Low temperature quantum dynamics of oxygen exchange reactions involving ^{17}O

G. Guillon, M. Lepers, P. Honvault

MARS group, Lab ICB, Physics Department,
*CNRS/Univ. de Bourgogne, **Dijon, France***

26e congrès general de la SFP 2023, July 3-7, Paris, France

OUTLINE

- Context: cold oxygen molecules
- PESs and quantum scattering methods
- Isotope exchange reactions: $^{17}O + ^{16}O_2$ & $^{16}O + ^{17}O_2$
- Symmetric reaction: $^{17}O + ^{17}O_2$
- Conclusions

Context & Motivation

- O_2 ($^3\Sigma_g^-$) is a natural candidate for magnetic trapping (simplest paramagnet)
- O_2 is of wide chemical interest

Friedrich *et al.* ***JCSFT*** (1998)

↓

Study of reactions involving O_2 in controlled low temperature environments

↓ ↓

Typical examples: $C + O_2 \rightarrow CO + O$
$O + O_2 \rightarrow O_2 + O$

Helium clusters or magnetic trap:
species not amenable to laser-cooling

- Carbon atoms have been magnetically co-trapped alongside O_2

Karpov *et al.* ***NJP*** (2020)

- $^{17}O_2$ particularly adapted for buffer gas cooling, because of richer rotational structure

Bohn ***PRA*** (2001)

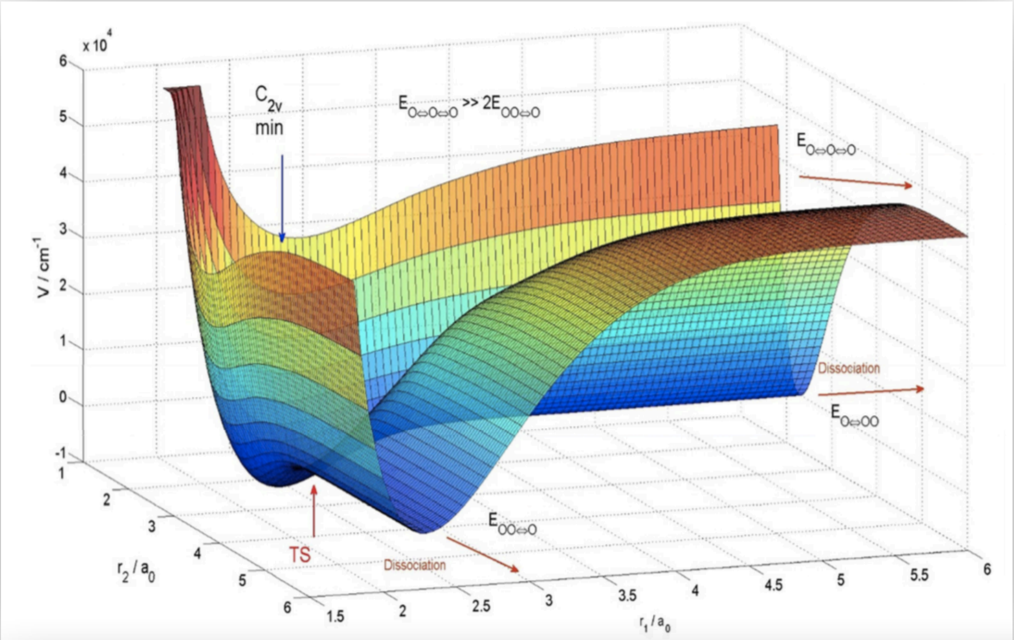
- Ortho- $^{17}O_2$ more amenable to magnetic trapping due to isolated high-field-seeking state with *N=0*: no trap loss due to crossing of magnetic levels (as happens in $^{16}O_2$)

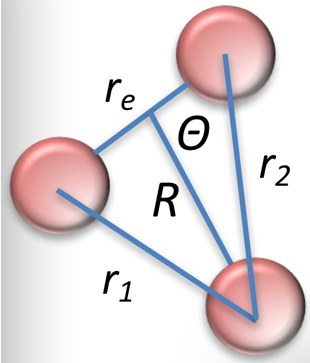
Bohn ***PRA*** (2000)

- $^{17}O_2$ has been shown to give collision rates with He comparable to that for CaH

Potential for O_3 ($^1A'$): TKTHS PES

Tyuterev *et al.* ***PRL*** (2014)

