

Femtosecond relaxation kinetics of highly excited M_{Na}^{**} states in CaF_2 at 3.2 eV and 4.7 eV

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Abstract Femtosecond (fs) laser pulses at variable delay times allowed us to track the fast non-radiative transitions between the manifold of highly excited M_{Na}^{**} states to the lower lying fluorescent M_{Na}^* state in CaF_2 . Two distinct M_{Na}^{**} states of the manifold at 3.16 eV ($M_{\text{Na}2}^{**}$) and 4.73 eV ($M_{\text{Na}3}^{**}$) were populated using the second (SH) and third harmonics (TH) of fs laser light at 785 nm. The population kinetics of the fluorescent M_{Na}^* state in the 2 eV excitation energy range was revealed by depleting its fluorescence centered at 740 nm using fundamental near infrared (NIR) fs laser pulses. The related time constants for $M_{\text{Na}2,3}^{**} \rightarrow M_{\text{Na}}^*$ relaxation amounted to 1.0 ± 0.14 ps and 3.0 ± 0.3 ps upon SH and TH excitation, respectively.

1 Introduction

Calcium fluoride (CaF_2) is one of the most important crystalline materials in terms of ultraviolet (UV) and vacuum ultraviolet (VUV) optics, since it shows a large energy gap of around 12 eV [1]. Even though it can be manufactured in extreme purity, traces of impurity atoms are sufficient to induce extrinsic lattice defects, which in turn affect its transmission, absorption, and laser damage behavior. During applications with high laser intensities, these defects become particularly crucial [2–6].

The investigation of defects in CaF_2 has a relatively long history [7–9], particularly with the M center [7, 10–13]. Sodium (Na)-stabilized M centers (M_{Na} centers) yield characteristic absorption bands around 600 nm, 385 nm, and 322 nm [13–15] and show fluorescence after absorption into these bands as well as upon ArF (193 nm) and F_2 laser excitation (157 nm) [16]. As a result, M_{Na} centers are of great importance for optical components applied in ArF laser lithography. Their concentration has to be minimized to obtain CaF_2 of a very high transmission and durability in the UV and DUV ranges. Furthermore, it is helpful to know the optical properties of the M_{Na} defects and their formation kinetics in order to suppress their effect on the transmission and the durability of CaF_2 crystals. However, the two-photon absorption (TPA) of CaF_2 exhibits a peculiarity (Fig. 1) [17, 18]: The TPA coefficients obtained with ArF laser excitation (30 ns pulses) show a pronounced increase with increasing M_{Na} concentration whereas the TPA coefficient obtained with the fourth harmonic of a femtosecond (fs) laser (197 nm, 350 fs) is independent of the M_{Na} concentration. In Fig. 1 the fluorescence signal amplitude height (“LIF signal”) around 740 nm recorded under identical conditions is used as a measure for the M_{Na} concentration.

It is assumed that the observed difference in TPA behavior obtained for short (ns) and ultrashort (<ps) laser pulses is related to the relaxation kinetics between optically pumped highly excited non-fluorescing states of the M_{Na}^{**} manifold and the relatively long-lived (lifetime of 23 ns [12], fluorescing M_{Na}^* state. Therefore, we looked for a measurement method to reveal the kinetics of radiationless $M_{\text{Na}}^{**} \rightarrow M_{\text{Na}}^*$ transitions (Fig. 2). As a first proof of principle, we applied pairs of femtosecond (fs) laser pulses at variable delay times. One pulse (second or third harmonic of the fs laser at 262 nm and 392 nm, respectively) was used to pump into the related

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M_{Na}^{**} state, and the other pulse (fundamental wavelength) to deplete (quench) the fluorescence of the M_{Na}^* state (Fig. 2).

