Ab-initio calculation of state-resolved cross sections and rate coefficients for electron-oxygen scattering

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Plan of the talk:

- Short introduction to the theoretical formalism for electron-molecule resonant scattering;

- State-resolved cross sections database for electron-oxygen scattering
  - Ab-initio electron-O2(X, v) cross sections;
  - Cross sections for $^1\Delta$, $^1\Sigma$ excited states of oxygen;

- Applications
  - Electron-vibration relaxation in oxygen plasmas;
  - Non-equilibrium model for inductively coupled plasmas discharges;
Some theoretical details

Let’s consider electron-molecule scattering with the presence of two (or more) interacting resonances:

\[
e^{-} + AB(v) \rightarrow AB_{1}^{-}, AB_{2}^{-} \rightarrow e^{-} + AB^{*}(w) \quad (VE')
\]
\[
\rightarrow A^{-} + B \quad (DA)
\]
\[
\rightarrow e^{-} + A + B \quad (DE)
\]
\[
e^{-} + AB^{+}(v) \rightarrow AB_{1}, AB_{2} \rightarrow A + B \quad (DR)
\]

The process can be described by two (or more) discrete electronic states, \(|d_1\rangle\) and \(|d_2\rangle\), embedded-in and interacting-with a single electronic continuum \(|\tilde{k}\rangle\)

\[
|\Psi\rangle \sim |d_1\rangle + |d_2\rangle + |\tilde{k}\rangle
\]

Resonant bound state

Interaction between electron and neutral molecule
The theory is developed in the \textit{projector-operators} formalism within Hilbert space:

\[ P = \int d \vec{k} \left| \vec{k} \right\rangle \left\langle \vec{k} \right|, \quad Q = |d_1\rangle\langle d_1| + |d_2\rangle\langle d_2| \]

\[ P + Q = 1, \quad P^2 = P, \quad Q^2 = Q, \quad PQ = QP = 0 \]

The electron-molecule effective Hamiltonian \( H = H_0 + U + V \) can be written as:

\[ H_0 = |d_1\rangle(T_N + V_0 + \epsilon_1)\langle d_1| + |d_2\rangle(T_N + V_0 + \epsilon_2)\langle d_2| + \int d \vec{k} \left| \vec{k} \right\rangle (T_N + V_0 + \epsilon_{\vec{k}}) \left\langle \vec{k} \right| \]

\[ U = |d_1\rangle U_{12} \langle d_2| + \text{h.c.} \]

\[ V = \int d \vec{k} \left| d_1 \right| V_{1k} \left\langle \vec{k} \right| + |d_2\rangle V_{2k} \left\langle \vec{k} \right| + \text{h.c.} \]

- \( V_0 \) is the neutral molecule potential with eigenvalues equation:
  \[ (T_N + V_0)\left| \nu \right\rangle = \epsilon_{\nu} \left| \nu \right\rangle \]

- \( \epsilon_{1,2} \) are the resonance positions respect to \( V_0 \)
- \( U \) describes the coupling between the discrete states
- \( V \) couples the discrete states with the continuum states
Schrödinger equation for electron-molecule scattering. \( \Psi \) is the complete wave function of the system with total energy \( E = \epsilon_k + \epsilon_v \):

\[
(H - E)|\Psi\rangle = 0
\]

Splitting \( |\Psi\rangle = P|\Psi\rangle + Q|\Psi\rangle \) into \( P \) e \( Q \) Hilbert subspace and projecting the Schrödinger equation, it obtains Lippmann-Swinger like equations for open-channel and closed-channel:

\[
P(H_0 + U - E)P|\Psi\rangle = -PVQ|\Psi\rangle
\]
\[
Q(H_0 + U - E)Q|\Psi\rangle = -QVP|\Psi\rangle
\]

Treating \( V \) as a perturbation the open-channel solution can be written as:

\[
P|\Psi\rangle = P|\epsilon_k\rangle|\nu\rangle + \frac{1}{P(E - H_0 - U)P}PVQ|\Psi\rangle
\]

The homogeneous solution represents asymptotically a free electron \( |\epsilon_k\rangle \) and a target molecule in vibrational level \( |\nu\rangle \)
By putting the open-channel solution into closed-channel equation, after some manipulations, one has the final vector equation for the two resonant wave functions $\tilde{\xi}(R) = (\xi_1, \xi_2)$:

$$(\mathcal{H} - E) \tilde{\xi}(R) + \int dR' \mathcal{K}(R, R', E) \tilde{\xi}(R') = -\tilde{V}_k \chi_v(R)$$

where $\tilde{V}_k = (V_{1k}, V_{2k})$ are the coupling potentials and

$$\mathcal{H} = \begin{pmatrix} T_N + V_1 & U_{12} \\ U_{21} & T_N + V_2 \end{pmatrix}$$