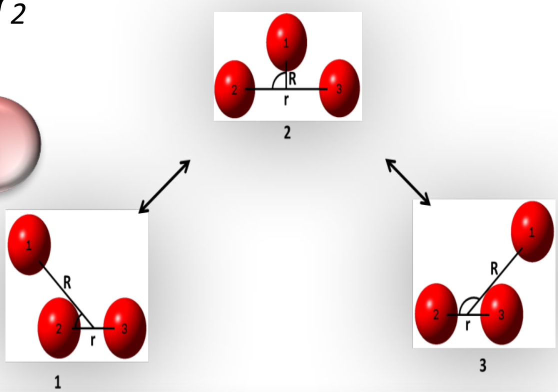


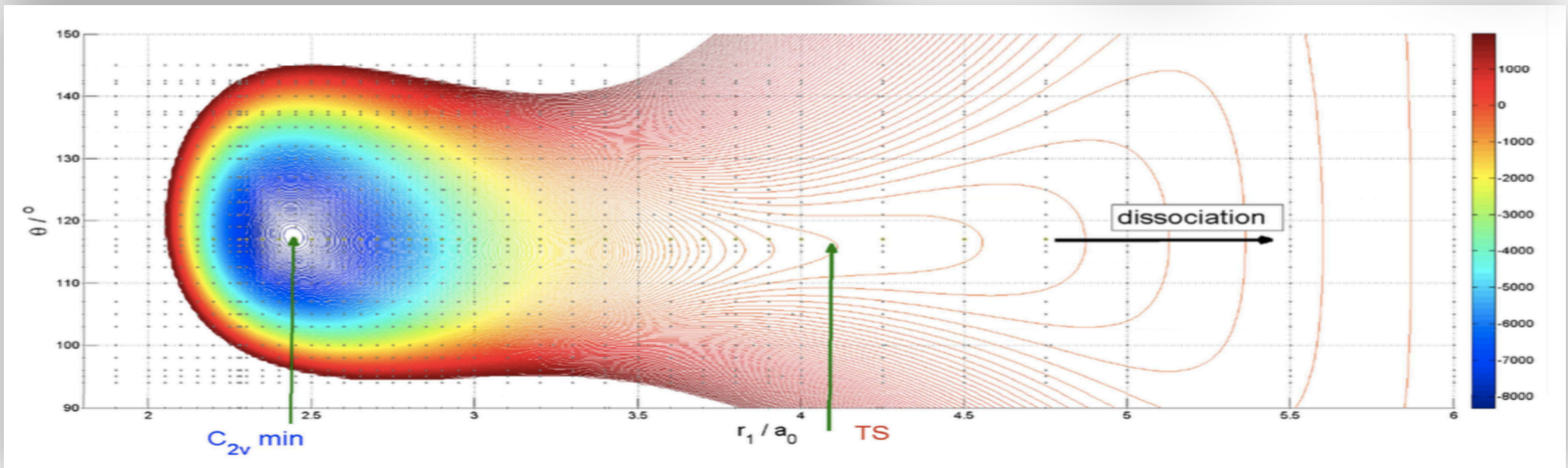


Global Minimum C_{2v} :

$r_e = 2.4\ a_0$

$\Theta_e = 117\ °$





D_e= 9220 cm^{-1}

Quantum reaction dynamics: TIQM formalism

Solution of the **T**ime-**I**ndependent **S**chrodinger **E**quation (**TISE**) $H\psi = E\psi$ for nuclei

Hamiltonian in democratic **hypers-pherical** (DHS) coordinates (1 distance, 5 angles):

$$H = -\frac{1}{2\mu\rho^5}\frac{\partial}{\partial\rho}\rho^5\frac{\partial}{\partial\rho} + \frac{\mathbf{\Lambda}^2}{2\mu\rho^2} + V(\rho,\theta,\phi)$$

hyper-radius ρ

angular momentum ***J*** projection on ppal axis: helicity Ω

$$\mathbf{\Lambda}^2 = \mathbf{\Lambda}_0^2 + \frac{4J_z^2}{\sin^2\theta} + \mathcal{R}$$

$$\mathbf{\Lambda}_0^2 = -\frac{4}{\sin 2\theta}\frac{\partial}{\partial\theta}\sin 2\theta\frac{\partial}{\partial\theta} - \frac{1}{\cos^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$\mathcal{R} = \frac{J_x^2 - J_z^2}{\cos^2\theta/2} + \frac{J_y^2}{\cos^2\theta} - \frac{2i\sin\theta J_y}{\cos^2\theta}\frac{\partial}{\partial\phi}$$

Coriolis coupling term

Define ρ-dependent basis functions (**surface-states**)

$$\Phi_{k\Omega}^{JM\epsilon_I\sigma}(\rho;\theta,\phi,\alpha,\beta,\gamma) = \varphi_k^{\epsilon_I\sigma\Omega}(\rho;\theta,\phi)N_\Omega^{JM\epsilon_I}(\alpha,\beta,\gamma)$$

global orientational function

Solution of **TISE** expanded in all angular d.o.f. but the hyper-radius ρ:

$$\Psi^{JM\epsilon_I\sigma}(\rho,\theta,\phi,\alpha,\beta,\gamma) = \frac{1}{\rho^{5/2}}\sum_{k\Omega}\Phi_{k\Omega}^{JM\epsilon_I\sigma}(\rho_m;\theta,\phi,\alpha,\beta,\gamma)f_{k\Omega}^{J\epsilon_I\sigma}(\rho_m;\rho)$$

Using this expansion in the **TISE** we are led to a set of **2nd order coupled equations** for $f_{k\Omega}^{J\epsilon_I\sigma}$

Quantum reaction dynamics: method

Computations within the time-independent formalism

- Calculations done with in-house **HYP3D** code: Launay *et al.* ***CPL*** (1990)

