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

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OUTLINE

• Context: cold oxygen molecules
• PESs and quantum scattering methods
• Isotope exchange reactions: $^{17}\text{O} + ^{16}\text{O}_2$ & $^{16}\text{O} + ^{17}\text{O}_2$
• Symmetric reaction: $^{17}\text{O} + ^{17}\text{O}_2$
• Conclusions
• $O_2$ ($^3\Sigma_g^-$) is a natural candidate for magnetic trapping (simplest paramagnet)
• $O_2$ is of wide chemical interest

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 $O_2$

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

• 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 $^{16}O_2$)

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

Karpov et al. *NJP* (2020)
Bohn *PRA* (2001)
Bohn *PRA* (2000)
Potential for $\text{O}_3 \left( ^1\text{A'} \right)$: TKTHS PES

Tyuterev et al. *PRL* (2014)

Global Minimum $C_{2v}$:

$\text{r}_e = 2.4 \text{ a}_0$

$\Theta_e = 117 \, ^\circ$

$D_e = 9220 \, \text{cm}^{-1}$
Quantum reaction dynamics: TIQM formalism

Solution of the Time-Independent Schrödinger Equation (TISE) $H\psi = E\psi$ for nuclei

Hamiltonian in democratic hyperspherical (DHS) coordinates (1 distance, 5 angles):

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

Define $\rho$-dependent basis functions (surface-states)

$$\Phi^{JMEI\sigma}_{k\Omega}(\rho; \theta, \phi, \alpha, \beta, \gamma) = \varphi^{E\sigma\Omega}_{k}(\rho; \theta, \phi) N^{JMEI}_{\Omega}(\alpha, \beta, \gamma)$$

Solution of TISE expanded in all angular d.o.f. but the hyper-radius $\rho$:

$$\Psi^{JMEI\sigma}(\rho, \theta, \phi, \alpha, \beta, \gamma) = \frac{1}{\rho^{5/2}} \sum_{k\Omega} \Phi^{JMEI\sigma}_{k\Omega}(\rho_m; \theta, \phi, \alpha, \beta, \gamma) f^{J\sigma}_{k\Omega}(\rho_m; \rho)$$

Using this expansion in the TISE we are led to a set of 2nd order coupled equations for $f^{J\sigma}_{k\Omega}$
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 $\rho$ to optimize overlap between internal DHS and external Jacobi
- Computation of surface-states basis at $\rho_m$-values (sectors) for all $\Omega$
- For each $J$, total $\psi$ expanded in this basis
- Resultant coupled equations solved using « log-derivative » propagator
- Numerically propagated $\psi$ matched to asymptotic form to obtain **T-matrix**
- Computations at numerous energies $E_c$

**Cross sections:**

$$\sigma_{v_j}^{v'_j}(E_c) = \frac{\pi}{(2j+1)\kappa_{v_j}^2} \sum_{J \Omega \Omega'} (2J+1) |T^{J}_{v'_j \Omega' v_j \Omega}|^2,$$

**Rate constants:**

$$k_{v_j}(T) = \sqrt{\frac{8k_BT}{\pi \mu_R}} \frac{1}{(k_BT)^2} \int_0^{\infty} E_c \sigma_{v_j}(E_c) e^{-E_c/k_BT} dE_c$$
Identical nuclei: the permutation symmetry problem

Basic assumption: no spin-dependent term in Hamiltonian

Write the total wave function as a simple tensor product

\[ \Psi = \psi_{el} \psi_{nuc.space} \psi_{nuc.spin} \]

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

$A + X_2$ $\rightarrow$ $A + X_2$ \hspace{1cm} (\alpha: \text{elastic/inelastic})

$AX + X$ \hspace{1cm} (\beta: \text{reactive})

2 final arrangements

2 $X$ nuclei with spin $s$ \hspace{1cm} (Nucleus $A$ not affected by permutation symmetry)

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

shape (or Young diagram)