$$\mathcal{K}(R, R', E) = \sum_v \chi^*_v(R) \chi_v(R') \left[ \hat{\Delta}(R, R', E - \epsilon_v) - \frac{i}{2} \hat{\Gamma}(R, R', E - \epsilon_v) \right]$$

$$\Gamma_{ij}(R, R', E - \epsilon_v) = 2\pi \int d\epsilon' \ V_{ik} \delta(E - \epsilon') \ V^*_{jk} \quad i, j = 1, 2$$

$$\Delta_{ij}(R, R', E - \epsilon_v) = \frac{1}{2\pi} P \int d\epsilon' \ \frac{\Gamma_{ij}(R, R', \epsilon')}{E - \epsilon_v - \epsilon'} \quad i, j = 1, 2$$
The nuclear dynamics, in the **full theory**, is governed by *complex, non-local* and *energy-dependent* operators.

The **local approximation** (the so-called ‘boomerang model’) of the full theory consists to make the following two *ansatz* in the kernel $\hat{K}$:

(spacing of the vibrational levels)

If $|v_n - v_m| \ll \epsilon_k \quad \forall \ n, m \quad \Rightarrow \quad E - v_n = \epsilon_k + v_i - v_n \approx \epsilon_k$

(resonance positions)

$\epsilon_k \approx \epsilon_1(R) = V_1(R) - V^0(R)$

$\epsilon_k \approx \epsilon_2(R) = V_2(R) - V^0(R)$

With these replacements the kernel $\hat{K}$ become *local* (=dependent on just one geometry) and *energy-independent*.

$$
\left(\begin{bmatrix} T_N + V_1 & U_{12} \\ U_{21} & T_N + V_2 \end{bmatrix} - \frac{i}{2} \hat{\Gamma}(R) - E \hat{1}\right) \tilde{\chi}(R) = -\tilde{V}_k \chi_v(R)
$$
The final resonant vibrational-excitation cross section for transition $\nu_i \rightarrow \nu_f$ and for electron energy $\epsilon$ is given by:

$$\sigma_{i,f}(\epsilon) = \frac{2s_r + 1}{2(2s + 1)} \frac{g_r}{g} \frac{64\pi^5 m^2 k_f}{\hbar^4} \frac{k_f}{k_i} |T_{11} + T_{22} + T_{12} + T_{21}|^2$$

where the $T$ matrix elements are given by

$$T_{pq} = \langle \chi_f | V_{pk_f} | \xi_q \rangle \quad p, q = 1, 2$$

For a two non-interacting resonances the cross section reduces to:

$$\sigma_{i,f}(\epsilon) = \frac{2s_r + 1}{2(2s + 1)} \frac{g_r}{g} \frac{64\pi^5 m^2 k_f}{\hbar^4} \frac{k_f}{k_i} (|T_{11}|^2 + |T_{22}|^2)$$

The corresponding rate coefficient, assuming for electrons a Maxwell distribution at temperature $kT$, is given by:

$$K_{i,f}(T') = \frac{2}{\sqrt{\pi}} (kT')^{-1.5} \int d\epsilon \ \epsilon \ \sigma_{i,f}(\epsilon) \ e^{-\epsilon/kT}$$
Resonant Vibrational-excitation cross section

e^− + AB(ν) → AB^− → AB(ν') + e^−
State-resolved cross sections database for electron-oxygen scattering
In order to describe the low-energy electron-$O_2(X^3\Sigma_g^-)$ resonant scattering it needs to include four resonant states, $^2\Pi_g$, $^2\Pi_u$, $^4\Sigma_u^-$, $^2\Sigma_u^-$ of $O_2^-$. Potential energy curves and resonance widths obtained from MOLPRO and R-matrix within aug-cc-pvQZ basis-set and MR-CI model. The $O_2$ target was represented using the corresponding orbital configurations: 3 core orbitals $(2a_g, 1b_{1u})^6$ of frozen electrons and 9 valence orbitals up to $(3a_g, 2b_{3u}, 2b_{2u}, 3b_{1u}, 1b_{2g}, 1b_{3g})^{10}$. For the scattering calculations:

$(2a_g, 1b_{1u})^6 (5a_g, 2b_{3u}, 2b_{2u}, 4b_{1u}, 2b_{2g}, 2b_{3g})^{11}$ and

$(2a_g, 1b_{1u})^6 (5a_g, 2b_{3u}, 2b_{2u}, 4b_{1u}, 2b_{2g}, 2b_{3g})^{10} (6a_g, 3b_{3u}, 3b_{2u}, 1b_{1g}, 5b_{1u}, 3b_{2g}, 3b_{3g}, 1a_u)^1$. 