- Body-fixed formalism
- Symmetry-adapted hyper-spherical harmonics
- Matching at large ρ to optimize overlap between internal DHS and external Jacobi
- Computation of surface-states basis at ρ_m-values (sectors) for all Ω
- For each ***J***, total ψ expanded in this basis
- Resultant coupled equations solved using « log-derivative » propagator
- Numerically propagated ψ matched to asymptotic form to obtain **T-matrix**
- Computations at numerous energies E_c

- **Cross sections:**

$$\sigma_{vj}^{v'j'}(E_c) = \frac{\pi}{(2j+1)\kappa_{vj}^2} \sum_{J\Omega\Omega'} (2J+1) \mid T^J_{v'j'\Omega' vj\Omega} \mid^2,$$

- **Rate constants:**

$$k_{vj}(T) \;=\; \sqrt{\frac{8k_BT}{\pi\mu_R}} \frac{1}{(k_BT)^2} \int_0^\infty E_c \sigma_{vj}(E_c) e^{-E_c/k_BT} dE_c$$

Identical nuclei: the permutation symmetry problem

Basic assumption: **no spin-dependent term in Hamiltonian**

Write the total wave function as a simple **tensor product**

$$\Psi = \psi_{\mathrm{el}}\,\psi_{\mathrm{nuc.space}}\,\psi_{\mathrm{nuc.spin}}$$

Total:
vs binary exchange:
- symmetric for bosons
- antisymmetric for fermions

Describes e-state (only one here)

Describes nuclear motion

Nuclear spin function

The **spin symmetry** restricts the **space symmetry** → Influence on observables (cross sections)

Two identical nuclei: $A + X_2$ type systems

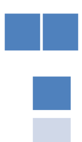
$A + X_2 \rightarrow$
- $A + X_2$ **(α: elastic/inelastic)**
- $AX + X$ **(β: reactive)**

2 final arrangements

2 **X** nuclei with spin *s* (Nucleus **A** not affected by permutation symmetry)

Total number of spin states: $(2s+1)^2$ Permutation group of 2 particles: $\boldsymbol{P_2}$

shape (or Young diagram)



$C_s \cong$	P_2	e	(12)
A’	[2]	1	1
A’’	[1²]	1	-1

Action of transposition (12) on nuclear spin function :

$$(12)\psi_{s_A m_A}\psi_{SM} = (-)^{2s+S}\psi_{s_A m_A}\psi_{SM}$$

$^{16}O^{16}O$ (66) and $^{17}O^{17}O$ (77) diatomics

$^{16}O^{16}O$ or $^{18}O^{18}O$ →

$$\psi_{^{16}O_2} = \psi_{el}\,\psi_{nuc.space}\,\psi_{nuc.spin}$$

$^{16}O/^{18}O$ (s = 0)

S = 0

(A') (bosons)

($\Lambda_{el} = {}^3\Sigma_g^-$)

$(-)^S$ **S even**

odd (ortho) *j* rot. levels

[(12)Ψ = -(-)^j ψ = ψ]

$^{17}O^{17}O$ →

$$\psi_{^{17}O_2} = \psi_{el}\,\psi_{nuc.space}\,\psi_{nuc.spin}$$

^{17}O (s = 5/2)

S = 5, 4 … 0

(A'') (fermions)

