Ab-initio calculation of state-resolved cross sections and rate coefficients for electron-O$_2$ and -N$_2$ scattering

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Plan of the talk:

Ab initio state-resolved cross sections database

- Atmospheric modelling: electron-O$_2$ and electron-N$_2$
- Astrophysics: electron-He$_2^+$
- Fusion plasma: electron-BeH$^+$

Main collaborators:
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I.F. Schneider (Université du Havre, France)
J. Tennyson (University College London, UK)
In order to describe the low-energy electron-\(\text{O}_2(\text{X}^3\Sigma_g^-)\) resonant scattering it needs to include four resonant states, \(^2\Pi_g, ^2\Pi_u, ^4\Sigma_u^-, ^2\Sigma_u^-\) of \(\text{O}_2^-\).

Potential energy curves and resonance widths obtained from MOLPRO and R-matrix within aug-cc-pvQZ basis-set and MR-CI model.

The \(\text{O}_2\) 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
\[(2a_g, 1b_{1u})^6 (5a_g, 2b_{3u}, 2b_{2u}, 4b_{1u}, 2b_{2g}, 2b_{3g})^{10} (6a_g, 3b_{3u}, 3b_{2u}, 1b_{1g}, 5b_{1u}, 3b_{2g}, 3b_{3g}, 1a_u)^1.\]
Table 1. Reduced mass ($\mu$), dissociation energy ($D_e$) and equilibrium distance ($R_e$) for O$_2$ and O$_2^-$ potentials. Electron affinity (eA) of O$_2$ and the crossing point ($R_c$) between the O$_2$ and O$_2^-$ 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>O$_2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ (a.u.)</td>
<td>14582.6</td>
<td></td>
</tr>
<tr>
<td>$D_e$ (eV)</td>
<td>5.10 (5.12 [20])</td>
<td>4.02 0.83 1.54 0.73</td>
</tr>
<tr>
<td>$R_e$ (a.u.)</td>
<td>2.92 (2.28 [20])</td>
<td>2.55 3.38 3.47 3.73</td>
</tr>
<tr>
<td>$R_c$ (a.u.)</td>
<td>—</td>
<td>2.34 3.20 3.03 3.25</td>
</tr>
<tr>
<td>eA (eV)</td>
<td>1.45 (1.46 [21])</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Calculated vibrational levels of O$_2$($X^{3}\Sigma_g^-$) molecule for rotational level $j = 1$. Energies are given in eV.

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\epsilon_p$</th>
<th>$v$</th>
<th>$\epsilon_p$</th>
<th>$v$</th>
<th>$\epsilon_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>14</td>
<td>2.435</td>
<td>28</td>
<td>4.280</td>
</tr>
<tr>
<td>1</td>
<td>0.196</td>
<td>15</td>
<td>2.587</td>
<td>29</td>
<td>4.382</td>
</tr>
<tr>
<td>2</td>
<td>0.388</td>
<td>16</td>
<td>2.735</td>
<td>30</td>
<td>4.476</td>
</tr>
<tr>
<td>3</td>
<td>0.573</td>
<td>17</td>
<td>2.881</td>
<td>31</td>
<td>4.565</td>
</tr>
<tr>
<td>4</td>
<td>0.756</td>
<td>18</td>
<td>3.024</td>
<td>32</td>
<td>4.651</td>
</tr>
<tr>
<td>5</td>
<td>0.937</td>
<td>19</td>
<td>3.164</td>
<td>33</td>
<td>4.730</td>
</tr>
<tr>
<td>6</td>
<td>1.117</td>
<td>20</td>
<td>3.301</td>
<td>34</td>
<td>4.794</td>
</tr>
<tr>
<td>7</td>
<td>1.291</td>
<td>21</td>
<td>3.436</td>
<td>35</td>
<td>4.847</td>
</tr>
<tr>
<td>8</td>
<td>1.461</td>
<td>22</td>
<td>3.568</td>
<td>36</td>
<td>4.898</td>
</tr>
<tr>
<td>9</td>
<td>1.629</td>
<td>23</td>
<td>3.696</td>
<td>37</td>
<td>4.938</td>
</tr>
<tr>
<td>10</td>
<td>1.796</td>
<td>24</td>
<td>3.821</td>
<td>38</td>
<td>4.960</td>
</tr>
<tr>
<td>11</td>
<td>1.960</td>
<td>25</td>
<td>3.942</td>
<td>39</td>
<td>4.976</td>
</tr>
<tr>
<td>12</td>
<td>2.122</td>
<td>26</td>
<td>4.059</td>
<td>40</td>
<td>4.987</td>
</tr>
<tr>
<td>13</td>
<td>2.281</td>
<td>27</td>
<td>4.172</td>
<td>41</td>
<td>4.994</td>
</tr>
</tbody>
</table>
\[ e^- + O_2(X^3\Sigma^-_g; \nu) \rightarrow O_2^- (^2\Pi_g, ^2\Pi_u, ^4\Sigma_u^-, ^2\Sigma_u^-) \rightarrow \begin{cases} 
\quad e^- + O_2(X^3\Sigma^-_g; \nu') & \text{(VE)} \\
\quad O(^3\Pi) + O^-(^2\Pi) & \text{(DA)} \\
\quad e^- + O(^3\Pi) + O(^3\Pi) & \text{(DE)} 
\end{cases} \]


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
\[ e^- + O_2(X^3\Sigma_g^-; \nu) \rightarrow O_2^-\left(2\Pi_g, 2\Pi_u, 4\Sigma_u^-, 2\Sigma_u^-\right) \rightarrow e^- + O_2(X^3\Sigma_g^-; \nu') \]

