Mutual neutralization of $Li^+ + D^-$: theoretical and experimental studies

T. Launoy [1,2], J. Liévin [1], J. Loreau [1], N. Vaeck [1] and X. Urbain [2]

[1] Laboratoire de Chimie Quantique et Photophysique, Université Libre de Bruxelles, 50, av. F. Roosevelt, CP160/09, 1050 Bruxelles, Belgium

[2] Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Chemin du Cyclotron 2, 1348 Louvain-la-Neuve, Belgium

Astrochemical context

Modelling of stellar atmospheres requires various detailed and accurate data on different processes such as the mutual neutralization (MN) of cation-anion pairs that can affect atomic species of interest.

Abundances of the chemical elements in stellar atmospheres are important parameters for understanding the universe and in particular stellar evolution, nucleosynthesis, galaxy evolution and so forth. Among all the possible reactions, neutralization plays an important role in atmospheric and astrophysical processes. Furthermore, due to the difficulty to accurately obtain experimental and theoretical data, there is a strong demand from the astrochemical community for information on the low energy cross section of processes involving H^- (or D^-).

Experimental setup

Merged beam experiments are ideal for the study of low energy interactions such as the mutual neutralization (MN) process [1].

We are currently looking at one of the simplest mutual neutralization reactions because the first galaxies and stars were formed from a mixture of H and ^4He with traces of ^2D and ^7Li [2]:

$$^7Li^+ + {}^2D^- \rightarrow Li^*(nl) + D$$

The setup in **Figure 1** was modified :

- Changing the ECR source to a HeatWave Labs source with coaxial heater for the $^7Li^+$ cation
- Using a laser to photodetach the $^2D^-$ anion to optimize the anion beam

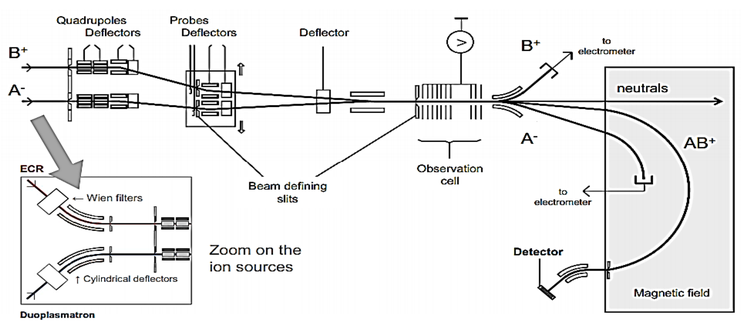

Figure 1. Schematic view of the merged beam setup (Louvain-la-Neuve, Belgium).

Theoretical methodology

We calculated the potential energy curves (PECs) of some excited states of the LiH molecule using the MOLPRO package [6] with various basis sets and with the MRCI+Q methodology (see **Figure 3**).

- Ion pair dissociation limit : $Li^+ (^1S) + H^- (^1S)$: $^1\Sigma^+$
  - To describe the MN process, only the potential energy curves of the $^1\Sigma^+$ states and the couplings between them are required.
- Basis set used for H^-:
  - aug-cc-pV5Z augmented by [3s,3p,2d,1f] Gaussian type orbitals (GTO) previously optimized [7].
- Basis set used for Li^+:
  - Slater type orbitals (STO) from the AUTOSTRUCTURE package [8] fitted by Gaussian type orbitals and using various methods for the coefficient expansion and the Gaussian exponents :
    a) Following the work of O-Ohata *et al.* [9]
    b) Following the work of Stewart [10]
    c) Using MATLAB
  - d) aug-cc-pCV5Z + an even-tempered basis set with a fictional atom
  - e) aug-cc-pCV5Z + an even-tempered basis set without a fictional atom
  - f) Basis set from Gim and Lee [11] including an effective core potential with a core polarization potential (ECP/CPP).
  - g) Basis set from Gim and Lee without the ECP/CPP.

Experimental results

We measured the Kinetic Energy Release (KER) and the mutual neutralization cross section at an average 7 meV average collision energy.

As seen in **Figure 2**, our apparatus gives access to the branching ratio among the accessible neutral channels of the lithium atom and could discriminate the Li(3p) and Li(3d) channels separated by only 44 meV.

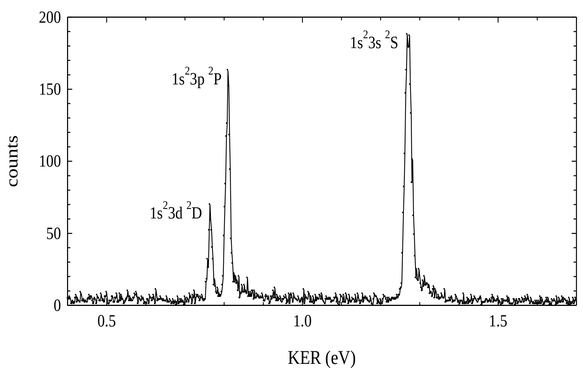

Figure 2. KER resulting from the mutual neutralization process between Li^+ and D^- at 7 meV.