S even

$-(-)^S$

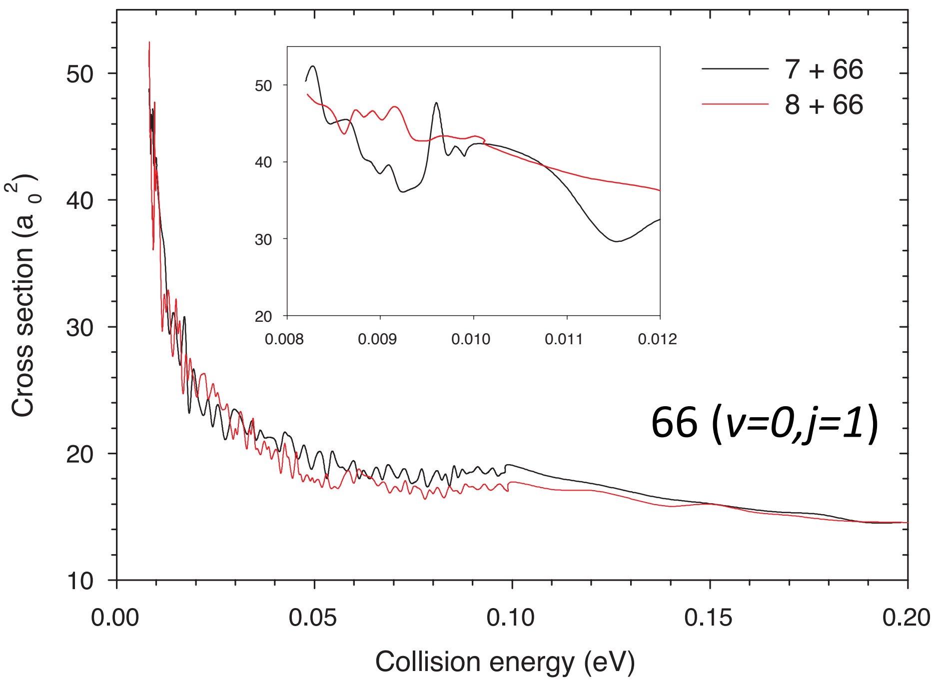
S odd

even (ortho) & odd (para) *j* rot. levels

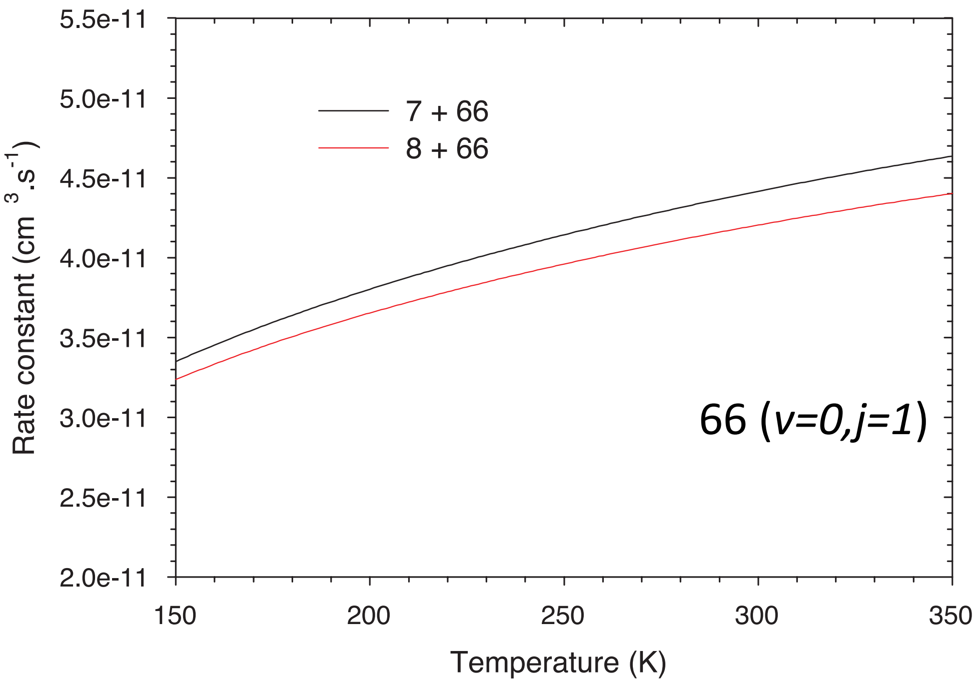
[(12)Ψ = (-)^j(-)^{S}ψ = -ψ]

The $^{17}O + ^{16}O^{16}O$ reaction

Cross sections



Rate constants



- ✓ 8 + 66 reaction is slightly more exothermic than 7 + 66
- ✓ 7 + 66 reaction is slightly faster

Collisions with $^{17}O^{17}O$ (77)

s=5/2 **fermions** ⇒ *(12)Ψ = (-)^j(-)^{S}ψ = -ψ*

⇓

6×6=36 spin states

Total nuclear spin **S**:

S	5	4	3	2	1	0
2S+1	11	9	7	5	3	1

S even: 15 spin states

para-$^{17}O_2$ or p77 j=1,3,5…

S odd: 21 spin states

ortho-$^{17}O_2$ or o77 j=0,2,4…

Cross sections for 6 + 77:

inelastic

$$\sigma_{\alpha\, v\, j \to \alpha\, v'\, j'} = \begin{cases} \frac{7}{12}\sigma^{\square\square}_{\alpha\, v\, j \to \alpha\, v'\, j'} & \text{6 + o77: } j \,\&\, j' \text{ even} \\ 0 & j + j' \text{ odd} \\ \frac{5}{12}\sigma^{\begin{smallmatrix}\square\\ \square\end{smallmatrix}}_{\alpha\, v\, j \to \alpha\, v'\, j'} & \text{6 + p77: } j \,\&\, j' \text{ odd} \end{cases}$$

