Abstract. The precise measurement of the chemical composition of stars is a fundamental problem relevant to many areas of astrophysics. State-of-the-art approaches attempt to unite accurate descriptions of microphysics, non-local thermodynamic equilibrium (non-LTE) line formation and 3D hydrodynamical model atmospheres. In this paper I review progress in understanding inelastic collisions of hydrogen atoms with other species and their influence on spectral line formation and derived abundances in stellar atmospheres. These collisions are a major source of uncertainty in non-LTE modelling of spectral lines and abundance determinations, especially for old, metal-poor stars, which are unique tracers of the early evolution of our galaxy.

Full quantum scattering calculations of direct excitation processes $X(\text{nl}) + H \leftrightarrow X(\text{n}'l') + H$ and charge transfer processes $X(\text{nl}) + H \leftrightarrow X^+ + H^-$ have been done for Li, Na and Mg [1,2,3] based on detailed quantum chemical data, e.g. [4]. Rate coefficients have been calculated and applied to non-LTE modelling of spectral lines in stellar atmospheres [5,6,7,8,9]. In all cases we find that charge transfer processes from the first excited S-state are very important, and the processes affect measured abundances for Li, Na and Mg in some stars by as much as 60%. Effects vary with stellar parameters (e.g. temperature, luminosity, metal content) and so these processes are important not only for accurate absolute abundances, but also for relative abundances among dissimilar stars.

1. Introduction

Precise relative and absolute stellar chemical abundances from spectroscopy are needed to address many fundamental problems in modern astrophysics, e.g. the chemical and dynamical evolution of the Galaxy, the solar system and its place in the Galaxy, and understanding stellar processes such as mixing and gravitational settling. In particular, old metal-poor stars play a key role in understanding the evolution of the early universe and the formation of the first structures. While distant quasars and galaxies probe the early universe directly, the information they provide is rather general. On the other hand, the compositions and kinematics of old long-lived stars in the Milky Way also probe the early universe in an indirect but very detailed manner (so called "galactic archeology" [10]). Old stars are generally characterised by a lack of heavy elements, often referred to in astrophysics as "metals", and thus such stars are "metal-poor" (since the elements heavier than Li have been produced during the chemical evolution of the universe, and were not present immediately after the Big Bang). Since the very first stars may no longer be observable, we must look for the chemical signatures of the first generations of stars in these old stars, which presumably were formed in subsequent generations.
We routinely observe spectral line strengths with precision of order 0.01 dex\(^1\) (~2%). Systematic errors dominate and relative abundances have estimated precision of typically an order of magnitude larger (>0.1 dex (>20%), even ~1 dex (a factor of 10). This considerably limits our ability to accurately interpret stellar chemical abundances. An example of this is shown in an abundance-abundance diagram in figure 1, taken from [11]. Here we see that chemical evolution models predict structure in the relative abundances of metal-poor stars on a scale of 0.01 dex – the thin filamentary structures indicate sequences of stars enriched by only one supernova, i.e. true second generation stars. Such structures would tell us a great deal about the first generations of stars and the early chemical evolution of the Galaxy. Comparison with observations is difficult since the observations have errors of approximately one order of magnitude larger.

![Figure 1. Abundance-abundance diagram showing ratios of Ti/Mg against Ca/Mg.](image)

The current state-of-the-art in stellar abundance analysis attempts advances on three main fronts: 1) accurate descriptions of microphysical processes, 2) three-dimensional hydrodynamical models of the stellar atmosphere, and 3) non-local thermodynamic equilibrium (non-LTE) descriptions of the radiative transfer, and connections between these three fields. In this review I focus on the particular problem of microphysical data needed for non-LTE modelling, especially inelastic collisional processes involving hydrogen atoms. Non-LTE modelling requires accurate descriptions of all microphysical processes on atoms, i.e. all radiative and collisional processes on the atom of interest in the stellar atmosphere. Although basic hand-waving arguments can be made that collisions with electrons are the most important collisional processes in stellar atmospheres (based on the relative speeds of perturbers and the efficiency of collisions expected from the Massey criterion, e.g. [12,13]), the importance of low-energy collisions with hydrogen atoms, usually at least four orders of magnitude more abundant than electrons in line forming regions of cool star atmospheres, has been a

\(^1\) "dex" indicates a logarithmic scale with base 10.