2 Experimental

The CaF_2 sample ($50 \times 50 \times 15 \text{ mm}^3$, provided by Schott Lithotec AG) was cut from an undoped high purity single

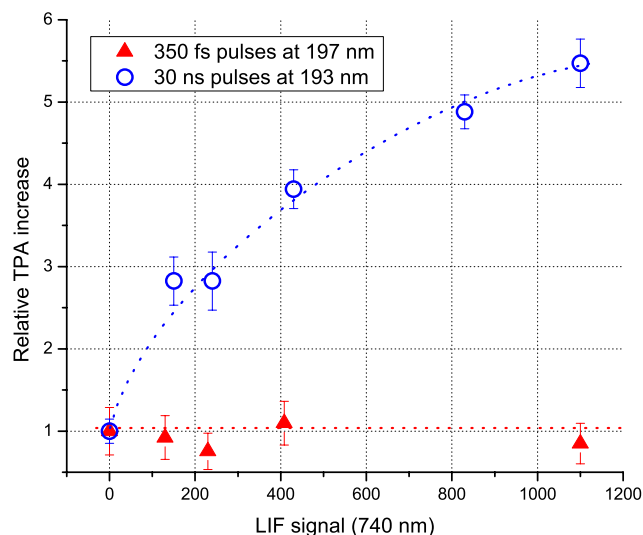


Fig. 1 Relative two-photon absorption (TPA) coefficients of CaF_2 single crystals with variable M_{Na} concentrations (given by the laser-induced fluorescence (LIF) signal at 740 nm obtained by ArF laser excitation (193 nm, 30 ns pulses) and fs laser excitation (197 nm, 350 fs) [17, 18])

Fig. 2 Fluorescence excitation spectrum of the M_{Na} center (left) and related energy level scheme showing the optical excitation and the non-radiative (k_2 and k_3) and fluorescing (LIF) relaxation pathways (right)

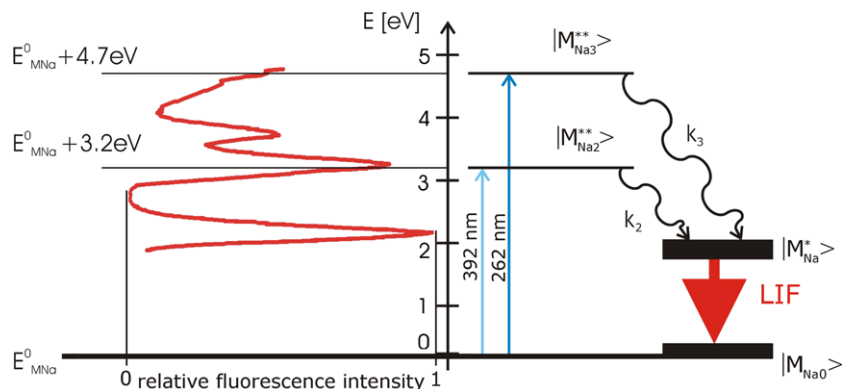
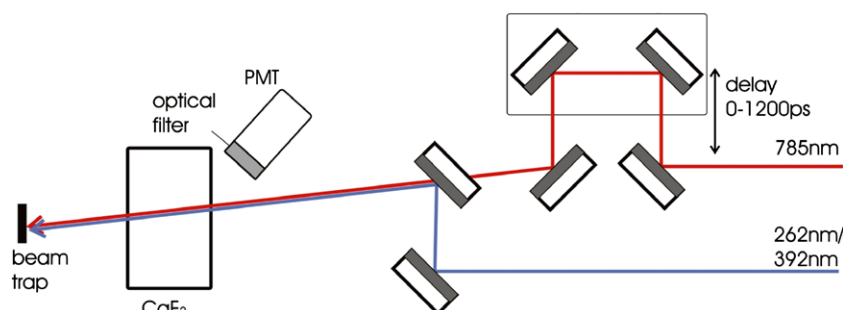


Fig. 3 Scheme of the experimental setup used for the NIR pulse delay time-dependent depletion of the M_{Na}^* fluorescence at 740 nm upon excitation at 392 nm (SH) or 262 nm (TH)



crystal with a residual Na contamination, caused by the manufacturing process and polished on its large surfaces. Prior to each fs laser experiment, $\sim 15,000$ ArF laser pulses were applied to generate the initial concentration of M_{Na} centers.