α = 6 +77

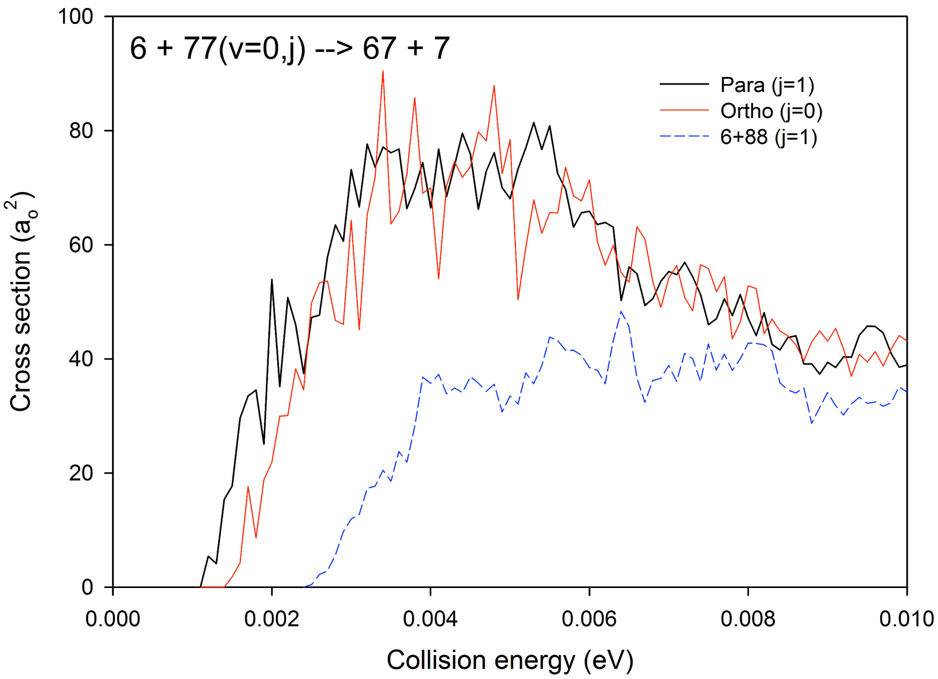
$$\sigma_{\alpha\, v\, j \to \beta\, v'\, j'} = \begin{cases} \frac{7}{12}\sigma^{\square\square}_{\alpha\, v\, j \to \beta\, v'\, j'} & j \text{ even} \\ \frac{5}{12}\sigma^{\begin{smallmatrix}\square\\ \square\end{smallmatrix}}_{\alpha\, v\, j \to \beta\, v'\, j'} & j \text{ odd} \end{cases}$$

reactive

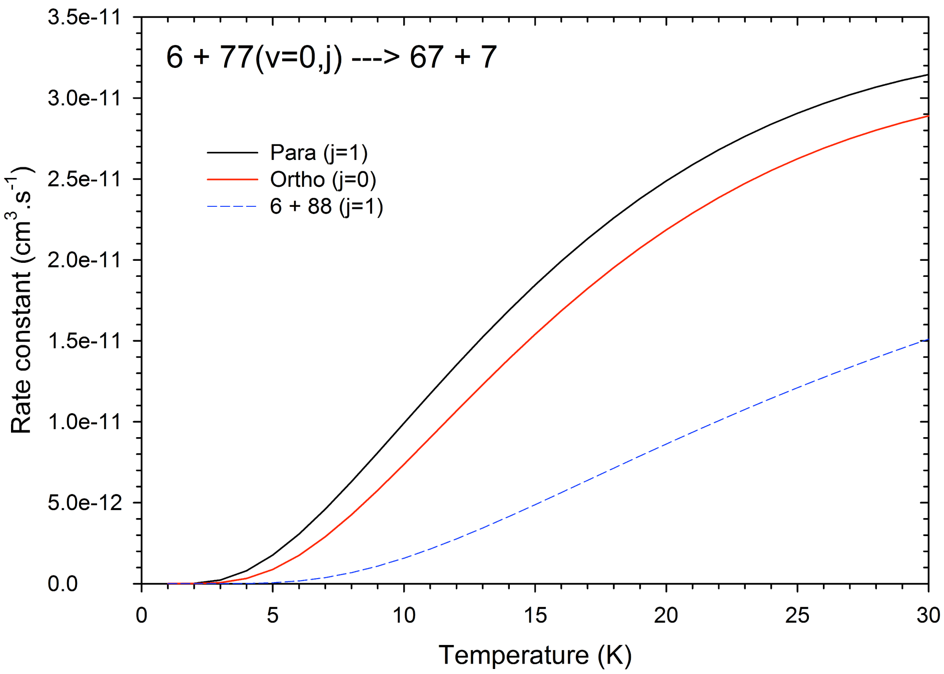
β = 6 +67

The ^{16}O + o/p-$^{17}O^{17}O$ reaction

Cross sections



Rate constants



- ✓ 6 + 88 reaction is slightly more endothermic than 6 + 77
- ✓ 6 + 77 reaction is much faster

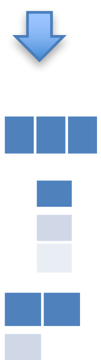
Three identical nuclei: $X + X_2$ type systems

$X + X_2$ ➔ $X + X_2$ Only one final arrangement (if E_c not too high)

3 **X** nuclei with spin *s* Total number of spin states: $(2s+1)^3$

Permutation group of 3 particles: $\boldsymbol{S_3}$

shape (or Young diagram)



$S_3 \simeq C_{3v}$	$(\bullet)(\bullet)(\bullet) \simeq e$	$3(\bullet)(\bullet\bullet) \simeq 3\sigma_v$	$2(\bullet\bullet\bullet) \simeq 2C_3$
$[3] \simeq A_1$	1	1	1
$[1^3] \simeq A_2$	1	-1	1
$[2, 1] \simeq E$	2	0	-1

This last 2-dimensional irrep. (Specht module) generated by
2 std polytabloids built on the std tableaux 1 2 / 3 and 1 3 / 2

Important for ortho-para conversions

Due to indistinguishibility of nuclei, we can have:

- **ELASTIC process**

$O + O_2(v=0, j) \longrightarrow O + O_2(v=0, j)$ (« pure » elastic)

$\longrightarrow O_2(v=0, j) + O$ (« rearranging »)

} Indistinguihable alternatives in QM

- **NONELASTIC process**

$O + O_2(v=0, j) \longrightarrow O + O_2(v'=0, j')$ (inelastic)