This work (7 meV) : $\sigma = 3.12\ 10^{-12}\ cm^2$

Theo. [3] (10 meV) : $\sigma = 3.5\ 10^{-12}\ cm^2$

Exp. [4] (0.7 eV) : $\sigma = 5\ 10^{-14}\ cm^2$

- Agreement with the theoretical results of Croft *et al.* [3] about the total cross section
- Disagreement between the measured branching ratio and the theoretical one [5]:
  - Higher proportions of the 3d channel by approximately 6%
  - Higher proportions of the 3s channel by approximately 5%
  - Lower proportions of the Li(3p) channel

Theoretical results

- Calculating the PECs and the Non-adiabatic coupling matrix elements (NACME), we looked into the influence of the basis set on the position of the avoided crossings that could explain the disagreement between our measured branching ratio and the theoretical ones from Croft *et al.* [5].

	2s-2p	2p-3s	3s-3p	3p-3d	3p-4s	3d-4s	4s-4p
a	6.7	10.9	21.4	32.5	34.4	34.5	-
b	3.5	5.5	11.2	17.1	-	18	33
c	6.9	11.1	22	34.4	-	35.9	-
d	7	11	20.6	29.4	-	31.5	-
e	6.7	11.2	20	29.3	29.9	30.1	-
f	7.1	11.3	18.8	26.7	26.8	27.2	46.3
g	7.1	11.3	18.5	26.4	26.4	26.7	47.4
Croft *et al.*[3]	7.3	11.3	22.1	34	-	36	91.2
Gim and Lee[11]	7	11	21	35	-	-	-
Méndez [12]	7 / 6.5	10.5 / 11	20.5 / 21.5	32 / 31	-	-	-

Figure 2. Position of the avoided crossing between LiH molecular states dissociating to Li*(nl) + H(1s) (see **Figure 3**) as a function of the basis set. The letters a,b,… refer to the basis set as previously explained. The data is based on NACME when possible.

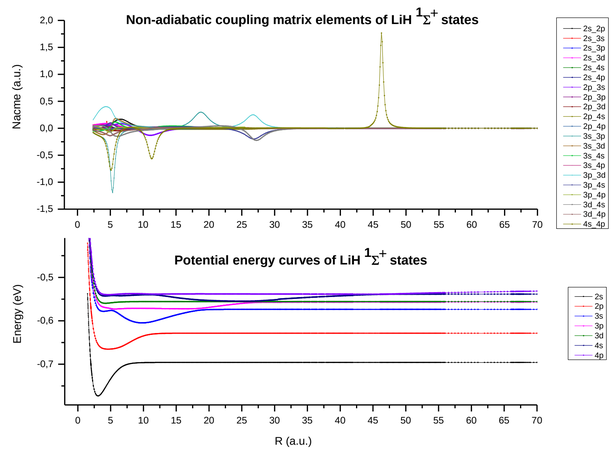

Figure 3. Non-adiabatic coupling matrix elements and potential energy curves of some molecular states of LiH calculated with the basis set from Gim and Lee [11].

Summary

- We measured the branching ratio and the total cross section of the mutual neutralization between $^7Li^+ + {}^2D^-$ at 7 meV.
- The cross section agrees with theoretical results whereas the experimental branching ratio are does not.
- Further experiments at higher collision energies are still needed to completely compare our results with the experimental study of Pear and Hayton [4] which was restricted to higher collision energies in the range of 0.7 to 316 eV.
- Potential energy curves of LiH were calculated using various basis sets in order to compute the cross section and the branching ratio in future research.

References

[1] Nkambule, S. M.; Elander, N.; Larson, Å.; Lecointre, J.; Urbain, X. *Phys. Rev. A* 2016, **93**, 32701.
[2] Stancil, P. C.; Lepp, S.; Dalgarno, *A. Astrophys. J.* 1996, **458**, 401.
[3] Croft, H.; Dickinson, A. S.; Gadéa, F. X. *Mon. Not. R. Astron. Soc.* 1999, **304**, 327–329.
[4] Peart, B.; Hayton, D. A. *J. Phys. B At. Mol. Opt. Phys.* 1994, **27**, 2551.
[5] Croft, H.; Dickinson, A. S.; Gadéa, F. X. *J. Phys. B At. Mol. Opt. Phys.* 1999, **32**, 81.
[6] MOLPRO, version 2015.1, a package of *ab initio* programs, H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, and others , see http://www.molpro.net.
[7] Loreau, J. ; Liévin, J. ; Palmeri, P. ; Quinet, P. ; Vaeck, N. *J. Phys. B At. Mol. Opt. Phys.* 2010, **43**, 065101.
[8] Badnell, N. R. *ApJS* 2006, **167**, 334.
[9] O-ohata, K. ; Taketa, H. ; Huzinaga, S. *J. Phys. Soc. Jpn.* 1966, **21**, 2306-2313.
[10] Stewart, R. F. *J. Chem. Phys.* 1970, **52**, 431–438.
[11] Gim, Y. ; Lee, C.-W. *J. Chem. Phys.* 2014, **141**, 144313.
[12] Méndez, L.; Cooper, I. L.; Dickinson, A. S.; Mó, O.; Riera, A. *J. Phys. B: At. Mol. Opt. Phys.* 1990, **23**, 2797

fnrs LA LIBERTÉ DE CHERCHER