The M_{Na} center enriched sample was excited by either the second (392 nm, SH) or third harmonic (262 nm, TH) of a pulsed titanium:sapphire laser (Coherent, Mira 900, amplified by a regenerative amplifier (Quantronix, Titan, $\tau_{\text{pulse}} = 150 \text{ fs}$, 5 Hz repetition rate). A second pulse at 785 nm (fundamental wavelength of the Ti:Sa laser) was used to deplete the M_{Na} fluorescence induced by the SH or the TH pulses, respectively (see Fig. 2). Both pulses hit the sample in a collinear arrangement with a delay of up to 1.2 ns varied in steps of 133 fs by an optical delay line (Fig. 3). For each pulse pair the M_{Na} center fluorescence at 740 nm was detected and spectrally integrated by a photomultiplier tube (PMT, Hamamatsu H6780-20). The PMT was shielded by a set of glass and interference filters in order to cut off the scattered fs laser light.

3 Results and discussion

Figure 4 shows the fluorescence depletion amplitude as a function of the delay time between the UV pump pulse at 392 nm (3.16 eV) or at 262 nm (4.73 eV) and the near infrared (NIR) depletion pulse at 785 nm (1.58 eV). To obtain the fluorescence depletion amplitude, the laser-induced fluorescence (LIF) signal around 740 nm upon combined pulse excitation (UV plus NIR) is normalized to the LIF signal

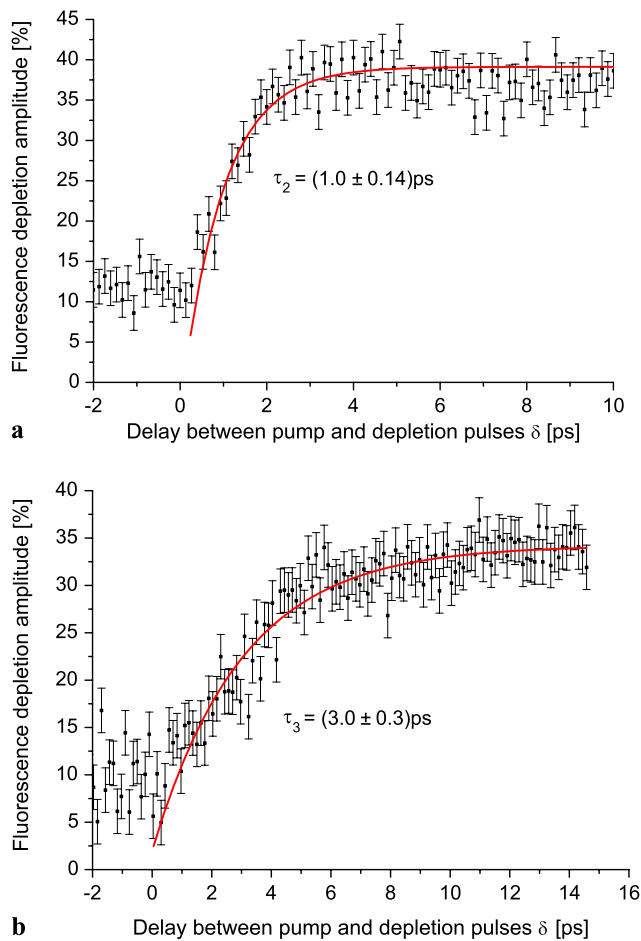


Fig. 4 Fluorescence depletion amplitude as a function of the delay time between the UV pump pulse and the NIR depletion pulse applying UV excitation (*top*) at 392 nm (3.16 eV) and (*bottom*) at 262 nm (4.73 eV)

upon pure UV fs laser excitation. The difference between this normalized LIF signal to unity is defined as the depletion amplitude. The error of each measurement point is assumed to be equal to the fluctuation of the measurement points at negative or very long NIR pulse delay times. The LIF signal as a function of the NIR vs. UV laser pulse delay (Fig. 4) can be fitted by a single exponential function. The time constants derived from the fits amount to 1.0 ± 0.14 ps for excitation at 392 nm and 3.0 ± 0.3 ps for excitation at 262 nm.

Looking at the LIF signal when the NIR fs laser pulse is preceding the UV fs laser pulse (negative delay times), about 10% fluorescence appears to be depleted for both UV excitation wavelengths. So far one cannot exclude the possibility that this effect is due to non-perfect signal deconvolution (LIF traces with and without NIR laser pulse). However, this fluorescence depletion offset does not interfere with the determination of the time constants of the radiationless transition. The highest fluorescence depletion amplitudes, on the other hand, amount to 34% and 40% upon

262 nm and 392 nm UV excitation, respectively. The fact that only a fraction of the fluorescence is depleted by the NIR pulses is attributed to the moderate NIR fs laser beam intensity. Using a higher pulse intensity, white light generation leading to unreasonable results would be observed.