\(^2\) The square bracket notation [X/Y] indicates a logarithmic dex scale where the solar ratio is at zero.
major source of uncertainty, e.g. [14]. This uncertainty becomes even more acute in old metal-poor stars where the abundance of hydrogen atoms may reach as much six orders of magnitude larger than that of electrons due to the scarcity of metals to provide electrons.

Thus, the question has been: does the greater abundance overcome the expected lower efficiency of hydrogen collisions with respect to electrons? About a decade ago there was quite little reliable information in this regard. There was one experimental result at intermediate energies [15], and one low-energy calculation [16] both for the Na(3s)+H → Na(3p)+H process, which demonstrated the importance of the avoided crossings with the ionic state. In astrophysics, the "Drawin formula" [14], an extension of a classical Thomson model, is still routinely employed for allowed transitions despite giving results four orders of magnitude too large for the Na(3s)+H → Na(3p)+H process. Ad hoc estimates are often used for forbidden transitions. In this paper I briefly review work to improve this situation by providing accurate data for inelastic hydrogen collisions for astrophysically important atoms and the impact the data have had on non-LTE stellar abundance analyses.

2. Physics of inelastic hydrogen collisions

The basic theory of atomic collisions has been reasonably well understood for some time [17]. However, the detailed calculation of accurate quantum-chemical data for quasi-molecules required as input to the relevant coupled-channel scattering equations, including for excited states, has been a major hurdle (see, for example, paper by Guitou et al. in these proceedings). Further, while the solution of the scattering equations in the standard adiabatic approach appears straightforward, it encounters difficulties such as the electron translation problem (see paper by Belyaev in these proceedings). Earlier studies such as [15,16] demonstrated, through comparison with the Landau-Zener model and detailed quantum scattering calculations, that the experimental data could be reasonably explained by nonadiabatic transitions associated with avoided crossings, also called pseudocrossings, in the NaH molecular potentials. At pseudocrossings, adiabatic potentials approach each other and the transition probabilities may become large even for slow collisions, despite that the Massey criterion based on atomic energy level spacings predicts the collisions to be nearly adiabatic.

Taking the particular case of low-lying states of NaH as an example, these pseudocrossings arise from interaction of the covalent Na+H and ionic Na'+H− configurations, and are thus called avoided ionic crossings. The adiabatic potentials showing these pseudocrossings are shown in figure 2, where we see clearly the influence of the ionic configuration, which strongly perturbs the potentials from their behaviour at large internuclear distance. Similar effects are seen in other quasi-molecules such as LiH (e.g. [18]) and MgH [4] (also Guitou et al. in these proceedings). Quantum scattering calculations for Li+H [1], Na+H [2] and Mg+H [3] including all or most states below the ionic state asymptotic limit have found this to be an important mechanism for nonadiabatic transitions.

The basic physical interpretation of this mechanism is that, in a given X+H quasi-molecule, starting from a covalent state with appropriate symmetry where the electrons are associated to their respective atoms, at avoided ionic crossings the valence electron associated with the atom X has a probability to tunnel to the H atom resulting in a predominantly ionic charge distribution X'+H−. Later during the collision at a different avoided crossing, there is a probability that the electron may tunnel back to a different covalent molecular state leading finally to a different final state of the atom A, and excitation or deexcitation X(nl)+H → X(n′l′)+H. The electron may also stay with the H atom leading to ion-pair production X+H → X'+H−. Calculations for Li+H, Na+H and Mg+H mentioned above have generally shown that large-valued cross sections for excitation are typically small compared with those for ion-pair production from certain states. This can be easily understood: a large-valued cross section for an excitation process results from passing two avoided ionic crossings, one of them (higher-lying) passed with a small transition probability, while for an ion-pair production process this region is passed with a large nonadiabatic transition probability due to small adiabatic energy splittings at highly excited crossings.
3. Comparison of results
Space does not permit a full comparison of all available cross section and rate coefficient results; a few key examples will be presented here, and the reader is referred to [20] for more thorough examination of the results for Li+H and Na+H and to [7] for Mg+H. In particular we note that figure 3 of [20] compares cross sections at low energy for Na(3s) + H → Na(3p) + H, the single case where experimental data is available. The quantum scattering calculations and the Landau-Zener model results agree quite well with experiment. Near the threshold, where there is no experimental data, the quantum scattering calculations show substantial differences depending on which quantum-chemical data are used. This highlights the sensitivity of the near-threshold cross sections to the uncertainties in the quantum-chemistry data, and gives an estimate of the uncertainties in the calculated cross sections. In this case the uncertainties seem to be around one or two orders of magnitude. However, it should be noted that the uncertainties vary strongly from transition to transition, and the transitions with the largest cross sections have the smallest uncertainties, as low as a factor of 2. Fortunately, these are the most important from an astrophysical perspective (see [6]).