**electron-$O_2(X, v)$ resonant scattering**
Table 1. Reduced mass ($\mu$), dissociation energy ($D_e$) and equilibrium distance ($R_e$) for $O_2$ and $O_3^-$ potentials. Electron affinity (eA) of $O_2$ and the crossing point ($R_e$) between the $O_2$ and $O_3^-$ potential energy curves are also given. Literature values, where available, are given in parentheses.

<table>
<thead>
<tr>
<th></th>
<th>$O_2$ ($X^3\Sigma_g^-$)</th>
<th>$2\Pi_u$</th>
<th>$2\Pi_g$</th>
<th>$4\Sigma_u$</th>
<th>$2\Sigma_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ (a.u.)</td>
<td>14582.6</td>
<td>4.02</td>
<td>0.83</td>
<td>1.54</td>
<td>0.73</td>
</tr>
<tr>
<td>$D_e$ (eV)</td>
<td>5.10 (5.12 [20])</td>
<td>4.02</td>
<td>0.83</td>
<td>1.54</td>
<td>0.73</td>
</tr>
<tr>
<td>$R_e$ (a.u.)</td>
<td>2.29 (2.28 [20])</td>
<td>2.55</td>
<td>3.38</td>
<td>3.47</td>
<td>3.73</td>
</tr>
<tr>
<td>$R_e$ (a.u.)</td>
<td>—</td>
<td>2.34</td>
<td>3.20</td>
<td>3.03</td>
<td>3.25</td>
</tr>
<tr>
<td>eA (eV)</td>
<td>1.45 (1.46 [21])</td>
<td>2.34</td>
<td>3.20</td>
<td>3.03</td>
<td>3.25</td>
</tr>
</tbody>
</table>

At energy below 2 eV the VE cross sections are dominated by $^2\Pi_g$ symmetry; comparison with Allan’s results

Resonance at 10 eV dominated by $^4\Sigma_u^-$ symmetry
Set of calculated cross sections for $j = 1$

and the corresponding rate coefficients
**Dissociative-electron-attachment**

\[ e^- + O_2 (X^3\Sigma^-; v) \rightarrow O_2 (^2\Pi_g, ^2\Pi_u, ^4\Sigma_u^-, ^2\Sigma_u^-) \rightarrow O(^3P) + O^- (^2P) \]

DeA cross section for \( v = 0 \) and \( j = 1 \)
Contributions from the four symmetries and comparison with some theoretical and experimental data present in literature
Set of calculated cross sections and the corresponding rate coefficients for some vibrational levels $\nu$ and for $J = 1$.
**Electron-impact dissociation:**

\[
e^- + O_2(X^3\Sigma^-; \nu) \rightarrow O_2^-(2\Pi_g, 2\Pi_u, 4\Sigma_u^-, 2\Sigma_u^-) \rightarrow e^- + 2\ O(^3\Pi)
\]

Set of vibrational-resolved cross sections and the corresponding rate coefficients for \( j = 1 \)
Effect of target rotation

Number of vibrational levels as a function of the rotational quantum number $j$

<table>
<thead>
<tr>
<th>$j$</th>
<th>$v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$0...41$</td>
</tr>
<tr>
<td>50</td>
<td>$0...33$</td>
</tr>
<tr>
<td>100</td>
<td>$0...23$</td>
</tr>
<tr>
<td>150</td>
<td>$0...9$</td>
</tr>
<tr>
<td>170</td>
<td>$0...2$</td>
</tr>
</tbody>
</table>

Thermal averaged energy of the ro-vibrational level $\varepsilon_{v,j}$:

$$
\bar{\varepsilon}_v(T_r) = \sum_j \varepsilon_{v,j}(2j + 1) \frac{e^{-\varepsilon_{v,j}/k_B T_r}}{Q_v(T_r)}
$$

$T_r$ is the rotational temperature
Thermal averaged vibrational-excitation cross section, $T_r$ is the rotational temperature:

$$\bar{\sigma}_{v,v'}(\epsilon, T_r) = \sum_j \sigma_{v,v',j}(\epsilon)(2j + 1) \frac{e^{-\epsilon_{v,j}/k_BT_r}}{Q_v(T_r)}$$

$j$-resolved cross section for $v = 0 \rightarrow v' = 1$

Thermal averaged rate coefficient by assuming the rotational temperature in equilibrium with electron temperature
Rotational $j$-resolved rate coefficients (solid lines) for dissociative-electron-attachment and for dissociative-excitation processes for $\nu = 0$ as a function of the electron temperature and Thermal averaged rate coefficient (dashed line) for $\nu = 0$ by assuming the rotational temperature in equilibrium with electron temperature
Cross sections for $^1\Delta$, $^1\Sigma$ excited states of oxygen*.

