Abstract. Rate coefficients for inelastic collisions between Li and H atoms covering all transitions between the asymptotic states Li(2s,2p,3s,3p,3d,4s,4p,4d,4f)+H(1s) and Li^+ + H^- are presented for the temperature range 2000–8000 K based on recent cross-section calculations. The data are of sufficient completeness for non-LTE modelling of the Li I 670.8 nm and 610.4 nm features in late-type stellar atmospheres. Non-LTE radiative transfer calculations in both 1D and 3D model atmospheres have been carried out for test cases of particular interest. Our detailed calculations show that the classical modified Drawin-formula for collisional excitation and de-excitation (Li^+ + H <-> Li^{+'} + H) over-estimates the cross-sections by typically several orders of magnitude and consequently that these reactions are negligible for the line formation process. However, the charge transfer reactions collisional ion-pair production and mutual neutralization (Li^+ + H <-> Li^++ + H^-) are of importance in thermalizing Li. In particular, 3D non-LTE calculations of the Li I 670.8 nm line in metal-poor halo stars suggest that 1D non-LTE results over-estimate the Li abundance by up to about 0.1 dex, aggravating the discrepancy between the observed Li abundances and the primordial Li abundance as inferred by the WMAP analysis of the cosmic microwave background.

Key words: Atomic data – Line: formation – Stars: abundances
Inelastic H+Li and H−+Li+ collisions and non-LTE Li I line formation in stellar atmospheres

P. S. Barklem1, A. K. Belyaev2, and M. Asplund3

1 Department of Astronomy and Space Physics, Uppsala University, Box 515 SE 751 20 Uppsala, Sweden
2 Department of Theoretical Physics, A. I. Herzen University, St. Petersburg 191186, Russia
3 Research School of Astronomy, Mt. Stromlo Observatory, Cotter Road, Weston, ACT 2611, Australia

Received; accepted

1. Introduction

Lithium abundances in stellar atmospheres are key observational parameters in astrophysics. They tell us much about stellar evolution and nucleosynthesis, Big Bang nucleosynthesis, and the role of cosmic rays in Galactic chemical evolution, to name a few (see Lambert 1993; Carlsson et al. 1994 and references therein). Stellar Li abundances are in practice determined from the 670.8 nm resonance line of Li I and in a few cases the 610.4 nm subordinate line. Thus, the ability to accurately interpret these lines is important. As Li I has a low ionization potential, non-local thermodynamic equilibrium (non-LTE) effects can be expected to be important (Steenbock & Holweger 1984; Carlsson et al. 1994; Asplund et al. 2003).

Steenbock and Holweger (1984) were the first to suggest that inelastic collisions with hydrogen might be important in thermalizing Li I. In photospheres of late-type stars neutral hydrogen atoms outnumber electrons by typically \( N_H / N_e \sim 10^4 \), even more in metal poor stars. Thus, weight of numbers may overcome the expectation that electron collisions are a more efficient thermalizing mechanism firstly due to their higher thermal velocity and therefore higher collision rate, and secondly since for speeds of interest electron cross sections are generally larger than those for neutrals since the neutral collisions are adiabatic while the electron collisions are not (e.g. Lambert 1993). In such photospheres \( kT \sim 0.2\text{–}0.6 \text{ eV} \) and thus for typical optical transitions the low energy collisions just above the threshold are most important in determining the collision rates. Steenbock & Holweger, in the absence of any better experimental or theoretical guidance, calculated the collisional excitation and ionization rates by modifying a formula from Drawin (1968) for H+H which is itself a modification of the classical Thomson formula for excitation by electrons (cf. Lambert 1993). In recent years some work has been devoted to improve these highly uncertain H collision cross-sections. Low-energy experimental data have been obtained (Fleck et al. 1991) and \textit{ab initio} calculations performed down to the threshold (Belyaev et al. 1999) for the Na+H system with good agreement between theory and experiment. However, these results are for only the very lowest states of this one system. For non-LTE calculations, estimates are required for transitions between all states which might affect the population of the states of interest. It is for this reason that the modified Drawin formula (often with a scaling factor determined astrophysically) is still often in use despite that it is known to overestimate the Na(3s)+H→Na(3p)+H collision rate by several orders of magnitude.

