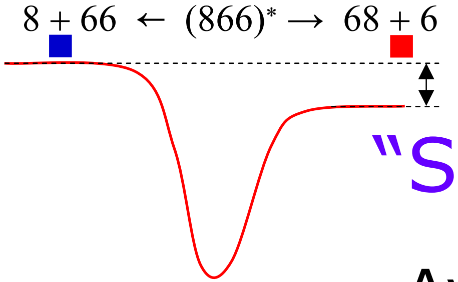
$$\Gamma_n^{\mathrm{J}}(\alpha)/\Gamma_n^{\mathrm{J}}(\beta) \sim \left|\delta^{(\alpha)}E_n^{\mathrm{J}} / \delta^{(\beta)}E_n^{\mathrm{J}}\right|$$

QUANTUM REC.RATES ARE ΔZPE-SENSITIVE!



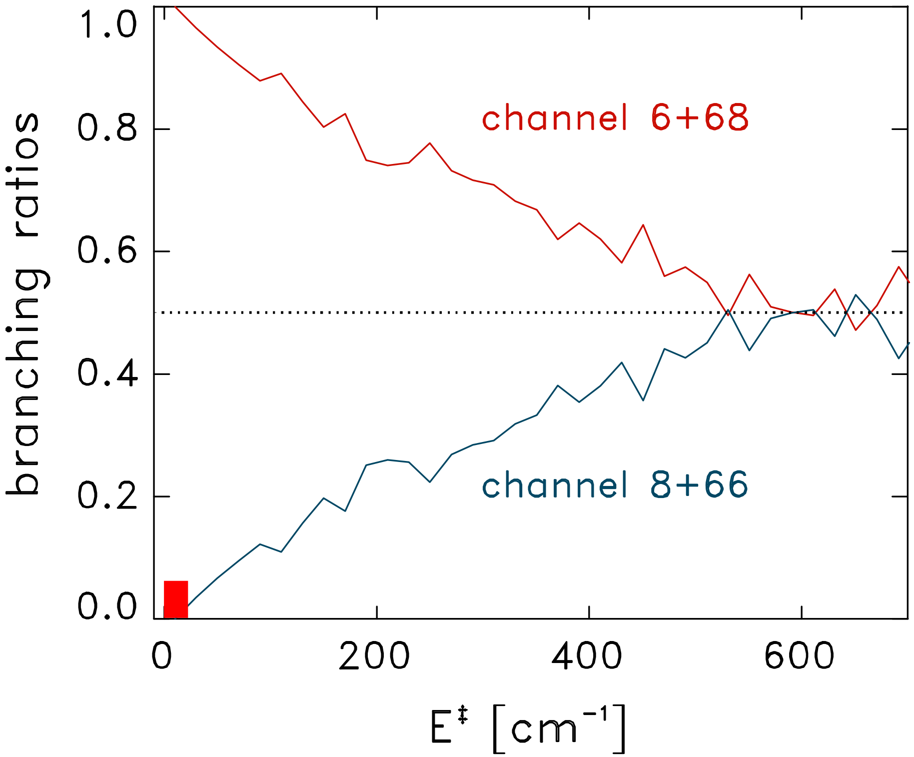
“SPREADING” OF ΔZPE EFFECT

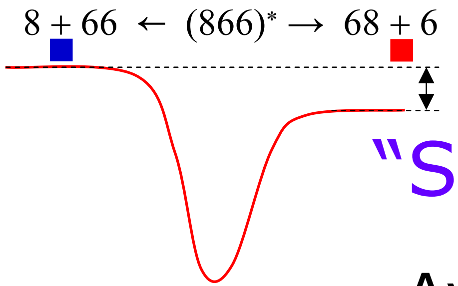




"SPREADING" OF ΔZPE EFFECT

Average branching ratios: $\left\langle \Gamma_n^J(\alpha) / \Gamma_n^J \right\rangle_{n,J}$





