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Time-resolved study of the plasma-plume emission during the nanosecond ablation of lithium fluoride

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ABSTRACT

The properties of the plasma-plume accompanying the pulsed laser ablation of lithium fluoride (LiF) at medium-vacuum conditions (4 Pa) were studied by a combination of spatially and temporally resolved optical emission spectroscopy. The laser-induced plasma at CO_2 laser intensities ranging from 0.18 to 4.7 GW × cm^{-2} was found strongly ionized in F^+, Li^+, F^{2+}, and F^{3+} species and rich in neutral lithium and fluorine atoms. The temporal behavior of excited Li atoms and ionized excited species F^+, Li^+, F^{2+}, and F^{3+} is reported. The results show a faster decay of the continuum emission and Li^+, F^{3+}, and F^{2+} ionic species than in the case of F^+ and neutral Li atoms. The velocity distributions of atomic and ionic species are obtained from time-of-flight measurements. Electron density and excitation temperature in the laser-induced plasma were estimated from the analysis of spectral data at various delay times from the CO_2 laser pulse incidence. From the intensity decay of Li^+, F^+, F^{2+} and F^{3+} with the delay time, we have estimated the three-body electron–ion recombination rate constants for these species.

1. Introduction

Lithium fluoride (LiF) is an important material used as a component of molten salts, specialized vacuum UV, UV, visible and IR optics (transmission range: 0.104–7 μm), in thermo luminescent dosimeters, in mixtures used in nuclear reactors and in polymer light-emitting diodes. It is the material with the most extreme UV transmission of all because it has the largest band gap [1] and is also used for X-ray monochromator plates where its lattice spacing makes it the most useful analysis crystal. In spite of its high transparency, when LiF is irradiated with short pulses of high-intensity laser radiation is no longer transparent. Laser-induced breakdown spectroscopy (LIBS) is a powerful growing technique used in different areas of research [2–6] (environmental science, detection and quantification of analytes in a large range of matrices, chemistry and reactivity, production of classical and novel materials, etc.). In all these applications, it is very important to understand the composition and the temporal evolution of the species in the plasma.

When a high-intensity laser beam is focused on a sample, it is well known that thermal processes occur, leading to a material melting, sublimation and ionization of the expanding hot plasma (spark) that evolves with time and the excited species relax further. In addition, the laser pulse interacts with the expanding vapor so that the temperatures of the excited species, electronic densities and charge states depend strongly on the laser pulse intensity. Several processes can occur in the laser-induced plasmas, such as electron ionization, radiative excitation and de-excitation, ion–atom charge transfer and three-body electron–ion recombination. Because of the transient characteristics of the plasma plume formed by laser-induced breakdown (LIB), optical emission spectroscopy (OES) technique with time and space resolution is especially suitable to obtain information about the behavior of the produced species as well as to study the dynamics of the plasma expansion.

The LIB technique in LiF has been studied by several researchers [7–10] using high-power lasers. Some detailed time-resolved studies of LIB plasmas in different samples have been reported recently by us [11–14].

In this paper, we report new results on wavelength- and time-resolved measurements of the optical emissions that accompany the plasma-plume arising in the CO_2 pulsed-laser ablation of LiF. The emission observed in the plasma region is mainly due to electronic relaxation of excited F, F^+, F^{2+}, F^{3+}, Li and Li^+ fragments. The time dependence and velocity distributions of space-integrated emission of some excited species are presented from time-of-flight (TOF) measurements using time-resolved OES. Intensities of some lines of F^+ were used for determining electron temperature, and their Stark-broadened profiles were employed to calculate electron density. The temporal behavior of intensity lines of Li^+, F^+, F^{2+} and F^{3+} has been employed for the estimation of the three-body electron–ion recombination rate constants for these species.

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2. Experimental procedure

The experimental setup and equipment used has been described elsewhere [13]. The laser beam from a transversely excited atmospheric (TEA) CO_2 pulsed-laser, with a pulse intensity of 0.18–4.7 GW × cm^{-2} at a wavelength of 10.591 μm, was focused (NaCl lens of 24 cm focal length) onto a LiF crystalline target at medium-vacuum conditions (P_{air} = 4 Pa). The laser-pulse intensity was varied with the aid of several calibrated CaF_2 attenuating plates. The measured focused-spot area was 7.85×10^{-3} cm^2. The optical emission from the laser-induced plasma was imaged 1:1 with a quartz lens (focal length 4 cm) onto the entrance slit of different spectrometers. The laser-induced LiF plasma emission was collected in a direction perpendicular to the incident laser beam at a fixed distance z along the plasma axis. To change the z distance, the target and the focusing NaCl lens were shifted in order to obtain a minimum focal spot area. The temporal history of the plasma was recorded by a gateable ICCD (Andor iStar DH-734). For time-resolved measurements, the ICCD detector is synchronized with the start of the laser pulse by adjusting the gate width time and the delay time. For better accuracy of the plasma temporal characterization, the measurements consist in the accumulation of 10 shots and a repetition rate of 1 Hz. The intensity response of the detection system was calibrated with a standard halogen lamp (Osram No. 6438, 6.6 A, 200 W).