Recently, calculations for Li+H collisions for all transitions between the states \( \text{Li}(2s,2p,3s,3p,3d,4s,4p,4d,4f) + \text{H}(1s) \) and \( \text{Li}^+ + \text{H}^- \) have been performed (Belyaev & Barklem 2003). This paper should be consulted for details and justification of the approaches used. In brief summary, on the basis of the interpretation of the experimental and theoretical results for Na+H (Fleck et al. 1991; Belyaev et al. 1999), non-adiabatic regions associated with avoided ionic crossings in the adiabatic potential curves are expected to provide the basic mechanism for the transitions at low energy. A simple physical interpretation of this process is that at certain separations during the collision the optical electron associated with the Li atom may tunnel to the H atom, leading to a predominantly ionic charge distribution \( \text{Li}^+\text{H}^- \) of the LiH quasi-molecule. Later, at another avoided crossing, the electron may tunnel back towards the Li atom into a different covalent charge distribution leading asymptotically to a different final Li state. The electron may also remain with the H atom leading to an ion-pair production reaction \( \text{Li}^+\text{H} \rightarrow \text{Li}^+\text{H}^- \). For the transitions between the lowest four states a fully quantum mechanical approach has been used, while for the transitions involving higher states, a multichannel Landau-Zener model has been used. The model approach is justified for the higher crossings where the requirements of the Landau-Zener model are better fulfilled.

For the charge transfer reactions \( \text{Li}^+ + \text{H} \rightarrow \text{Li}^+ + \text{H}^- \), referred to as ion-pair production and mutual neutralization, our calculations use the model approach. More elaborate calculations, using a diabatic molecular expansion method, have been made by Croft et al. (1999b). This process has a remarkably large cross section near the threshold in alkali-hydrogen systems, particularly to and from the first excited state. This has been predicted theoretically (Bates & Boyd 1956; Janev & Radulović 1978; Croft et al. 1999a; Dickinson et al. 1999) and...
is consistent with experiment (Peart & Hayton 1994). Despite
that this process has been known to be remarkably efficient in
various fields (e.g. plasma physics, early universe chemistry)
for some time, to our knowledge this is the first time it has
been considered in a stellar atmosphere application of Li.

2. Collision rate coefficients

The rate coefficients \( \langle \sigma v \rangle \) for excitation and de-excitation
\( \text{H}(1s) + \text{Li}(nl) \rightarrow \text{H}(1s) + \text{Li}(n'l') \), and the charge transfer reactions
\( \text{Li}(nl) + \text{H} \rightarrow \text{Li}^+ + \text{H}^- \) are presented in Table 1. The data
have been obtained by integrating a Maxwellian velocity distri-
bution with cross-sections from Belyaev & Barklem (2003)
in the case of excitation and de-excitation, and from Croft
et al. (1999b) in the case of mutual neutralization, with ion-pair
production cross-sections obtained via the principle of detailed
balance. Thus the data represent, in our opinion, the best avail-
able estimates. Note that all forward and backward rates were
computed separately, but should be connected by the detailed
balance relation. Inspection of the data reveals the remarkably
large rate coefficients for \( \text{Li}(nl) + \text{H} \rightarrow \text{Li}^+ + \text{H}^- \), particularly for the
\( n = 3 \) states.

For the temperatures here the uncertainty in the rate coeff-
ficients is determined by the uncertainty in the cross sections
near the threshold. The uncertainty in the input cross sections
is discussed in detail in the relevant papers. In summary, the ac-
curacy for transitions between the lower states (2s, 2p and 3s) is
estimated to be better than a factor of 2. For the excitations in-
volving higher states the data are expected to be accurate within
an order of magnitude. Comparison with experimental results
for the total neutralization cross-section with \( \text{D}^- \) (which uses
the same interaction potentials as for \( \text{H}^- \)) finds the theoretical
result about 20% greater at the lowest measured energy 0.68
eV (see Croft et al. 1999a), with a general trend of the dis-
agreement becoming larger at lower energies, recalling that the
collision energies of importance here are \( E \approx 0.2 - 0.6 \text{eV} \).

Lambert (1993) presented unpublished estimated rate coeffi-
cients for the \( 2s \rightarrow 2p \) transition computed by Allen & Dick-
inson. Our data are roughly an order of magnitude smaller.

Comparisons were made with the modified Drawin formula
for all optically allowed transitions at 5000 K. Except for an ex-
traordinary \( 3s \rightarrow 4p \) transition, the Drawin formula gives a rate coeffi-
cient between roughly one and six orders of magnitude greater
than our result. This reinforces the view that the Drawin for-
mula typically greatly over-estimates the collisional efficiency,
as judged by the available (admittedly rather scant) evidence.

3. Application to non-LTE formation of Li lines

To assess the impact of the data on the interpretation of
stellar spectra, we have performed non-LTE calculations for
Li in cases of particular interest using the MULTI-code for
1D statistical equilibrium problems (Carlsson 1986) and the
MULTI 3D-code (Botnen 1997; Botnen & Carlsson 1999; As-
plund et al. 2003) for the 3D case. The adopted model atom is
the 21-level atom compiled by Carlsson et al. (1994). To test the
impact of the new data three model atoms were used, namely
the original model atom with no H collisions \((\text{nH})\), the model
with the new H collision data added \((\text{wH})\), and a model with the
H collision rates halved \((\text{w0.5H})\); the LTE results have been
obtained with the same codes using an atom with extremely
large collisional cross-sections to ensure consistency with the
non-LTE calculations. The 1D model atmospheres are from the
MARCS code (Gustafsson et al. 1975 and subsequent updates).
The 3D models and calculations are as detailed in Asplund
et al. (1999, 2003). Calculations were performed for the Sun,
the metal-poor subgiant HD140283 and the metal-poor turnoff
star HD84937. Equivalent widths for the 670.8 nm line are pre-
presented in Table 2. Departure coefficients for the lower states in
the 1D non-LTE models for the Sun and HD140283 are pre-
presented in Fig. 1.