*Thanks to David Schwenke (NASA Ames (US)) for supplying the potential energy curves
- State-resolved cross sections can be obtained by splitting procedure from the global cross section;

- By setting $Y, Y' = \{X^3\Sigma_g^-, a^1\Delta_g, b^1\Sigma_g^+\}$ the excited states of $O_2$ and by $v, v'$ the corresponding vibrational levels, in order to split the global cross section $\sigma_{Y'Y}^{exp}$ into vibrational-resolved cross section $\sigma_{Y'v}^{Y'v'}$ the following formula can be used:

$$
\sigma_{Y'v}^{Y'v'}(\epsilon) = q_{Y'v}^{Y'v'} \sigma_{Y'Y}^{exp} \left( \epsilon \frac{\Delta E_{Y'v}}{\Delta E_{Y'v}^0} \right),
$$

where $\epsilon$ is the electron energy,

$$
q_{Y'v}^{Y'v'} = \left| \langle \psi_{v'}^{Y'} | \psi_Y^{Y} \rangle \right|^2,
$$
the Frank-Condon factor and

$$
\Delta E_{Y'v}^{Y'} = |\epsilon_{v'}^{Y'} - \epsilon_{v}^{Y}|,
$$
is the threshold energy for the $Y, v \rightarrow Y', v'$ transition

Experimental global cross section for $e + O_2(X, \, ^1\Delta, \, ^1\Sigma)$
Application: Electron-vibration relaxation in oxygen plasmas

\[ e + O_2(X^3\Sigma^-; \nu, j) \leftrightarrow e + O_2(X^3\Sigma^-; w, j), \quad (VE) \]

- State-to-State vibrational kinetics
- Vibrational relaxation time is comparable to chemical relaxation: vibrational non-equilibrium

\[ \frac{dn_{\nu}}{dt} = n_e \sum_{w \in \nu} [k_{w,\nu} n_w - k_{\nu,w} n_\nu], \quad \nu \in \mathcal{V}, \]

V. Laporta, K.L. Heritier and M. Panesi, Chemical Physics 472 (2016) 44–49
• Time evolution of non-equilibrium vibrational distribution function:

• Vibrational relaxation time:
Inductively Coupled Plasma (ICP) torches have a wide range of possible applications which include deposition of metal coatings, synthesis of ultra-fine powders, generation of high purity silicon and testing of thermal protection materials for atmospheric entry vehicles.

In the computational model, the electromagnetic induction equation is solved together with the set of Navier-Stokes equations; A state-to-state thermo-chemical non-equilibrium formulation is used for the chemical reactions.

In its simplest configuration, an ICP torch consists of a quartz tube surrounded by an inductor coil made of a series of parallel current-carrying rings.
\begin{align*}
\partial_t \rho_i + \nabla \cdot [\rho_i (u + \mathbf{V}_i)] &= M_i, \quad \omega_i \quad [i \in S], \quad (2) \\
\partial_t (\rho u) + \nabla \cdot (\rho u \otimes u + p \mathbb{I}) &= \nabla \cdot \tau + J \times B, \quad (3) \\
\partial_t \rho E + \nabla \cdot (\rho H u) + \sum_i \rho_i \mathbf{V}_i \cdot h_i &= \tau : \nabla u - \nabla \cdot q + J \cdot E, \\
\partial_t \rho e_{ev} + \nabla \cdot (\rho e_{ev} u) + \sum_i \rho_i \mathbf{V}_i e_{ev,i} &= -\nabla \cdot q_{ev} + \Omega^{ET} + \Omega^C + \Omega^{VT} + J \cdot E, \quad (2)
\end{align*}

pressure = 10^5 \text{ Pa} \\
\text{Power} = 5 \times 10^4 \text{ W/m}
Results at equilibrium:
Outlook...

- Complete sets, state-resolved, of vibrational-excitation, dissociative-electron-attachment and dissociative-excitation cross sections and rate coefficients for electron-oxygen scattering are supplied for plasma description purposes;

- Next step will be the updating to *ab-initio* calculations for state-resolved cross sections for excited states $^1\Delta$ and $^1\Sigma$ of oxygen;

- Calculations for electron-$\text{O}_2^+$ scattering for dissociative recombination process;

- Developing of a self-consistent kinetic code for inductively-coupled-plasma;

- All cross sections are available to PHYS4Entry data base: http://users.ba.cnr.it/imip/cscpal38/phys4entry/database.html
Thank you for your attention

Acknowledgments:

• Prof. Roberto Celiberto (Politecnico di Bari, Italy)
• Prof. Jonathan Tennyson (University College London, UK)
• Prof. Marco Panesi (University of Illinois, IL, US)
• Dr. Alessandro Munafo (University of Illinois, IL, US)