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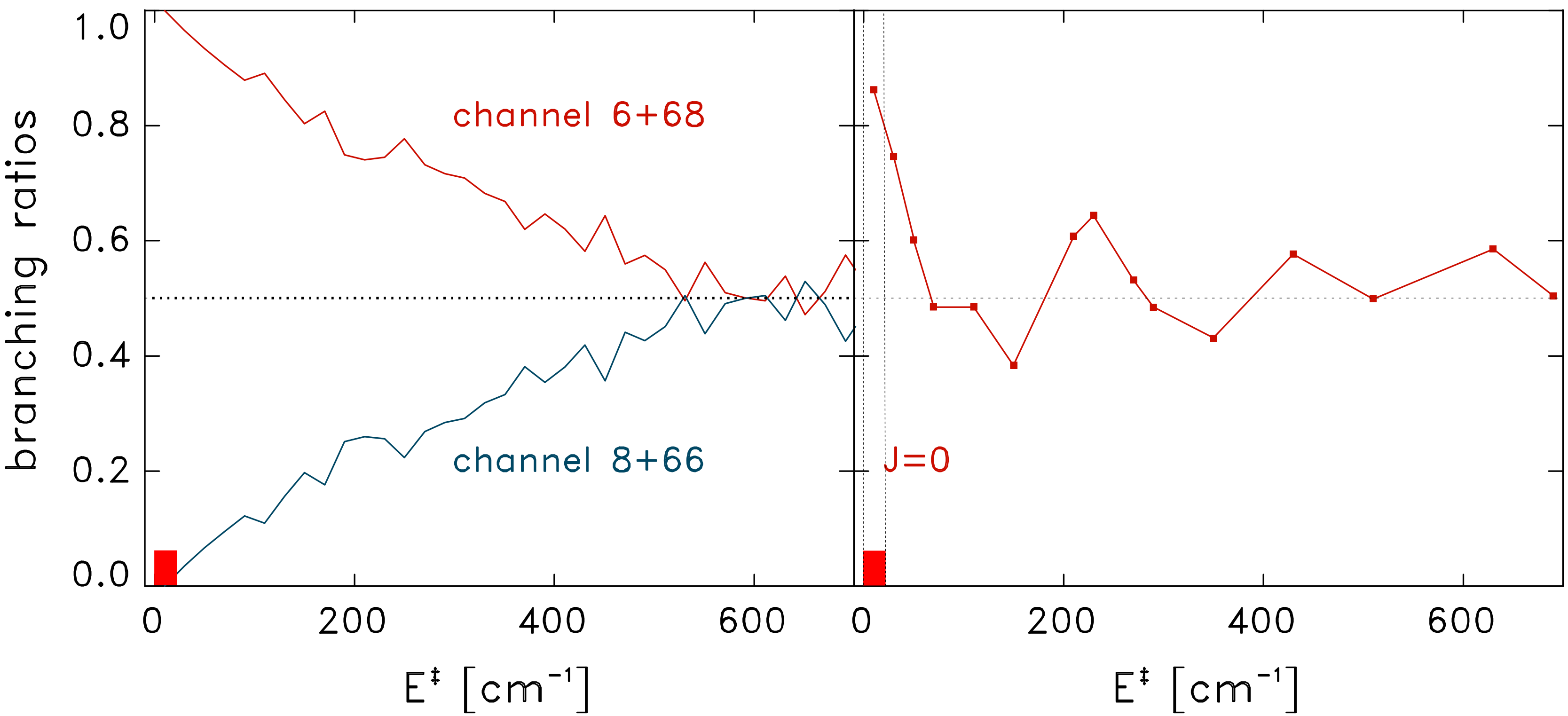
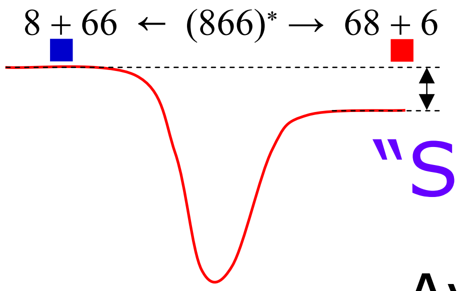


Non-statistical energy distribution



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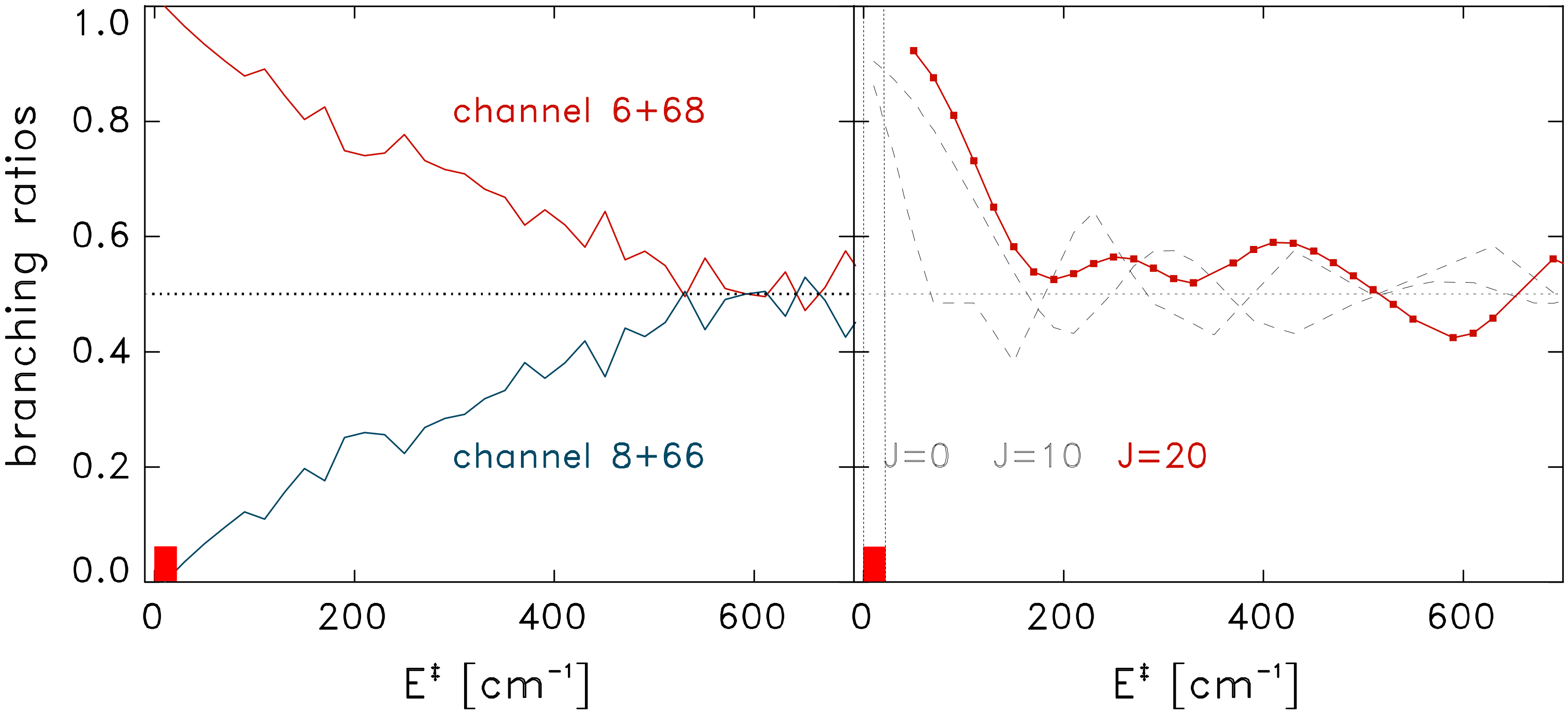
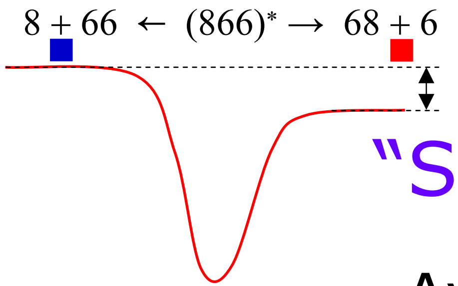