$\longrightarrow O_2(v'=0, j') + O$ (rearranging)

} Ibid. with $j' \neq j$

Computation of spin weights (uncoupled representation)

Simply count the **spin** states:

$$T^3(V) = V \otimes V \otimes V$$

d–dimensional space for one nuclei

$$d = \dim V = 2s + 1$$
$$d = 6 \text{ for } s = 5/2$$

$$d^3 = (2s+1)^3 = 6^3 = 216$$

decomposes as:

$$T^3(V) = P^3(V) \oplus \Lambda^3(V) \oplus M^3(V) \oplus \widetilde{M}^3(V)$$

three-nuclei tensor space

totally symmetric tensor space

totally antisymmetric tensor space

mixed symmetries modules

components:

$$n_{A_1} = \tau(d,3) = \binom{d+3-1}{d-1} = \frac{(d+2)!}{(d-1)!3!}$$

components:

$$n_{A_2} = \binom{d}{3} = \frac{d!}{(d-3)!3!}$$

components obtained from:

$$2n_E = d^3 - n_{A_1} - n_{A_2}$$

$$n_{A_1} = \frac{(d)(d+1)(d+2)}{6} = \frac{(2s+1)(2s+2)(2s+3)}{6} = 56,$$

$$n_{A_2} = \frac{(d-2)(d-1)(d)}{6} = \frac{(2s-1)(2s)(2s+1)}{6} = 20,$$

$$n_E = \frac{(d-1)(d)(d+1)}{3} = \frac{(2s)(2s+1)(2s+2)}{3} = 70,$$

Weight for cross Sections:

$$w_{A_1} = \frac{n_{A_1}}{n_{A_1} + n_E}$$

$$w_E = \frac{n_E}{n_{A_1} + n_E}$$

Example: $^{17}O + {}^{17}O^{17}O$, all nuclei are fermions, s=5/2

In general, decomposition of nuclear motion upon S_3 irreps:

$$\psi_{\text{nuc.space}} \equiv \psi = c_{A_1}\psi^{A_1} + c_{A_2}\psi^{A_2} + c_E\psi^E$$

We distinguish two processes:

$$7 + \text{o}77 \longrightarrow \begin{cases} 7 + \text{o}77 & (\alpha) \\ \text{p}77 + 7 & (\beta) \end{cases}$$

A_2 forbidden asymptotically

$$\psi_{\text{nuc.space}} \equiv \psi_{\text{o}} = c_{A_1}\psi^{A_1} + c_E\psi^E$$

$$7 + \text{p}77 \longrightarrow \begin{cases} 7 + \text{p}77 & (\alpha) \\ \text{o}77 + 7 & (\beta) \end{cases}$$

A_1 forbidden asymptotically

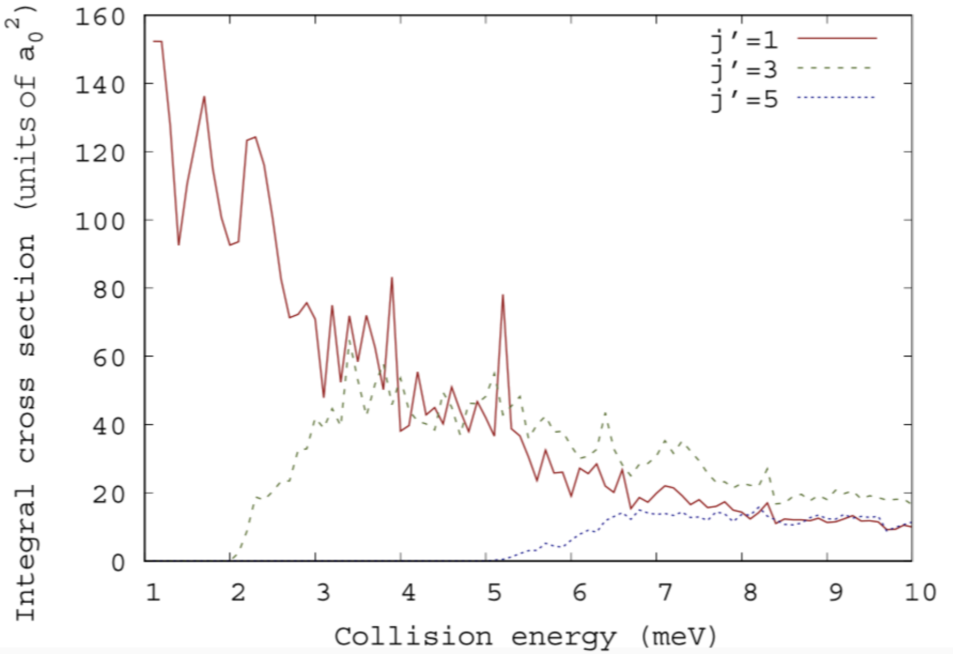
$$\psi_{\text{nuc.space}} \equiv \psi_{\text{p}} = c_{A_2}\psi^{A_2} + c_E\psi^E$$

