Ultracold collisions in spin-polarised Li + Li$_2$

Marko T. Cvitaš, Pavel Soldán, and Jeremy M. Hutson
Department of Chemistry, University of Durham, England
Pascal Honvault and Jean-Michel Launay
UMR 6627 du CNRS, University of Rennes, France
Introduction

- The possibility of producing vibrationally excited molecules at temperatures as low as 100 nK by photoassociation in an atomic Bose-Einstein condensate has been recently demonstrated [Wynar et al., Science 287, 1016 (2000)].
- The lifetime of molecules produced in a trap depends crucially on atom-molecule collision rates.
- We have set out to compute inelastic and reactive rate coefficients in the spin-polarised Li + Li$_2$ system.
- We have computed the quartet PES of the lithium trimer and performed the scattering calculations for collision energies in the range from 1 nK to 1 K.
Potential energy surface

- *Ab-initio* points were calculated at the RCCSD(T) level using the cc-pV5Z basis set on 273 configurations for Li₃.
- The surface shows a dramatically strong non-additivity in the well region.

Potential minima in different arrangements

<table>
<thead>
<tr>
<th>Arrangement</th>
<th>$V_{\text{tot}}$</th>
<th>$V_3$</th>
<th>$r_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}_2$</td>
<td>-334.05 cm⁻¹</td>
<td></td>
<td>4.170 Å</td>
</tr>
<tr>
<td>$\text{Li}<em>3$: $D</em>{\infty h}$</td>
<td>-964.99 cm⁻¹</td>
<td>-354.87 cm⁻¹</td>
<td>3.780 Å</td>
</tr>
<tr>
<td>$\text{Li}<em>3$: $D</em>{3h}$</td>
<td>-4018.52 cm⁻¹</td>
<td>-5244.88 cm⁻¹</td>
<td>3.105 Å</td>
</tr>
</tbody>
</table>

We carried out electronic energy calculations using the MOLPRO package [written by H.-J. Werner and P. J. Knowles,]
Fitting the surfaces

- Lithium dimer PE curve was interpolated using the RP-RKHS method with dispersion coefficients of Dalgarno et al. [Phys. Rev. A 54, 2824 (1996)]
- Non-additive part of the surface was fitted to a form in the symmetric coordinates, similar to the one used previously by Murrell et al. [Mol. Phys. 92, 63 (1997)], for C\textsubscript{2v} geometries (161 points fitted, 53 parameters), with the Axilrod-Teller form of long-range interaction.
- Fit was found satisfactory for the D\textsubscript{3h} and D\textsubscript{∞h} configurations, while not being able to describe the violent variation of the potential at the near-collinear arrangements.

Total potential in Jacobi coordinates for cos \( \vartheta = 0 \)  
Total potential in the valence coordinates for collinear arrangements
Deep well due to the large non-additive part of the potential is a chemical bonding effect rather than the dispersion driven effect. To some extent it is still present at the Hartree-Fock level. Electron-correlation effect lowers the value of the pairwise-additive part significantly.

RCCSD(T) (first column) and RHF (second column) energies in the D_{ooh} (first row) and D_{3h} (second row) with the aug-cc-pVTZ basis set.
Reactive scattering calculations

- We used general reactive scattering code written by J.-M. Launay.
- It solves the time-independent Schrödinger equation by coupled-channel approach with use of hyperspherical democratic coordinates. Hyperangular degrees of freedom are expanded in a set of hypersurface states which are evaluated by variational expansion onto a basis of pseudo-hyperspherical harmonics.
- Hyperradial equations involving 285 ro-vibrational states were propagated outwards to the distance of 45 bohrs. The PHS harmonics basis was extended up to K=90.
- Inelastic and reactive cross-sections were converged. Elastic cross-sections are uncertain up to approx. 20% due to the non-vanished long-range couplings.
- Asymptotic matching was performed to the solution of \(-C_6 / R^6\) potential for the incident channel, neglecting the anisotropy of the potential in the outer region.
- Asymptotic diatomic rovibrational basis of Li\(_2\) included \(v=0, 1, \ldots, 7\) (\(j_{\text{max}} = 33, 30, 28, 24, 22, 18, 14, 10\)).
• Elastic cross-sections tend to a constant as collision energy (T) approaches zero following the Wigner’s threshold law.

• Onset of temperature independence of the elastic cross-sections is in mK regime.
• Quenching rate coefficients are three orders of magnitude larger than the elastic, in the ultracold regime.

• Quenching rate coefficient \((k=\sigma v)\) tends to a constant in the zero energy limit (Wigner’s threshold law).

• Rate coefficients and cross-sections for elastic and quenching events do not depend strongly on the initial vibrational level.
• Reactive and inelastic rate coefficients are remarkably similar for the vi=1, j=0 initial state and differing always by less than an order of the magnitude.
Partial cross-sections

- Partial reactive and inelastic cross-sections for quenching to a vibrational manifold are monotonously decreasing with the initial kinetic energy (T) in the ultracold regime.
- Relative efficiency of the single, double and triple de-excitation processes is of the same order of magnitude.
Low-energy scattering behaviour

- In the range of applicability of Wigner’s threshold laws, elastic and quenching cross-sections can be characterised by the complex scattering length [Balakrishnan et al., Chem. Phys. Lett. 280, 5 (1997)].

\[ \sigma_v^{\text{elastic}} = 4\pi |a|^2 \]

\[ \sigma_v^{\text{inel+react}} = -\frac{4\pi}{k} \text{Im}(a) \]

Scattering length for the \( v=1, j=0 \) state:

\[ a = (2.71 - 2.54 i) \times 10^{-7} \text{ cm} \]
vi=1, \( j_i=0 \); vf=0, \( j_f=\) all accessible
Future work

- Improvement of the non-additive fit of the quartet lithium PES and potential sensitivity analysis in the cold regime.
- Extension to J > 0 in order to include states that are initially rotationally excited.
- Inclusion of magnetic fields and hyperfine effects.
- Investigation of other alkali systems.