<table>
<thead>
<tr>
<th>$C_s \cong$</th>
<th>$P_2$</th>
<th>$e$</th>
<th>$(12)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'$</td>
<td>[2]</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A''$</td>
<td>$[1^2]$</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Action of transposition $(12)$ on nuclear spin function:

$$ (12) \psi_{s_A m_A} \psi_{SM} = \left(-\right)^{2s+S} \psi_{s_A m_A} \psi_{SM} $$
\( ^{16}\text{O}^{16}\text{O} \) (66) and \( ^{17}\text{O}^{17}\text{O} \) (77) diatomics

\( ^{16}\text{O}^{16}\text{O} \) or \( ^{18}\text{O}^{18}\text{O} \)

\[ \psi_{^{16}\text{O}_2} = \psi_{\text{el}} \psi_{\text{nuc. space}} \psi_{\text{nuc. spin}} \]

\( ^{16}\text{O}^{18}\text{O} \) (s = 0)

\( S = 0 \)

\( \Lambda_{\text{el}} = 3\Sigma^- \)

odd (ortho) \( j \) rot. levels

\([ (12)\psi = -(-)^j \psi = \psi ] \)

\( ^{17}\text{O}^{17}\text{O} \)

\( ^{17}\text{O}^{18}\text{O} \) (s = 5/2)

\( S = 5, 4 \ldots 0 \)

\( \Lambda_{\text{el}} = 3\Sigma^- \)

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

\([ (12)\psi = -(-)^j(-)^S \psi = -\psi ] \)
The $^{17}\text{O} + ^{16}\text{O}^{16}\text{O}$ reaction

Cross sections

Rate constants

✓ $8 + 66$ reaction is slightly more exothermic than $7 + 66$
✓ $7 + 66$ reaction is slightly faster
Collisions with $^{17}\text{O}^{17}\text{O}$ (77)

$s=5/2$ fermions $\Rightarrow (12)\psi = (-)^{S+1}\psi = -\psi$

$6\times6=36$ spin states

Total nuclear spin $S$:

<table>
<thead>
<tr>
<th>S</th>
<th>5</th>
<th>4</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>2S+1</td>
<td>11</td>
<td>9</td>
<td>7</td>
<td>5</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

S even: 15 spin states

para-$^{17}\text{O}_2$ or p77 $j=1,3,5...$

S odd: 21 spin states

ortho-$^{17}\text{O}_2$ or o77 $j=0,2,4...$

Cross sections for 6 + 77:

Inelastic

\[
\sigma_{\alpha \nu j \rightarrow \alpha \nu' j'} = \begin{cases} 
\frac{7}{12} \sigma_{\alpha \nu j \rightarrow \alpha \nu' j'} & 6 + o77: j & j' \text{ even} \\
0 & j & j' \text{ odd} \\
\frac{5}{12} \sigma_{\alpha \nu j \rightarrow \alpha \nu' j'} & 6 + p77: j & j' \text{ odd} 
\end{cases}
\]

Reactive

\[
\sigma_{\alpha \nu j \rightarrow \beta \nu' j'} = \begin{cases} 
\frac{7}{12} \sigma_{\alpha \nu j \rightarrow \beta \nu' j'} & j \text{ even} \\
\frac{5}{12} \sigma_{\alpha \nu j \rightarrow \beta \nu' j'} & j \text{ odd} 
\end{cases}
\]
The $^{16}\text{O} + \text{o/p-}^{17}\text{O}^{17}\text{O}$ reaction

Cross sections

Rate constants

$6 + 77(v=0,j) \rightarrow 67 + 7$

- $6 + 88$ reaction is slightly more endothermic than $6 + 77$
- $6 + 77$ reaction is much faster
Three identical nuclei: $X + X_2$ type systems

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

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

Permutation group of 3 particles: $S_3$

shape (or Young diagram)

<table>
<thead>
<tr>
<th>$S_3 \simeq C_{3v}$</th>
<th>$(\bullet)(\bullet)(\bullet) \simeq e$</th>
<th>$3(\bullet)(\bullet\bullet) \simeq 3\sigma_v$</th>
<th>$2(\bullet\bullet\bullet) \simeq 2C_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3] $\simeq A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>[1$^3$] $\simeq A_2$</td>
<td>1</td>
<td>$-1$</td>
<td>1</td>
</tr>
<tr>
<td>[2, 1] $\simeq E$</td>
<td>2</td>
<td>0</td>
<td>$-1$</td>
</tr>
</tbody>
</table>