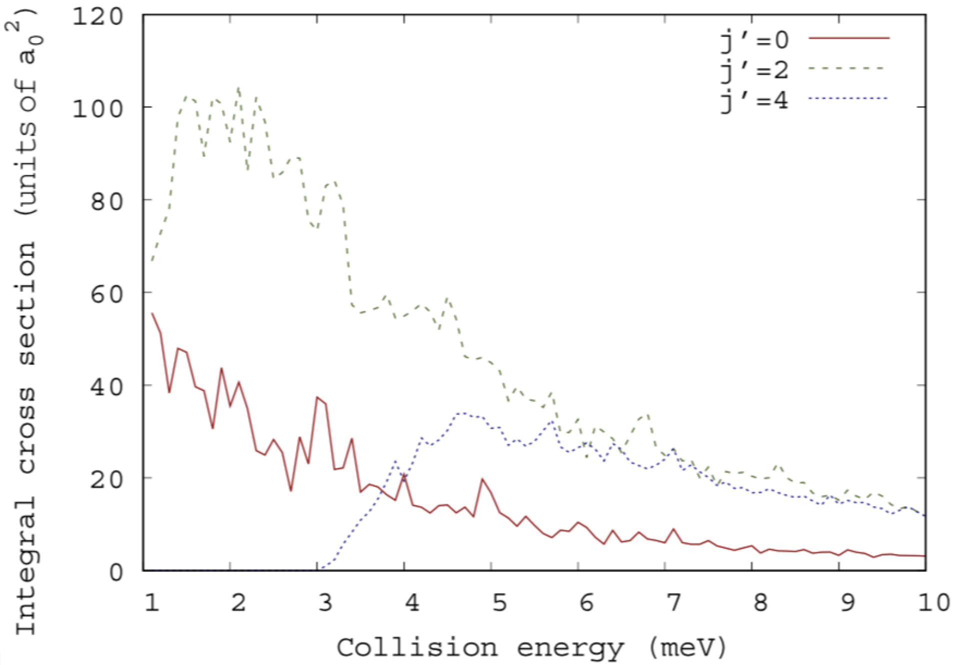
Due to nonzero spin, possibility of **ortho-para transitions**

Spin-weighted cross sections:

$$\sigma_{\alpha\ v\ j\to\alpha\ v'\ j'} \begin{cases} \frac{4}{9}\sigma^{A_1}_{\alpha\ v\ j\to\alpha\ v'\ j'} + \frac{5}{9}\sigma^{E}_{\alpha\ v\ j\to\alpha\ v'\ j'} & [j,\ j'\ \text{even}] \\ \frac{2}{9}\sigma^{A_2}_{\alpha\ v\ j\to\beta\ v'\ j'} + \frac{7}{9}\sigma^{E}_{\alpha\ v\ j\to\alpha\ v'\ j'} & [j,\ j'\ \text{odd}] \\ \frac{5}{9}\sigma^{E}_{\alpha\ v\ j\,\text{even}\to\alpha\ v'\ j'\text{odd}} \\ \frac{7}{9}\sigma^{E}_{\alpha\ v\ j\,\text{odd}\to\alpha\ v'\ j'\text{even}}. \end{cases}$$

Results: ^{17}O + o/p$^{17}O^{17}O$: pure state-to-state ICSs





Ortho-para conversion

7 + o77(*j=0*) → 7 + p77(*j'* odd)

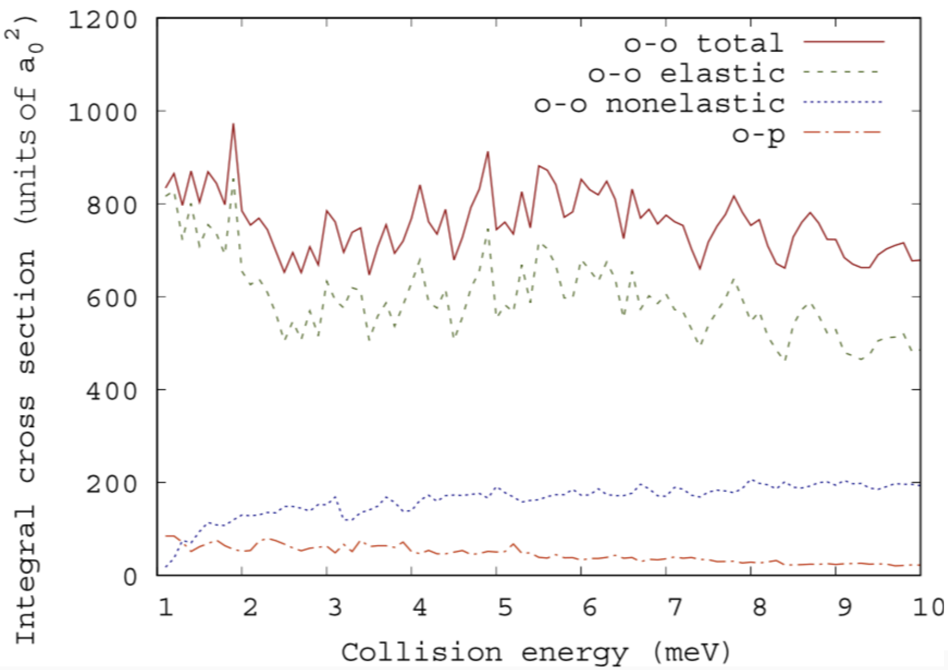
- Each ICS has a threshold (slightly endothermic processes)
- General decrease with E_c after first threshold increase