Set of calculated cross sections for \( j = 1 \)

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

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

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

Set of calculated cross sections and the corresponding rate coefficients for some vibrational levels \( v \) and for \( j = 1 \).
Electron-impact dissociation:

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

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>$v_j$</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 $\epsilon_{v,j}$:

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

$T_r$ 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

Thermal averaged rate coefficient
Rotational $j$-resolved rate coefficients (solid lines) as a function of the electron temperature and Thermal averaged rate coefficient (dashed line) by assuming the rotational temperature in equilibrium with electron temperature

**dissociative-electron-attachment**

**dissociative-excitation**
Application: Electron-vibration relaxation in oxygen plasmas

\[ e + O_2(X^3\Sigma^{-}_g; \nu, j) \rightleftharpoons e + O_2(X^3\Sigma^{-}_g; w, j), \]  

\[ \text{(VE)} \]

- 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:

- Equilibrium distribution
- Non-equilibrium distribution

• Vibrational relaxation time:

\[
\frac{d E_{vib}}{dt} = \frac{E^*_{vib} - E_{vib}}{\tau_e},
\]

\[\tau_e = P_e \tau \]
electron-N\textsubscript{2} resonant scattering

The resonance at 2.3 eV in electron-N\textsubscript{2} scattering is described in term of the resonant state N\textsubscript{2}\textsuperscript{-} (X \textsuperscript{2}\Pi\textsubscript{g})

The quantum chemistry codes MOLPRO and R-Matrix have been used to calculate potential energy curves, resonance width:

\textbf{cc-pvQZ basis set} \hspace{1cm} \textbf{MR-CI model}

\textbf{CAS (1}\sigma\textsubscript{g}, 1}\sigma\textsubscript{u})^4(2}\sigma\textsubscript{g}, 2}\sigma\textsubscript{u}, 1}\pi\textsubscript{u}, 3}\sigma\textsubscript{g}, 1}\pi\textsubscript{g}, 3}\sigma\textsubscript{u})^{10} 128 configurations

V. Laporta \textit{et al.}, Plasma Sources Sci. Technol. 23, 065002 (2014)
V. Laporta \textit{et al.}, Plasma Sources Sci. Technol. 21, 055018 (2012)
Vibrational-excitation process:

\[ e^- + N_2(X^1\Sigma^+_g; \nu, J) \rightarrow N_2^- (X^2\Pi_g) \rightarrow e^- + N_2(X^1\Sigma^+_g; \nu', J) \]
Elastic transitions ($v \rightarrow v$) 

Inelastic transitions ($20 \rightarrow v$) 

$VE$ cross sections parameterized on $N_2$ rotational quantum number $J$
**Electron-impact dissociation:**

\[ e^- + N_2(X \ ^1\Sigma^+; \nu, J) \rightarrow N_2(X \ ^2\Pi_g) \rightarrow e^- + 2 N(4S) \]
Electron-vibration relaxation in nitrogen plasmas

\[ e^- + N_2(X^1\Sigma^+_g; \nu, J) \rightarrow N_2(X^2\Pi_g) \rightarrow e^- + N_2(X^1\Sigma^+_g; \nu', J) \]

- Time evolution of non-equilibrium vibrational distribution function:
\[ \frac{dE_{\text{vib}}}{dt} = \frac{E_{\text{vib}}^* - E_{\text{vib}}}{\tau_e}, \]

**FIG. 8.** Vibrational relaxation time as a function of electron temperature for different values of the initial vibrational temperature \( T_v \). The values are obtained by solving the full set of kinetics equations.
electron-He$_2^+$ dissociation cross sections

\[ e + \text{He}_2^+ (X^2\Sigma_u^+, v = 0 - 23) \rightarrow e + \text{He}_2^+ (A^2\Sigma_g^+) \rightarrow e + \text{He} + \text{He}^+, \]
Figure 4. AN cross sections for processes starting from different \( \text{He}_2^+ \) vibrational levels \( \nu \).
electron-BeH\(^+\) Dissociative Recombination cross sections

V Laporta, K Chakrabarti, R Celiberto, RK Janev, JZs Mezei, S Niyonzima, J Tennyson and IF Schneider, PPCF 59, 045008 (2017)
\[ e^- + \text{BeH}^+(X \,^1\Sigma^+; \nu^+, j^+) \rightarrow \text{BeH}^{**} \rightarrow e^- + \text{BeH}^+(X \,^1\Sigma^+; w^+, j^+), \] (VE)

\[ e^- + \text{BeH}^+(X \,^1\Sigma^+; \nu^+, j^+) \rightarrow \text{BeH}^{**} \rightarrow \text{Be}^*(n) + \text{H}^\text{(2S)}, \quad n = 1, \ldots, 12, \] (DR)

\[ e^- + \text{BeH}^+(X \,^1\Sigma^+; \nu^+, j^+) \rightarrow \text{BeH}^{**} \rightarrow e^- + \text{Be}^+\text{(2S)} + \text{H}^\text{(2S)}, \] (DE)
Work in progress...

- We are planning with our collaborations to calculate *ab initio* cross sections for the main elementary processes for electron-molecule scattering (dissociative attachment, dissociative excitation, dissociative recombination and vibrational excitation);

- Work is in progress on electron-CO$_2$ scattering, electron-N$_2^+$, improvement of electron-NO….

Thank you for your attention