The changes of the LIF signal (depletion amplitudes) in Fig. 4 are considered as a measure of the M_{Na}^* population at the time of the NIR laser pulse impact: It is assumed that fluorescence depletion occurs via stimulated emission, an optically linear process, by the fundamental laser wavelength, which is very similar, e.g., to stimulated emission depletion (STED) in ultrahigh resolution microscopy [19]. Stimulated emission propagates along the fundamental laser beam and therefore will not reach the PMT (see Fig. 3). Due to the linearity, the fluorescence depletion amplitude at a given delay time is directly proportional to the actual concentration of M_{Na}^* centers. In addition the delay times of the NIR laser pulse (<20 ps) are much shorter than the spontaneous fluorescence lifetime of 23 ns [12], so that spontaneous emission during the UV-NIR pulse delay is negligible, and the depleting pulse therefore interacts with the initial concentration of M_{Na}^* centers, contributing to the fluorescence. As a result, the observed change of the LIF signal, i.e., the M_{Na}^* concentration on the ps time scale (Fig. 4), reflects the non-radiative transition $M_{Na2,3}^{**} \sim M_{Na}^*$, and the time constants in Fig. 4 represent the relaxation rate constants k_2 and k_3 depicted in Fig. 2. Due to the exponential decay behavior of the M_{Na}^{**} state, the non-radiative $M_{Na2,3}^{**} \sim M_{Na}^{**}$ transition is regarded as a direct transition without long-lived intermediate energy levels.

The M_{Na}^{**} relaxation time evidently increases with the energy gap between the M_{Na}^{**} and M_{Na}^* states. This gap lies in the 1.3 ± 0.2 eV range for excitation by 3.16 eV photons (392 nm, k_2) and around 2.8 ± 0.2 eV for excitation by 4.73 eV photons (262 nm, k_3), as shown in Fig. 2. The uncertainty results from the difference between the emission wavelength (740 nm) and the longest excitation wavelength (600 nm). Therefore, the M_{Na}^* and M_{Na0} states are displayed as thick lines in Fig. 2.

However, both radiationless transition times can be clearly resolved by the measurement system and lie within the expected range between the fs and ns laser pulse durations. The different behavior of the TPA coefficients at different pulse durations for CaF_2 crystals with a different M_{Na} concentration, as shown in Fig. 1, can now be understood: For long pulses (ns range) the M_{Na} centers will be excited by single photon absorption into a state of the M_{Na}^{**} manifold. Since the non-radiative relaxation is fast compared to the pulse duration, they relax to the M_{Na}^* state within the pulse duration, and the M_{Na}^* species can be excited within the same pulse. This subsequent single photon absorption has the same features in these experiments as a TPA and therefore affects the TPA coefficient. However, for short pulses

(fs range), the non-radiative relaxation is much slower than the pulse duration, and the M_{Na}^* species cannot be excited by the laser pulse. Therefore, the M_{Na} centers do not affect the TPA coefficients measured with fs pulses.

Summarizing, our experimental findings represent a valuable example of examining a small change in lattice defect concentration based on Na atoms of <ppm level concentrations in a high-purity CaF_2 single crystal. Laser-induced fluorescence is a nearly background-free tool to detect the defect centers and—together with fs laser-induced depletion—their excited states' kinetics. The excited state kinetics provides valuable information on the energy flow within the CaF_2 crystals, in both the M_{Na} centers as well as between M_{Na} centers and the CaF_2 lattice. Initially the electronic degrees of freedom of the M_{Na} centers are excited, and possibly also some vibrational degrees of freedom. It appears challenging and rewarding to investigate the relaxation kinetics (energy dissipation) of the M_{Na}^{**} excited state manifold over the very broad accessible energy range from 2 eV to at least 8 eV. For this excitation energy range laser-induced fluorescence at 740 nm emission wavelength has been demonstrated so far.

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