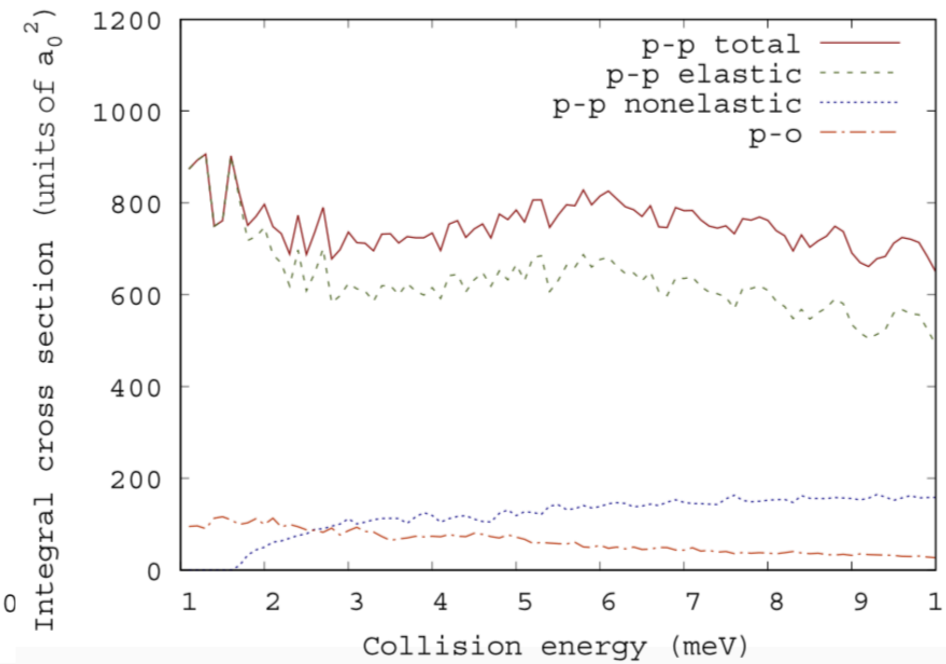
Para-ortho conversion

7 + p77(*j=1*) → 7 + o77(*j'* even)

- No threshold for the first (*j'=0*, red) ICS (exothermicity)
- Second (*j'=2*, green) ICS presents a threshold and dominates for all range of low energies

Results: $^{17}O + {}^{17}O^{17}O$: spin averaged ICSs





$$7 + \mathrm{o}77(j=0) \longrightarrow \begin{cases} 7 + \mathrm{o}77(j') & (\sigma^{\mathrm{oo}}_{j=0\to j'}) \\ \mathrm{p}77(j') + 7 & (\sigma^{\mathrm{op}}_{j=0\to j'}) \end{cases}$$

$$7 + \mathrm{p}77(j=1) \longrightarrow \begin{cases} 7 + \mathrm{p}77(j') & (\sigma^{\mathrm{pp}}_{j=1\to j'}) \\ \mathrm{o}77(j') + 7 & (\sigma^{\mathrm{po}}_{j=1\to j'}) \end{cases}$$

$$\sigma_{j\to j'} = \begin{cases} \sigma^{\mathrm{oo}}_{j\to j'} = \frac{4}{9}\sigma^{A_1}_{j\to j'} + \frac{5}{9}\sigma^{E}_{j\to j'} \; [j' \text{ even}] \\ \sigma^{\mathrm{op}}_{j\to j'} = \frac{5}{9}\sigma^{E}_{j\to j'} \; [j' \text{ odd}]. \end{cases}$$

$$\sigma_{j\to j'} = \begin{cases} \sigma^{\mathrm{pp}}_{j\to j'} = \frac{2}{9}\sigma^{A_2}_{j\to j'} + \frac{7}{9}\sigma^{E}_{j\to j'} \; [j' \text{ odd}] \\ \sigma^{\mathrm{po}}_{j\to j'} = \frac{7}{9}\sigma^{E}_{j\to j'} \; [j' \text{ even}]. \end{cases}$$

Parity conserving reaction huge compared to
to o-p transition, because of inclusion of elastic process

Global o-p or p-o process comparable
with nonelastic one at low energy

Summary

- **Oxygen isotope $^{17}0$ exchange reactions:**

- Low temperature reactive collision rates for 7 + 66, 6 + o/p77
- Comparison with more "standard" reactions 8 + 66 and 6 + 88
- Huge difference in behavior between 88 and o/p77
- Low temperature reactive collision cross sections for 7 + o/p77
- Proper spin-symmetry rates for ortho-para conversion of $^{17}O_2$
- Propensity for parity conservation of rot. levels ("elastic" scattering)

Outlook

- **Same exchange processes in the presence of a static magnetic field:**

- Effect on electronic speen (low field)
- Effect on nuclear spin of ^{17}O (strong field)

Acknowledgments

- Pascal Honvault
- Maxence Lepers

- Richard Dawes
- Vladimir Tyuterev

Thanks for your attention !