3. Results and discussion

3.1. Identification of the plasma species

Fig. 1 displays a low-resolution OES of the LIB in LiF compared with the atomic/ionic lines of F, F^+, F^{2+}, F^{3+}, Li and Li^+ along with the assignments of atomic/ionic lines of fluorine and lithium and relative intensities [15]. In this experiment, the laser delivers 734 mJ at 10.591 μm, leading to an estimated power of 43.9 MW, intensity (power density or irradiance) of 1.5 GW × cm^{-2}, fluence of 93.5 J cm^{-2}, photon flux of 7.1×10^{28} photon × cm^{-2} × s^{-1}, and electric field of 0.74 MV × cm^{-1} on the focal position. It is noteworthy to observe F^{3+} species but some emission lines observed at 217.144, 229.829 and 245.692 nm can only be due to F^{3+} species. Strong F^+, Li and Li^+ lines dominate the spectrum indicating the high ionization of LiF produced by LIB. In order to get more insight into LIB LiF plasma and to obtain an unambiguous assignment of the emission, we have scanned the spectra at high-resolution (≈0.01 nm). As an example, Fig. 2 shows different emission spectra from laser-induced (1.5 GW × cm^{-2}) LiF plasma and the fine structure of some F^{2+} lines ($2s^22p^2(^3P)3p\ ^4D^0_{J'} \rightarrow 2s^22p^2(^3P)3s\ ^4P_{J''}$; $2s^22p^2(^3P)3p\ ^2D^0_{J'} \rightarrow 2s^22p^2(^3P)3s\ ^2P_{J''}$). A schematic illustration of the observed fine structure of these F^{2+} lines is also presented. The relative separations of the energy term and line components are drawn to scale from data given by NIST Atomic Spectral Database [15].

3.2. Plasma excitation temperature measurements

The excitation temperature T_{exc} was calculated according to the well-known Boltzmann plot method [16,17] by using the relative intensities of several F^+ lines from the time-integrated spectrum. An example of this plot is shown in Fig. 3a. The spectral line wavelengths, the energies of the upper levels, statistical weights, and transition probabilities used for these lines were obtained from NIST [15]. The obtained excitation temperature was 37,800 ± 3500 K. The data errors are due to the uncertainty in intensities, wavelengths and transition probabilities.

The excitation temperature was also estimated at different delay times (Fig. 3b) using the simplified Boltzmann method considering only two lines of F^{2+} at 288.8 and 293.3 nm. One observes that the excitation temperature is elevated up to 37,600 K at a delay time of 0.4 μs. When the time is greater than 0.6 μs the temperature decreases. The decreasing of the excitation temperature is due to the expansion of the plasma. During this expansion, the thermal energy is converted into kinetic energy, and the plasma cools down rapidly.

3.3. Effect of the laser irradiance

The emission of the LiF plasma plume as a function of the laser intensity is shown in Fig. 4. The different bands of the first negative system of $N_2^+(B^2\Sigma_u^+–X^2\Sigma_g^+)$ and the second positive system of $N_2(C^3\Pi_u–X^3\Pi_g)$ are observed. In addition, the assignment of the rotational spectrum (P_1, P_2, R_1, R_2, $^RQ_{12}$ and $^PQ_{21}$ branches) of 0–0 $B^2\Sigma_u^+–X^2\Sigma_g^+$ band of N_2^+ is shown [18,19]. An increase of the atomic/ionic and molecular emission intensity growing laser irradiance was observed. At higher laser power densities, the spectral lines are more broadened than at lower power densities as a result of the high pressure associated with the plasma. It

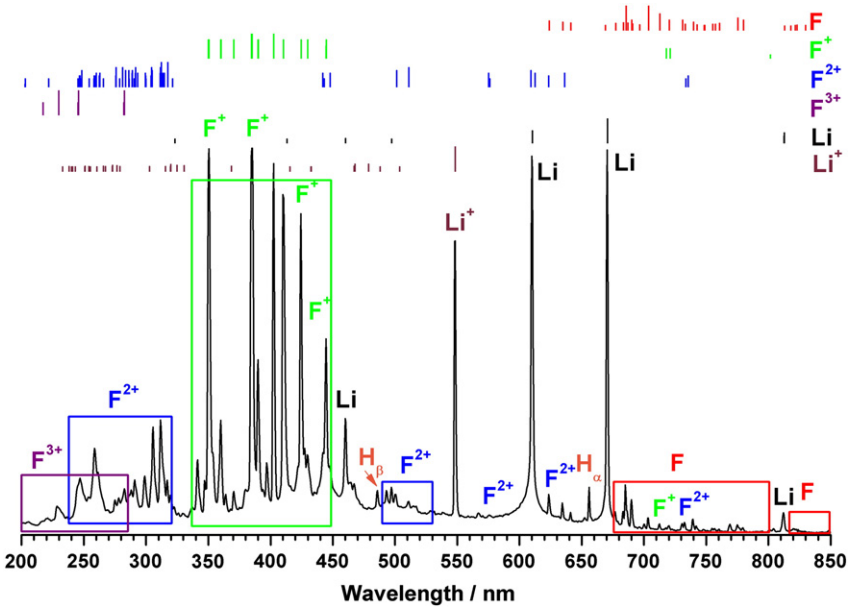

Fig. 1. An overview of the LIB emission spectrum of LiF plasma induced by a TEA-CO_2 high-power pulsed laser (1.5 GW × cm^{-2}) excited by the line 10P(20) at λ = 10.532 μm, compared with atomic/ionic line positions and relative intensities listed at NIST of F, F^+, F^{2+}, F^{3+}, Li and Li^+.