Non-statistical energy distribution

J-contribution



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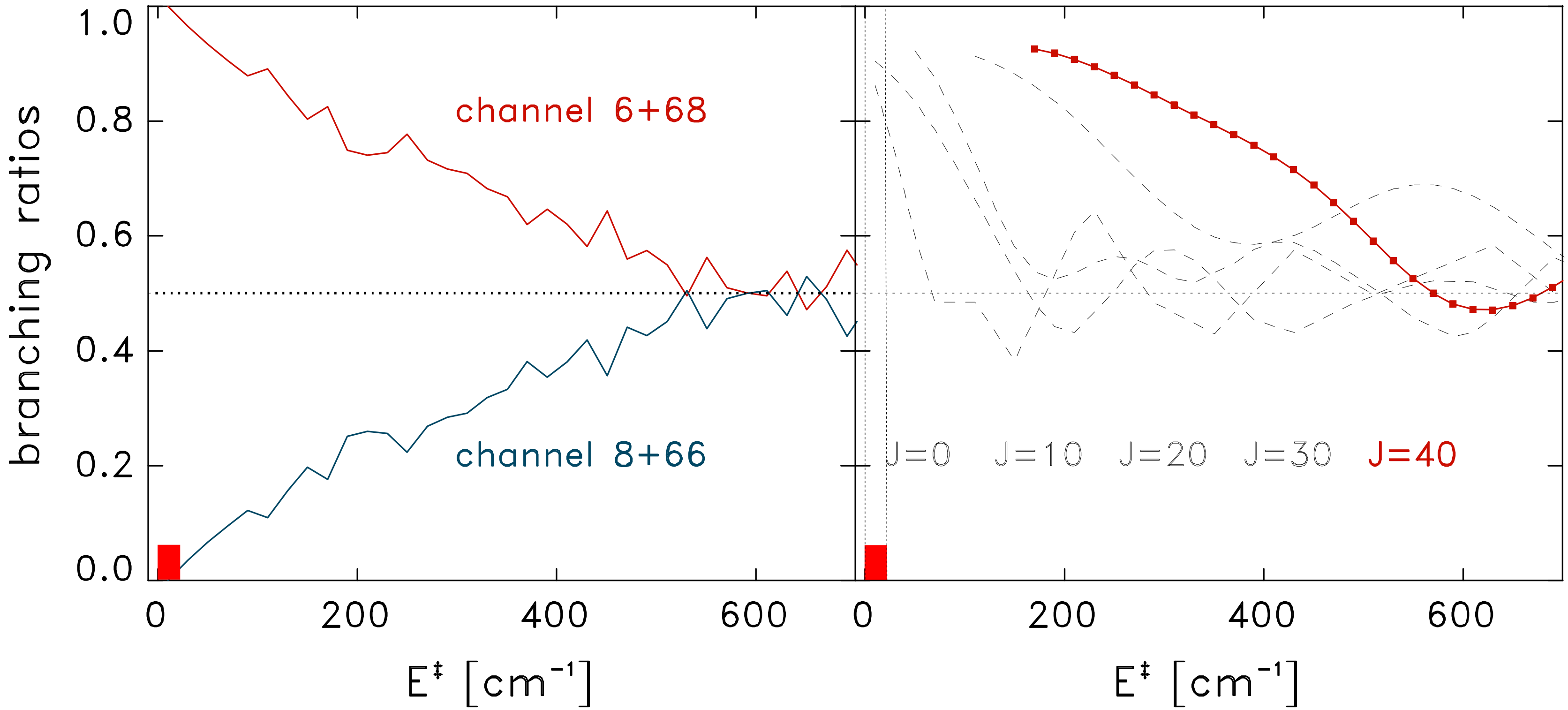

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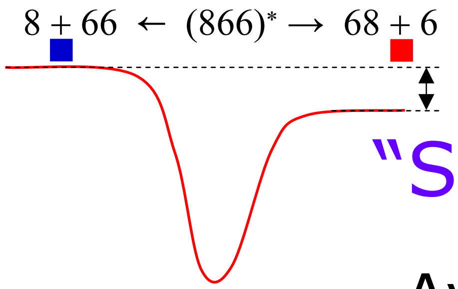

