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Abstract. This work highlights a potential pitfall associated with using optical emission to estimate the expansion velocity of material in laser ablation plumes, specifically when the monitored emission involves transition to a state that is present in high number density. Comparisons of time-gated, spatially resolved, images of the Li(3d → 2p) and Li(2p → 2s) emissions arising in the nanosecond 248 nm pulsed laser ablation of LiF enabled estimation of the distribution of ground state Li atoms in the plume. Analysis of these images revealed that the density of Li(2p) atoms in the early stages of the plume expansion was sufficiently high that even the Li(3d → 2p) emission profiles show evidence of radiation trapping.

1. Introduction
Optical emission measurements are often used to provide an estimate of the expansion velocity of material in the plumes produced during pulsed laser ablation (PLA [1]). However, this technique is not a direct measure of the velocity. Assumptions regarding how the emission profile reflects the distribution of the emitting species must be made. The propagation velocities of electronically excited species deduced from optical emission measurements generally differ slightly from those obtained by time of flight mass spectrometry, which raises questions regarding the formation mechanisms of these excited species.

There have been relatively few PLA studies of alkali halides, [2, 3, 4, 5, 6]. In this paper we investigate the 248 nm nanosecond PLA of LiF and discuss the problems associated with using optical emission measurements to obtain the expansion velocities of Li species in the plume of ablated material, concentrating on the effect of radiation trapping when the monitored emission involves transition to a state that is present in high number density.

2. Experimental Details
The apparatus consisted of a stainless steel vacuum chamber which was evacuated to a pressure of 1 × 10^{-6} Torr. The incident laser beam propagated through a side arm, in the xy-plane at 45° to the target surface normal - here defined as the x-axis. The target, a sintered disk of 99.9 % pure LiF, was rotated during the experiments in order to avoid repeated ablation of the same spot. A KrF cavity (Lambda-Physik EMG150MSC), provided pulses of 15 ns duration at 248 nm. The typical pulse energy (and fluence) employed was ~47 mJ/pulse (12.5 J/cm^2). To record spatially resolved optical emission spectra (OES) the emission was focused onto a quartz fibre directed so as to view a column along the y-axis. A second method of recording the plume emission involved imaging the evolving spatial distributions of selected emitting species by using an intensified-CCD camera in time-gated detection mode, decoupling it from the spectrometer and collecting either the total emission, or just the fraction transmitted through a suitably chosen narrow bandpass filter. Details of the experimental setup are presented elsewhere [7].
3. Results and Discussion

Figure 1 shows OES spectra covering the wavelength range 570 - 700 nm taken at different distances $x$ from the laser-target interaction region (in the range 0–28 mm), by capturing emission in a 1 $\mu$s time gate delayed by $t = 120$ ns after the start of laser excitation. This spectral region is dominated by two Li I spectral lines. The relevant portion of the Grotrian diagram of neutral Li is shown inset. Other Li I emissions were observed in other spectral regions of the spectrum, most notably the $3s \rightarrow 2p$ transition at 812.6 nm, but all were much weaker than the 610.4 nm and 670.8 nm emissions (henceforth termed the Li a and Li b emissions, respectively). The Li a emission dominates the OES spectrum and the ratio of the Li a to Li b emission intensities decreases with increasing $x$. This is at first sight surprising, given that the emitting (3d) states responsible for Li a emission lie higher in energy. The explanation for these differences lies in the fact that the Li b emission terminates at the ground (2s) state, and so can be re-absorbed if there is a significant population of ground state neutral Li atoms.

![Figure 1. OES spectra recorded at distances $x$ from the laser spot (in the range 0–28 mm), by capturing emission in a 1 $\mu$s time gate delayed by $t = 120$ ns after the start of laser excitation. Note: only the region around the two main Li I spectral lines is shown. Inset: portion of the Grotrian diagram for Li I.](image)

Before discussing the temporal evolution of the optical emission from the plume, it is important to reflect on the time-scales involved. The radiative lifetimes of these excited states is typically tens of ns. However, here, it will be shown that Li I emissions are still readily detectable after $>10$ lifetimes. A mechanism for populating the observed emitting levels after the ablation event is thus required. Recombination of Li$^+$ ions and electrons, stabilised by a third body, (or Li$^+$ neutralisation by electron transfer from F$^-$ ions) constitutes one obvious sources of excited neutral Li atoms. As suggested previously, [8] such electron ion recombination (EIR) is likely to proceed via highly excited Rydberg states, and subsequent radiative cascade via the monitored transitions and, ultimately, to the ground electronic state. In this scenario, the observed distribution of emitting neutrals will reflect the degree to which the overall Li$^+$ and e (or F$^-$) distributions overlap in space and time. As commented previously, Li b emission can be re-absorbed by ground state Li atoms, whereas the Li a emission connects two excited states, neither of which are expected to have large steady state populations. Comparing time gated images of the Li a and Li b emissions thus allows estimation of the extent of radiation trapping and thus some insight into the evolving distribution of ground state Li atoms in the
plume.