Although quantitatively different, the overall effects of the
H collisions are similar in the 1D and 3D cases. Almost all
of the difference resulting from the inclusion of the H colli-
sion data is caused by the reaction \( \text{Li}(3s) + \text{H} \rightarrow \text{Li}^+ + \text{H}^- \). Re-
moving all H collisions but this reaction results in equivalent
widths within 1\% of the results for the \( \text{wH} \) model. This reaction
causes a stronger collisional coupling between the ionization
stages, nearly thermalizing the \( 3s \) state. Photon suction (Bruls
et al. 1992) results in the other levels being affected, in particu-

\[ \begin{align*}
\text{H}(1s) + \text{Li}(nl) & \rightarrow \text{H}(1s) + \text{Li}(n'l') \\
\text{Li}(nl) + \text{H} & \rightarrow \text{Li}^+ + \text{H}^- \\
\end{align*} \]
Table 1. Rate coefficients $\langle \sigma v \rangle$, in units of cm$^3$ s$^{-1}$, for the processes H(1s)+Li(nl)→H(1s)+Li(n'l'), or where indicated H(1s)+Li(nl)→H + Li$^+$ (1s$^2$) and H + Li$^+$ (1s$^2$)→H(1s)+Li(n'l'), for selected temperatures in the range $T = 2000$–$8000$ K. Asterisks indicate transitions where the calculated cross sections are unreliable.

<table>
<thead>
<tr>
<th>Initial state nl</th>
<th>1s</th>
<th>2s</th>
<th>3s</th>
<th>1s'</th>
<th>2s'</th>
<th>3s'</th>
</tr>
</thead>
<tbody>
<tr>
<td>3s</td>
<td>3.79–17</td>
<td>1.74–13</td>
<td>7.80–11</td>
<td>1.30–12</td>
<td>1.78–13</td>
<td>2.51–14</td>
</tr>
<tr>
<td>2s</td>
<td>1.70–18</td>
<td>1.72–10</td>
<td>1.22–11</td>
<td>2.32–11</td>
<td>5.00–12</td>
<td>1.38–13</td>
</tr>
<tr>
<td>3s</td>
<td>3.79–10</td>
<td>5.15–10</td>
<td>1.97–09</td>
<td>2.00–10</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>3p</td>
<td>3.79–11</td>
<td>1.56–10</td>
<td>1.72–11</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>2d</td>
<td>9.07–07</td>
<td>1.48–11</td>
<td>1.67–11</td>
<td>7.31–12</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>3f</td>
<td>2.60–07</td>
<td>5.87–12</td>
<td>3.18–12</td>
<td>5.42–12</td>
<td>5.10–13</td>
<td>*</td>
</tr>
<tr>
<td>H$^+$ + Li$^+$</td>
<td>4.12–13</td>
<td>2.65–11</td>
<td>1.07–07</td>
<td>5.39–08</td>
<td>5.34–09</td>
<td>7.63–12</td>
</tr>
</tbody>
</table>

Table 2. Predicted flux equivalent widths (in pm=10 mÅ) for the 670.8 nm line in the Sun, HD140283 and HD84937 based on 1D and 3D models, in both LTE and non-LTE. Results are shown for various model atoms as described in the text. Note that the 3D results shown are based on only one snapshot and hence are not appropriate for direct comparison with the 1D cases.

<table>
<thead>
<tr>
<th>Star</th>
<th>$T_{\text{eff}}$ [K]</th>
<th>parameters</th>
<th>log $\epsilon_{\text{Li}}$</th>
<th>$W_{\text{LTE}}$ nH</th>
<th>$W_{\text{NLTE}}$ nH</th>
<th>$W_{\text{LTE}}$ wh</th>
<th>$W_{\text{NLTE}}$ wh</th>
<th>$W_{\text{LTE}}$ wH</th>
<th>$W_{\text{NLTE}}$ wH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sun</td>
<td>5777</td>
<td>log $g$ = 4.00</td>
<td>0.85</td>
<td>1.14</td>
<td>0.40</td>
<td>0.38</td>
<td>0.37</td>
<td>0.55</td>
<td>0.40</td>
</tr>
<tr>
<td>HD140283</td>
<td>6590</td>
<td>3.75–25</td>
<td>2.00</td>
<td>1.31</td>
<td>1.44</td>
<td>1.57</td>
<td>1.55</td>
<td>1.79</td>
<td>1.26</td>
</tr>
<tr>
<td>HD84937</td>
<td>6330</td>
<td>4.04–22.5</td>
<td>2.00</td>
<td>1.31</td>
<td>1.44</td>
<td>1.57</td>
<td>1.55</td>
<td>1.79</td>
<td>1.26</td>
</tr>
</tbody>
</table>