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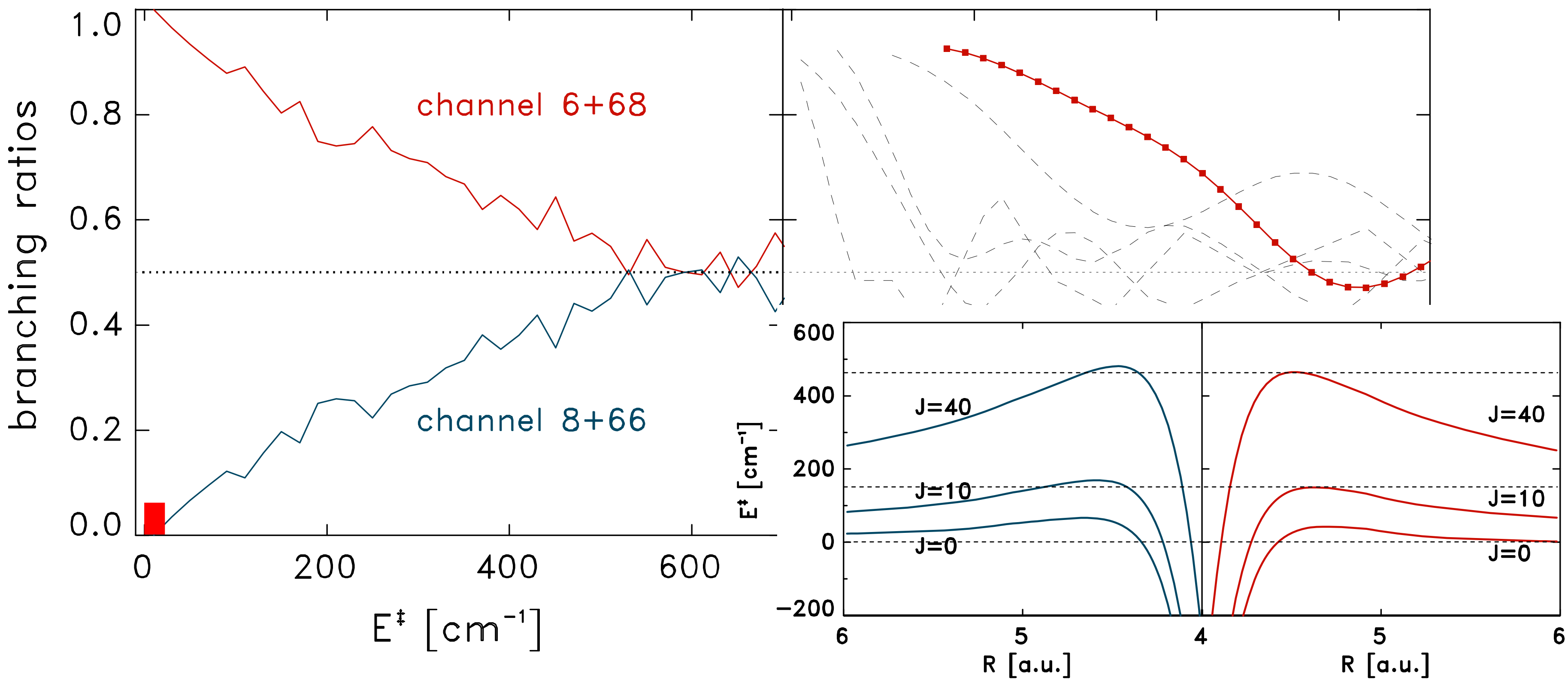
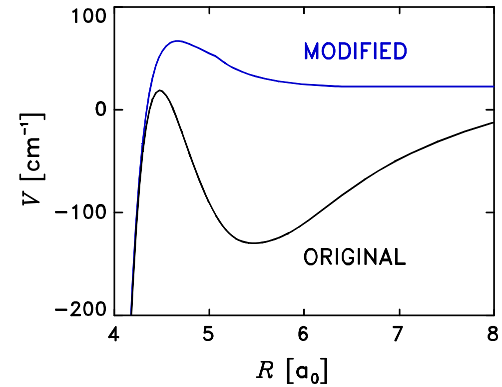


Non-statistical energy distribution

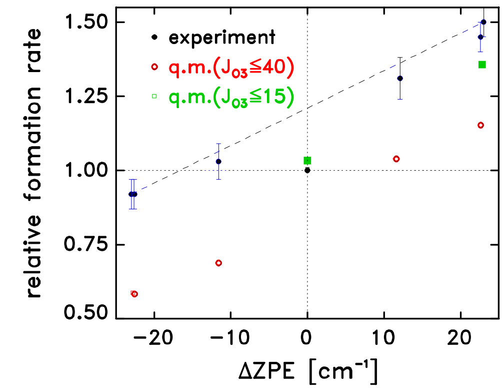
J-contribution: centrifugal barriers shifted by ΔZPE

SUMMARY

- Modified potential + narrow resonances

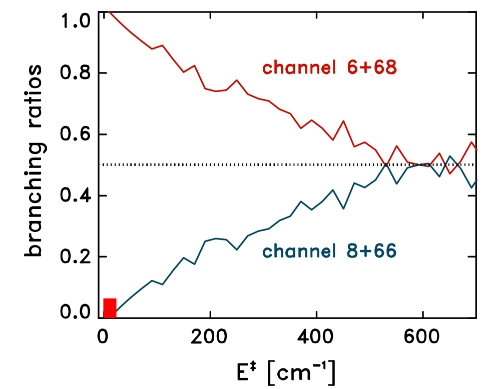


- Experimental pressure dependence OK.



- Relative formation rates:
  depend ~linearly on ΔZPE

- ΔZPE controls partial widths
  over a broad energy range



- The “symmetry”effect IsE-2 (at ΔZPE=0)?

REDUCTION OF THE RECOMBINATION DYNAMICS

Full scattering problem: $$O + O_2 + Ar \rightarrow O_3 + Ar$$

State-specific "Lindemann mechanism":

…Association: $$O + O_2 \rightarrow O_3^*(n)$$

…Stabilization: $$O_3^*(n) + Ar \xrightarrow{P(n,n')} O_3 + Ar$$

Collisional deactivation efficiency for various resonances?

$$k_{\mathrm{rec}}(n) = \boxed{P(n \rightarrow \mathrm{bound})} \frac{\omega \Gamma_n}{\omega + \Gamma_n}$$

COLLISIONAL DEACTIVATION OF RESONANCES

Close coupling scattering calculations for E_{coll} = 200 cm^{-1}.