This last 2-dimensional irrep. (Specht module) generated by 2 std polytabloids built on the std tableaux $\begin{matrix} 1 & 2 \\ 3 & 2 \end{matrix}$ and $\begin{matrix} 1 & 3 \\ 3 & 2 \end{matrix}$

Important for ortho-para conversions
Due to indistinguishibility of nuclei, we can have:

**ELASTIC process**

\[
O + O_2 (v=0, j) \rightarrow O + O_2 (v=0, j) \text{ (« pure » elastic)}
\]

\[
\rightarrow O_2 (v=0, j) + O \text{ (« rearranging »)}
\]

**NONELASTIC process**

\[
O + O_2 (v=0, j) \rightarrow O + O_2 (v'=0, j') \text{ (inelastic)}
\]

\[
\rightarrow O_2 (v'=0, j') + O \text{ (rearranging)}
\]
Computation of spin weights (uncoupled representation)

Simply count the spin states:

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

decomposes as:

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

- three-nuclei tensor space
- totally symmetric tensor space
- totally antisymmetric tensor space
- mixed symmetries modules

# components:

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

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

$$n_E = \binom{d-1}{d+1} = \frac{(2s+1)(2s+2)(2s+3)}{6} = 56,$$

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

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

$$d = \dim V = 2s + 1$$

$$d = 6$$ for $$s = 5/2$$

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

Weight for cross Sections:

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

$$\omega_E = \frac{n_E}{n_{A_1} + n_E}$$
Example: $^{17}\text{O} + ^{17}\text{O}^{17}\text{O}$, 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:

$$7 + o77 \quad \rightarrow \begin{cases} 7 + o77 \quad \text{(}\alpha\text{)} \\ p77 + 7 \quad \text{(}\beta\text{)} \end{cases} \quad \begin{array}{l} \text{A}_2 \text{ forbidden asymptotically} \\ \psi_{\text{nuc.space}} \equiv \psi_0 = c_{A_1} \psi^{A_1} + c_E \psi^E \end{array}$$

$$7 + p77 \quad \rightarrow \begin{cases} 7 + p77 \quad \text{(}\alpha\text{)} \\ o77 + 7 \quad \text{(}\beta\text{)} \end{cases} \quad \begin{array}{l} \text{A}_1 \text{ forbidden asymptotically} \\ \psi_{\text{nuc.space}} \equiv \psi_p = c_{A_2} \psi^{A_2} + c_E \psi^E \end{array}$$

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

**Spin-weighted cross sections:**

$$\sigma_\alpha v j \rightarrow \alpha v' j' \begin{cases} \frac{4}{9} \sigma^{A_1}_\alpha v j \rightarrow \alpha v' j' + \frac{5}{9} \sigma^{E}_\alpha v j \rightarrow \alpha v' j' [j, j' \text{ even}] \\ \frac{2}{9} \sigma^{A_2}_\alpha v j \rightarrow \beta v' j' + \frac{7}{9} \sigma^{E}_\alpha v j \rightarrow \alpha v' j' [j, j' \text{ odd}] \\ \frac{5}{9} \sigma^{E}_\alpha v j \text{ even} \rightarrow \alpha v' j' \text{ odd} \\ \frac{7}{9} \sigma^{E}_\alpha v j \text{ odd} \rightarrow \alpha v' j' \text{ even}. \end{cases}$$
Results: $^{17}\text{O} + \text{o/p}^{17}\text{O}^{17}\text{O}$: pure state-to-state ICSs

**Ortho-para conversion**

$7 + \text{o}77(j=0) \rightarrow 7 + \text{p}77(j' \text{ odd})$

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

**Para-ortho conversion**

$7 + \text{p}77(j=1) \rightarrow 7 + \text{o}77(j' \text{ even})$

- 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: $^{17}\text{O} + ^{17}\text{O}^{17}\text{O}$: spin averaged ICSs

Parity conserving reaction huge compared 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** $^{17}$O 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)
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