1 Note that it is not appropriate to directly compare the equivalent widths in Table 2 to estimate the net abundance difference between 1D and 3D as the 3D results are here only shown for one snapshot. The proper procedure is to add the 3D non-LTE corrections obtained here to the 3D LTE corrections published by Asplund et al. (1999) based on a long time-sequence with better numerical resolution.
Li abundances and the predicted primordial Li abundance from Big Bang nucleosynthesis. High-redshift deuterium measurements and analyses of the cosmic microwave background yield a relatively high baryon density of the Universe (e.g. Burles et al. 2001). In particular, the recent WMAP analysis (Bennett et al. 2003) corresponds to a primordial Li abundance of $\log\epsilon_{\text{Li},p} = 2.69 \pm 0.13$ based on standard Big Bang nucleosynthesis (Burles et al. 2001). The small amount of scatter in observed halo Li abundances is very difficult to reconcile with uniform stellar Li depletions of 0.4 dex or more. Likewise, it would require improbably high effective temperatures to resolve the disagreement. Clearly, halo stars and their spectrum formation are not as well understood as perhaps thought.

4. Discussion

We have found that while excitation and de-excitation by inelastic H collisions are not important in thermalizing Li, the charge exchange reactions involving the Li$(3s)$ state, are quite important. This mechanism is almost certainly important also in other alkalis (Na, K, Rb etc), where large cross-sections are also found (Dickinson et al. 1999; Janev & Radulović 1978). For other elements, further detailed calculations will be required to determine whether inelastic H collisions, including excitation and charge exchange, are important. The main obstacle for such calculations at present is the quantum chemical potentials and couplings required for a large number of molecular states. Though systems of avoided ionic crossings exist in all metal hydride quasi-molecules, we note other mechanisms may be important. As suggested by Lambert (1993), the importance of details in the molecular dynamics, such as avoided ionic crossings, in this process makes a simple general recipe impossible, in contrast to collisional broadening and depolarization by H where such effects play a lesser role (Anstee & O’Mara 1995; Barklem & O’Mara 2001; Derouich et al. 2003). \textit{Ab initio} potentials for alkaline-earth-hydrides are possible with current techniques (Chambaud & Lévy 1989). However, some cases of particular astrophysical interest such as O+H and Fe+H present a considerable challenge.

\textit{Acknowledgements.} We are indebted to F.X. Gadéa and A.S. Dickinson for providing us with the quantum chemical data used in computing the cross sections, and their results for mutual neutralization. We thank D. Kiselman for encouraging us to investigate inelastic H collisions. We gratefully acknowledge support from the Swedish Research Council, the Swedish Royal Academy of Sciences, the Göran Gustafsson Foundation and the Australian Research Council.

\textbf{References}

Anstee, S. D., & O’Mara, B. J. 1995, 253, 549
Asplund, M., Nordlund, Å., Trampedach, R., & Stein, R.F. 1999, 346, L17
Asplund, M., Carlsson, M., & Botnen, A.V. 2003, 399, L31
Belyaev, A. K., Grosser, J., Hahne, J., & Menzel, T. 1999, 60, 2151
Belyaev, A. K., & Barklem, P. S. 2003, submitted
Bennett, C. L., Halpern, M., Hinshaw, G., et al., 2003, in press
Bonifacio, P. 2002, 395, 515
Bruls, J. H. M. J., Rutten, R.J., & Shchukina, N. G. 1992, 265, 237
Burles, S., Nollett, K. M., & Turner, M. S. 2001, 552, L1
Carlsson, M., Rutten, R. J., Bruls, J. H. M. J., & Shchukina, N. G. 1994, 288, 860
Croft, H., Dickinson A. S., & Gadéa, F. X. 1999b, 304, 327
Derouich, M., Sahal-Bréchot, S., Barklem, P. S., & O’Mara, B. J. 2003, 404, 763
Drawin, H. W. 1968, Z. Phys., 211, 404
Gustafsson, B., Bell, R. A., Eriksson, K., & Nordlund, Å. 1975, 42, 407
Janev, R. K., & Radulović, Z. M. 1978, 17, 889
Steenbock, W., & Holweger, H. 1984, 130, 319

P. S. Barklem et al.: Inelastic H+Li and H$^-$+Li$^+$ collisions in stellar atmospheres 5