"Breathing sphere" approximation [angle-averaged V(Ar-O_3)]

All bound and many resonance states of non-rotating O_3

...Stabilization: $O_3^*(n) + \mathrm{Ar} \xrightarrow{P(n,n')} O_3 + \mathrm{Ar}$

Collisional deactivation efficiency for various resonances?

$$k_{\mathrm{rec}}(n) = P(n \rightarrow \mathrm{bound}) \frac{\omega \Gamma_n}{\omega + \Gamma_n}$$

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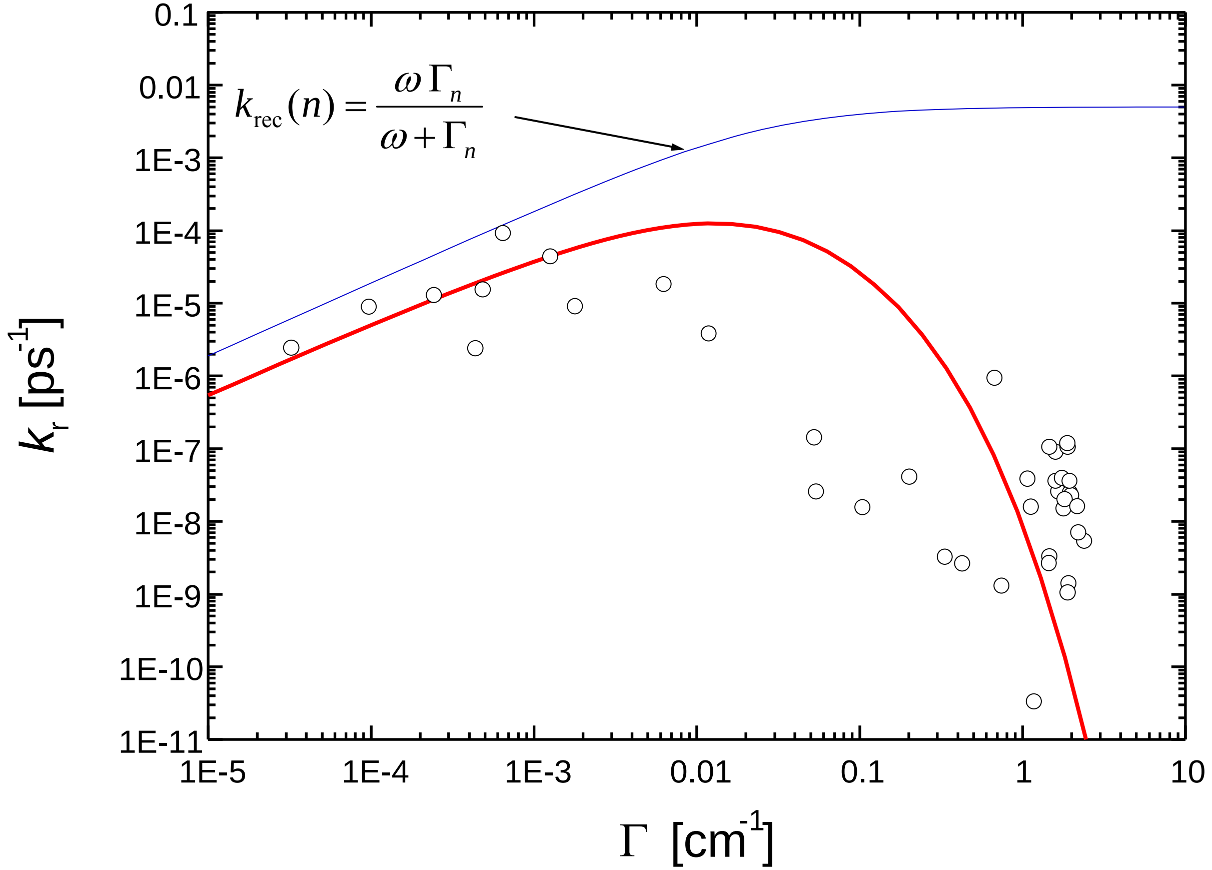