Figure 2 shows a series of wavelength filtered CCD images (viewed along $y$) of the plume. The images were all collected using a 20 ns time gate but at different delays: $t = 120$ ns for images (a)–(d), $t = 520$ ns for (e)–(h) and $t = 800$ ns for (i)–(l). Images (a), (e) and (i) are unfiltered images, whereas (b), (f) and (j) are taken through a 610 nm filter that transmits just the Li a emission, (c), (g) and (k) with a 670 nm filter, which select the Li b emission, and (d), (h) and (l) using a long pass filter that only transmits wavelengths $> 780$ nm, thereby sampling predominantly the 812.4 nm Li I emission. Comparing figures 2i, j and l, it is clear that the distribution of the total OES signal mirrors that of Li a and the $> 780$ nm (mainly 812.6 nm Li I) emissions. The Li b emission shows a strikingly different time evolution, however. At early time, the Li b emission appears to peak at an $x$-value behind the maximum of the Li a image. At $t \sim 520$ ns, the distribution shows a double maximum along the $x$-axis (see figure 2g). The first is closer to the laser-target interaction region than the peak of the Li a emission, the second more distant. The relative intensities of the leading (i.e. further from the ablation spot) and trailing maxima evolve with increasing $t$, so that by $t \sim 800$ ns the Li b emission profile again shows a single maximum that is significantly further forward than the peak in the Li a emission profile recorded at the same $t$.

As previously, [8] estimates of the mean velocities $\langle v \rangle$ of the emitting components in the plume could be derived as follows. The emission intensity profiles along the $x$-axis of each of the captured time gated CCD images were first analysed, and the peak (or peaks) found. The peak positions ($x_{\text{peak}}$) were plotted as a function of time delay $t$ for both the Li a and Li b emissions. Results for the Li a, shown in figure 3a, fit to a reasonable straight line, the gradient of which implies a value of $\langle v \rangle = 10.9 \pm 0.4$ km/s for the emitting species. Figure 3b shows the corresponding plot for the Li b (670 nm) emission. The Li b intensity profiles generally show two maxima, the relative intensities of which are seen to swap over at $t \sim 600$ ns. Only the $x_{\text{peak}}$ value of the predominant peak is plotted in the $x_{\text{peak}}$ versus $t$ plot displayed in figure 3b - hence the discontinuity around $t \sim 600$ ns.

Figure 3. Plots of $x_{\text{peak}}$ versus $t$ for the emissions (a) filtered at 610 nm, (b) filtered at 670 nm.

Figure 4. Attenuation profiles at $t = 280$ ns (a), 600 ns (b) and 800 ns (c).

Here, the optical emission is dominated by transitions of neutral Li. We postulate that these arise mainly as a result of neutralisation of Li$^+$ ions, by EIR. However, we should now consider the distributions of ground-state material in the plume. The plume images filtered so as to
select the Li a (3d→2p) and Li b (2p→2s) emissions are dramatically different. Given the short radiative lifetimes of the 3d and 2p levels (relative to the observation times), we can envisage no reason why the true distribution of Li*(3d) or Li*(3s) atoms should differ significantly from that for Li*(2p). The Li a transition terminates on an excited state(2p), the steady state number density of which will be much lower than that of the ground state. Its intensity profile should thus be much less affected by radiation trapping. Differences between the Li a and Li b images recorded at any given t might thus provide some insight into the distribution of ground state Li atoms at that time. A first estimate of the attenuation profile was obtained dividing the intensity versus x distribution of the Li a emission by that of the Li b emission. Before division the profiles were scaled to match at large x. Figure 4 shows three attenuation profiles so derived. The t = 280 ns profile (figure 4(a)) is quite sharp, and peaks ahead of x_{peak} for the corresponding Li a emission. By t = 600 ns (figure 4(b)) the attenuation profile is much broader and shows a hint of bimodality, and by t = 800 ns the profile is broader still, and appears to peak at smaller x than the x_{peak} value observed at 600 ns. This long time attenuation profile is much closer to the shifted Maxwellian velocity distribution that is characteristic of most ablation plumes. [1]

The seemingly unphysical nature of the ground state velocity distribution implied by the attenuation profiles derived at short t, highlights a shortcoming of the preceding analysis - namely the assumption that the Li a emission is immune to the effects of self-absorption. Radiation trapping will be most important in the densest regions of the plume, i.e. at early t, before the ablated material has expanded into an ever increasing volume. The self-absorption considered thus far is of Li b emission, but the net effect of the emission - re-absorption cycle is to maintain an excessive (relative to local thermal equilibrium) population in the 2p state which will serve to attenuate the 3d→2p and 3s→2p emissions in the densest regions of the plume. The effect of such re-absorption is imperceptible in the t = 800 ns profile (figure 4(c)) - where the plume density is lowest, but is responsible for the central dip in the t = 600 ns profile (figure 4(b)) and the apparent dramatic loss of ‘attenuation’ (and thus the implied absence of ground state Li atoms) at small x in the t = 280 ns profile (figure 4(a)). Thus, the sharp peak in the deduced attenuation profile is a consequence of the method used to estimate the attenuation. At small t, both the Li a and Li b signals are affected by re-absorption, so their ratio no longer represents simply the attenuation by ground state Li atoms.

In conclusion, we highlight a potential pitfall associated with OES measurements of the velocity of species in ablation plumes, specifically when the emission involves a transition to a state that is present in high number density. Radiation trapping in such cases can result in very misleading spatial and temporal emission profiles.

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