The rate coefficients for Mg+H collisions are plotted against transition energy, $\Delta E$, in figure 3. These plots are similar to those presented for Li+H and Na+H in [20], and include rate coefficients from quantum scattering calculations (upper panel) and those predicted by the commonly used Drawin formula (lower panel). Rate coefficients for charge transfer processes (ion-pair production) are shown in addition to those for excitation. A fit to the data for excitation processes is shown (dotted line), and the fits for Li+H and Na+H from [20] are shown for comparison (dashed lines). We emphasise that the actual data have a large scatter around these fits, and their purpose is to indicate the general behaviour. The most notable aspect of the Drawin formula results is that of the 21 excitation transitions considered, only 5 are optically allowed and can be calculated with the Drawin formula. This is due to the fact that Mg has two valence electrons leading to the presence of singlet and triplet spin terms, between which optical transitions are forbidden. As seen in Li and Na, there is a tendency for the Drawin results to be generally larger than those from quantum scattering calculations by a few orders of magnitude with a significant variation, here ranging from zero to four orders of magnitude larger.
Figure 3. Rate coefficients at 6000 K for excitation and ion-pair production processes in Mg+H collisions, plotted against the transition energy $\Delta E$. Different symbols are used to denote the initial state of the transition following the key given in the upper panel. The upper panel shows the results from this work based on detailed quantum scattering calculations [3]. Symbols inside circles refer to ion-pair production processes (IPP); i.e. the final state is the ionic state Mg$^{+}$+H$^{-}$. The dotted line shows a linear fit to the data for excitation processes (i.e. excluding ion-pair production), which is repeated in the lower panel to aid comparison. The dashed lines show the fits to the corresponding data for Li and Na from [20]. The lower panel shows the results of the Drawin formula, and the inset shows the ratio with the quantum scattering calculations. Optically forbidden transitions, where the Drawin formula is not applicable, are shown in the bottom of the panel.
4. Effects on line formation and stellar abundances

The effects on non-LTE line formation calculations and thus on measured stellar abundances has been examined for Li and Na in [8] and [9]. Work on Mg is presently underway. The most important result is that in both Li and Na it has been found that direct excitation and deexcitation processes, \( X(nl)+H \rightarrow X(n' l')+H \) where \( X \) is the atom of interest, are of little consequence for the statistical equilibrium. However, charge transfer processes, \( X(nl)+H \rightarrow X^++H^- \), particularly where \( nl \) corresponds to the first excited S-state, are important. The resulting effects on abundance corrections in solar-type stars are typically small, of order a few 0.01 dex (2%). In giants the influence is larger, of order 0.05 dex (~12%), and even larger still in metal-poor stars reaching of order 0.1–0.2 dex (25–60%). Thus, these processes are important for accurate absolute abundances, and also for accurate relative abundances of different elements and among dissimilar stars. An example of the evolution of the corrections for Li is shown in figure 4. This shows the increasing importance of hydrogen collision processes as one goes to the lowest metallicities, i.e. the oldest stars which trace the earliest times of the universe.

![Figure 4. Effects on abundance corrections for Li in giant stars with metallicity. The dotted line shows the mean correction found (i.e. considering all possible stellar temperatures) and the full line shows the maximum correction found. Data taken from [8].](image)

5. Conclusion and future

Inelastic processes involving collisions with hydrogen atoms, including charge transfer processes, have been found to be important in cool stellar atmospheres and have significant effects on measured abundances, especially in old metal-poor stars. Thus, accurate data for these processes is very important for understanding the nature of the early universe via galactic archeology. Accurate calculations have now been performed for Li, Na and Mg, and calculations for other astrophysically important elements such as Ca, O and Fe-group elements are planned. Tests of the data directly via measurements of the mutual neutralisation cross sections are planned at the DESIREE experiment [21]. The data and the line formation models can also be tested indirectly via spatially resolved observations on the sun, e.g. [22], and observations for Li and Mg lines were recently obtained at the Swedish Solar Telescope.
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