COLLISIONAL DEACTIVATION OF RESONANCES

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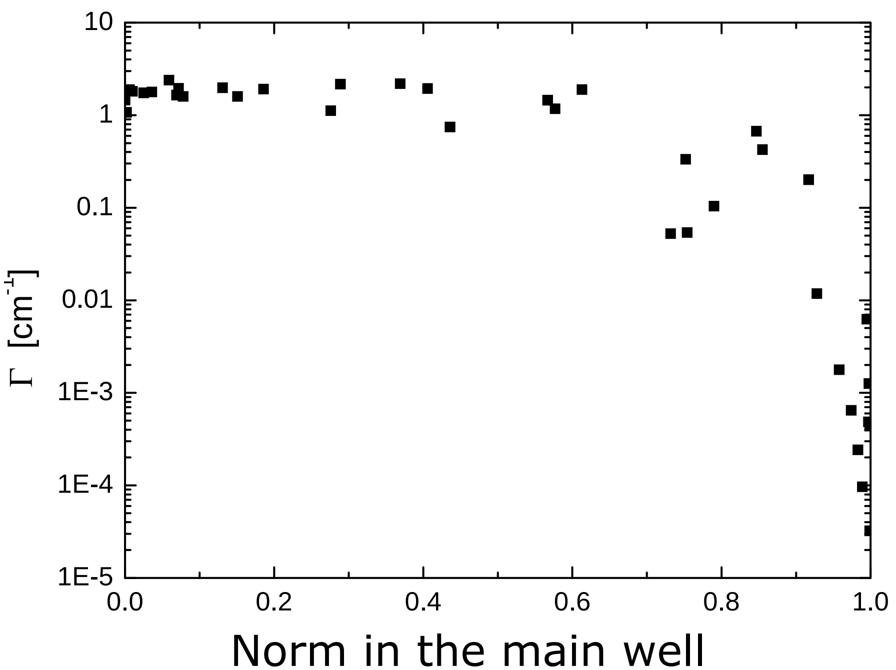
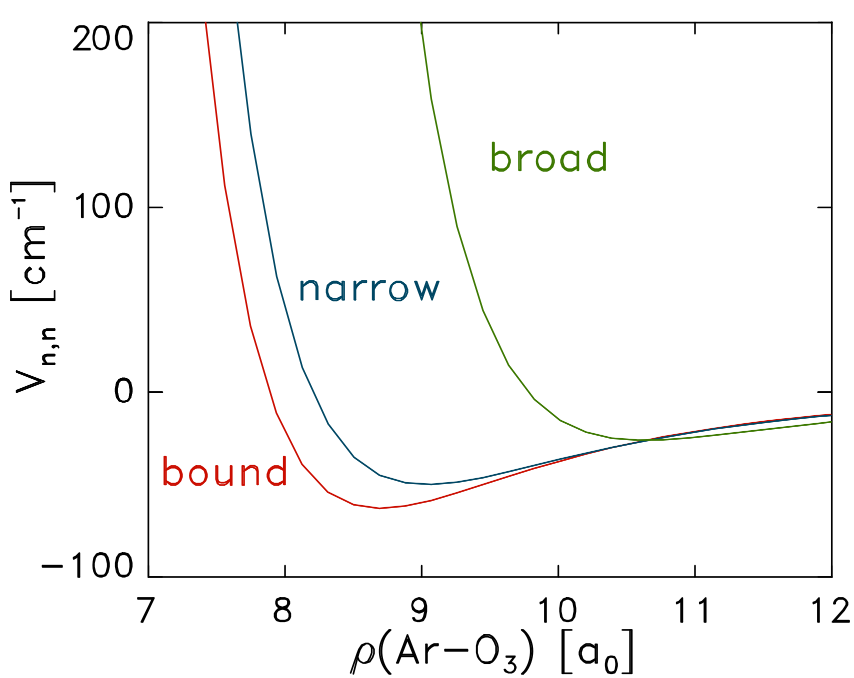
Broad resonances live outside the main well



Bound states for them are effectively screened



MANY THANKS TO:

Reinhard Schinke Mikhail Ivanov

Christof Janssen Konrad Mauersberger

OVERVIEW REFERENCES:

Ozone/Photodissociation: PCCP **9** 2044 (2007).

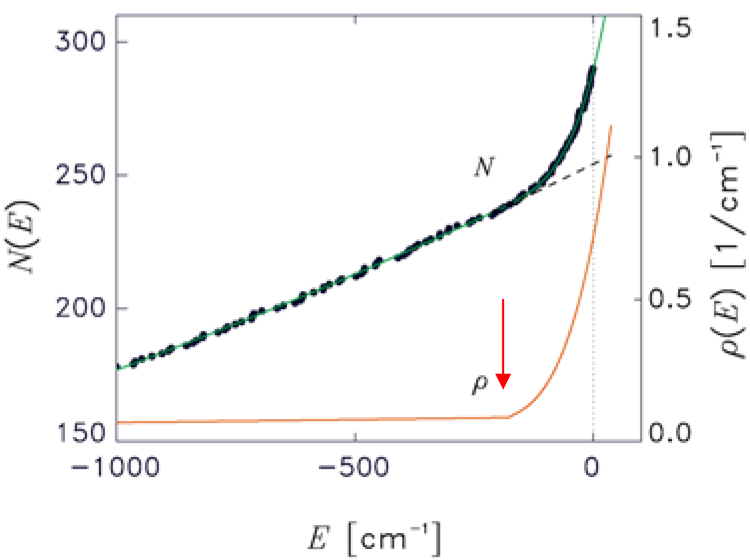
Ozone/Formation-Exchange-Isotope effect:
Ann. Rev. Phys. Chem. **57** 625 (2006)

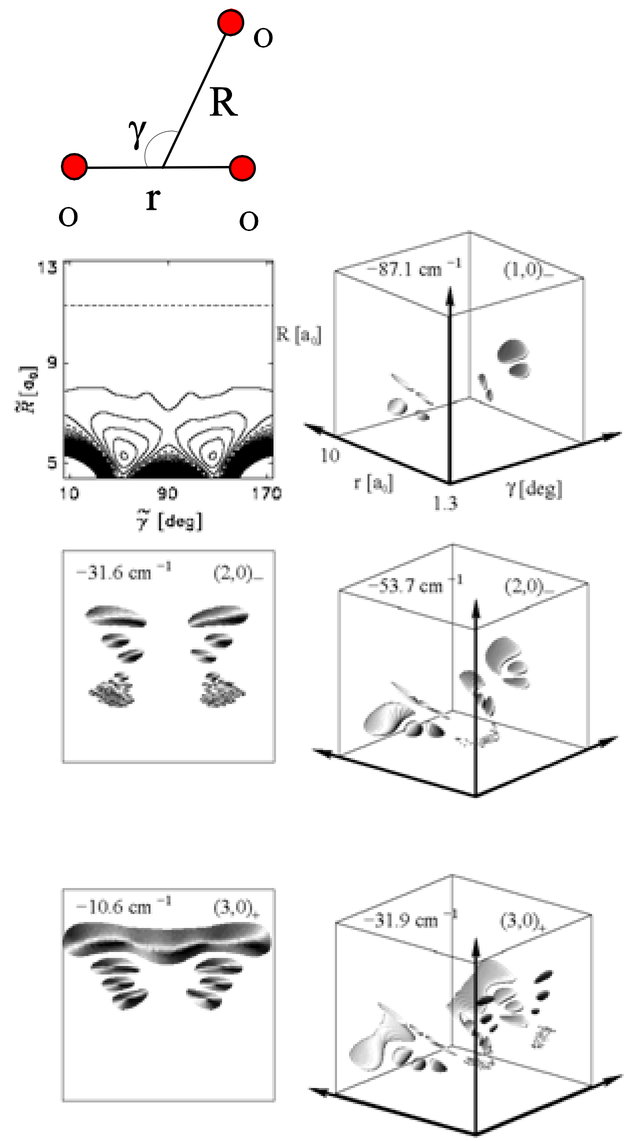
OZONE SPECTRUM AT THRESHOLD: vdW STATES

Each vdW well: a double minimum

Two small vibrational frequencies

High threshold density of states



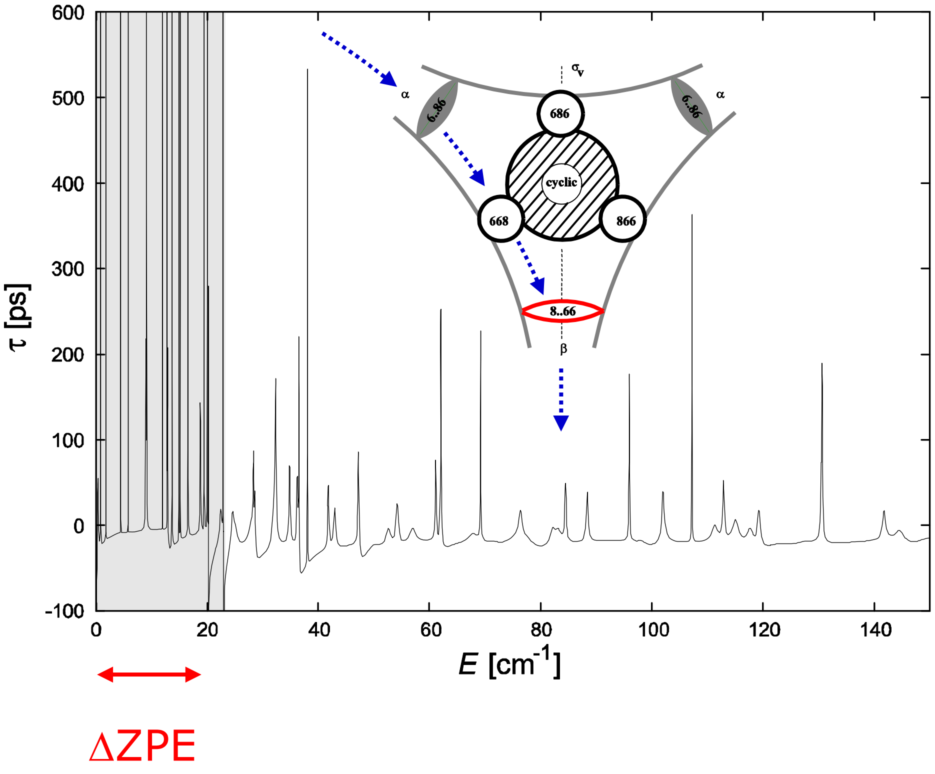


VdW STATES IN ASSOCIATION/STABILIZATION

Contribute?

= early explanation of IsE-1:

Babikov et al. 2003 (6+88)



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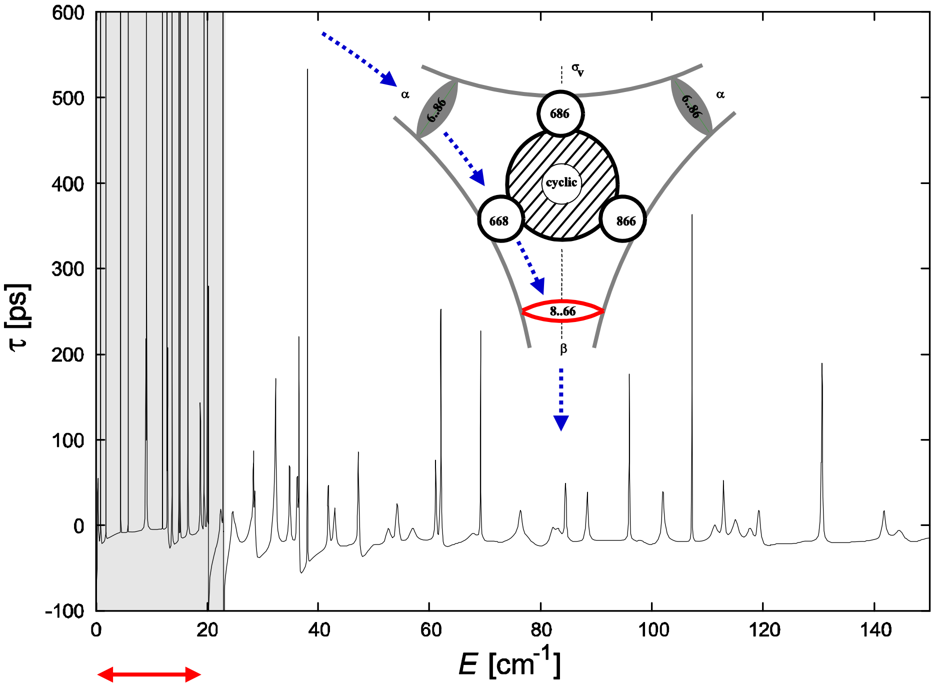


ΔZPE

Do not contribute?

Delocalized threshold states:

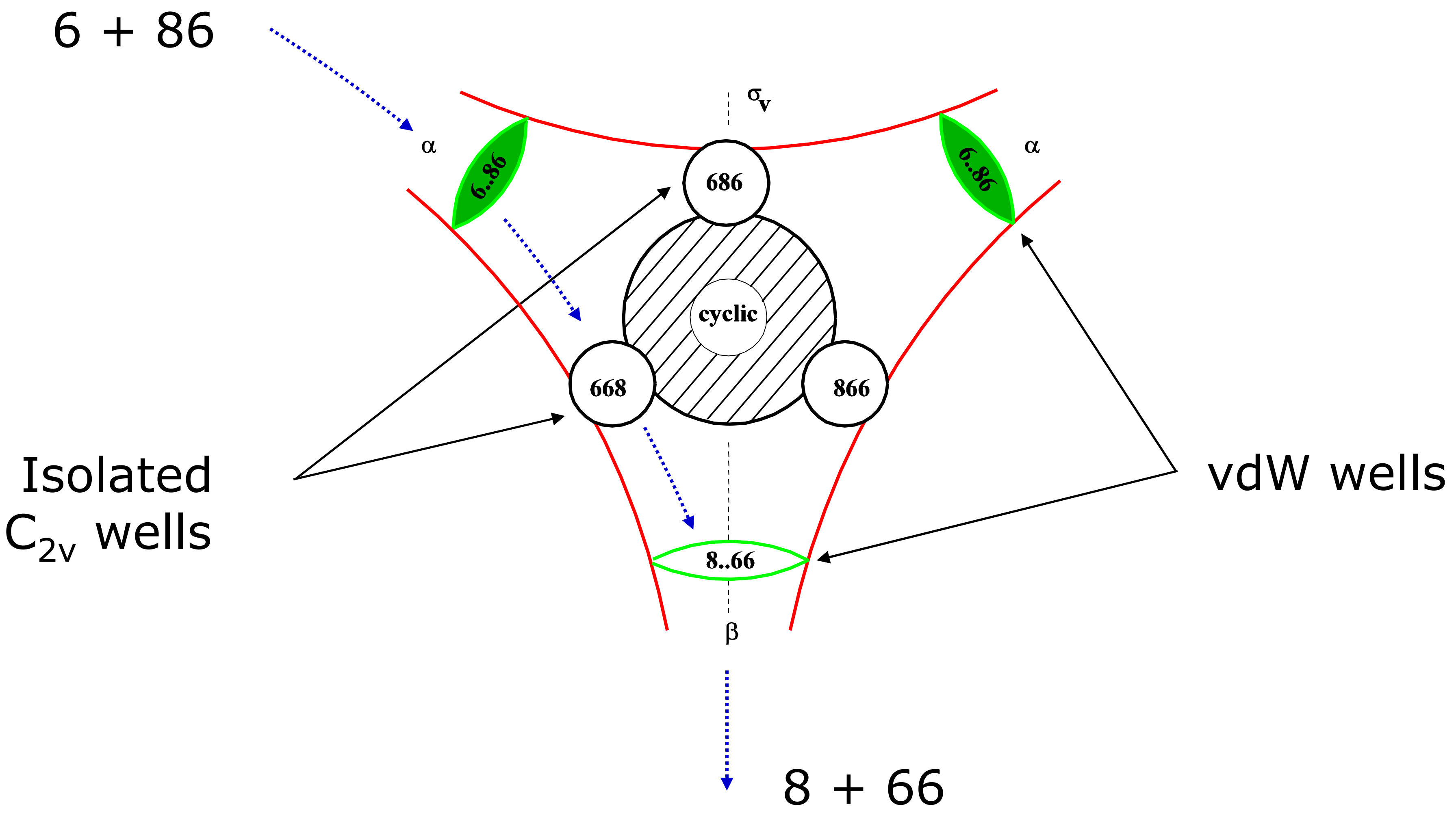
-Low stabilization probability in collisions O_3+(M=Ar)

-Disappear for thermal J>>1

⇕

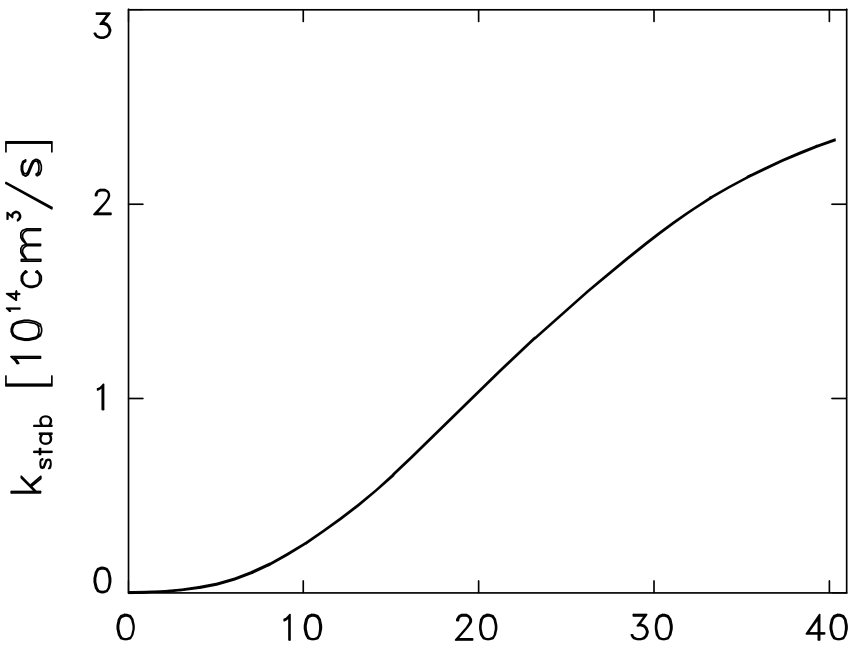
Irrelevant for recombination, but make calculations difficult!

SCHEMATIC REPRESENTATION OF THE PES



Q.M. RECOMBINATION RATE FOR 6-6-6 OZONE

Convergence vs. J_{O3}:



Total angular momentum of ozone

Pressure dependence:

Theory vs. experiment