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Fluorescence Intensity Time Trajectories of F_2 Centers in LiF Crystal

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ABSTRACT

It is known that fluorescence intensity time trajectories have a number of peculiar properties for a single molecule. The observed lack of repeatability of recording from one F_2 center to another, the absence of "on"/"off" states blinking, the change of the "off" state of the F_2 center with a triplet energy level depending on the change in the intensity of the exciting radiation are not typical for a single center. Duration of "off" stateon fluorescence intensity time trajectories of F_2 center (tens of seconds and even a few minutes) contradicts known data related to single centers. Arguments are given to prove that fluorescence intensity time trajectories of F_2 centers have features of ensemble behavior. Physicochemical reactions of destruction and reduction of F_2 centers occur in the luminous points with color centers under a laser beam.

Keywords: *Fluorescence; F_2 color centers; LiF; Single molecule spectroscopy; Photobleaching*

INTRODUCTION

Single-molecule spectroscopy (SMS)has been developing for over 30 years and has great interest to scientists working in the fields of chemistry, physics, biology and medicine. Not much research on fluorescence of a single impurity molecules and color centers in solids and transparent crystals are known, for example [1–4].

The use of lithium fluoride crystals in dosimetry and laser physics, in the field of fundamental researches and practical application of color centers induced by high-intensity femtosecond laser pulses [5-8] is widely known.

It is known that *F* color centers in alkali halide crystals consist of anion vacancies with trapped electrons in them. This is how *F*, F_2, F_3, F_4 and more complex F_n centers are formed, as well as charged *F* color centers that have an excess or missing electron. Color centers undergo photobleaching under the influence of light [9-11].

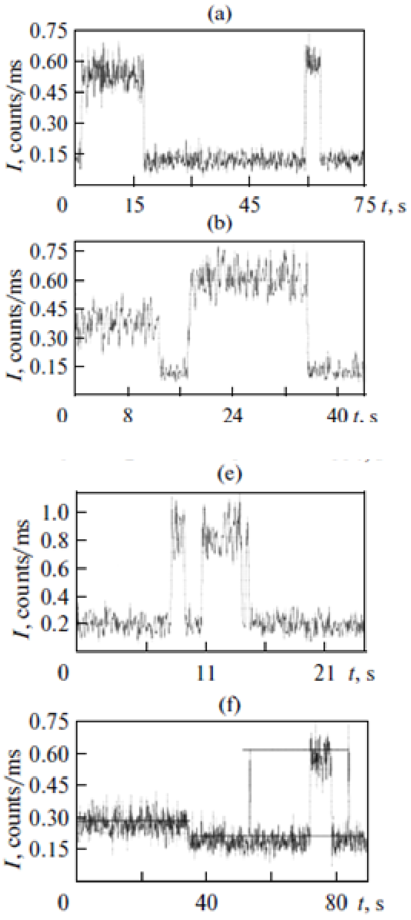
The authors of [1–4] believe that they observe the luminescence of single F_2 centers; however, their conclusions are based on not fully substantiated assumptions. In this paper, the authors consider it necessary to make some comments that will help to come to more realistic conclusions.

MATERIAL AND METHODS

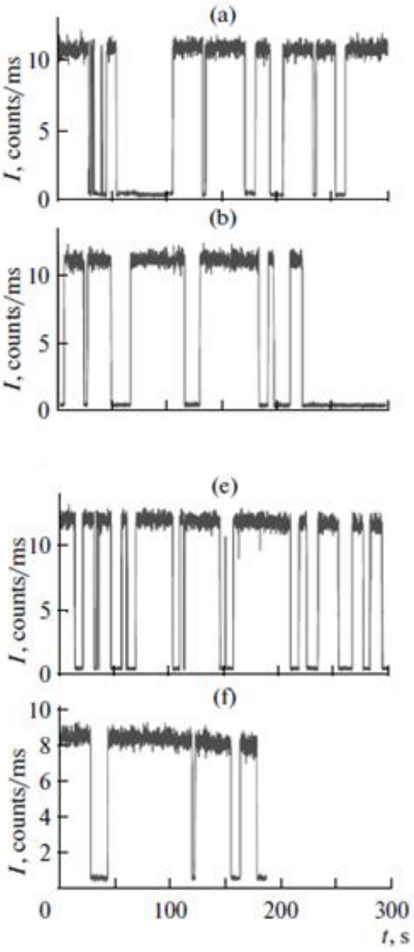
In [1, 2], γ-irradiated LiF crystals were investigated (the irradiation dose and the impurity composition of the crystals are not reported), subjected to gradient annealing (the conditions and temperatures of annealing are not given). It is only reported that in the annealed crystal, a region was selected where single F_2 centers were detected during scanning. The F_2 center consists of two adjacent anion vacancies (located along the C_2 axis) in the lattice of the LiF crystal that captured two electrons. The spectral absorption (at λ_{abs}=445 nm) and luminescence (at λ_{em}=670 nm) bands of the F_2 center are described by a linear oscillator oriented along one of six possible C_2 axes. The experiments on recording luminescence from single F_2 centers in LiF were carried out by means of Micro Time 200 (Pico Quant GmbH) laser scanning confocal fluorescence microscope. To excite luminescence, a diode laser with a wavelength of 470 nm was used, which operates in the pulsed mode with a pulse repetition rate of 5 and 10 MHz and pulse duration of about 60 ps. During the luminescence, a 690 ± 35 nm light filter was used. The exciting radiation was linearly polarized. The laser beam was directed along the normal to the crystal surface - the (100) plane. The orientation of the polarization vector of the exciting radiation around the beam axis along one of the crystallographic axes (either along [010] - orientation 0 °, or along [011] - orientation 45°) was carried out by rotating the crystal by the appropriate angle. A diode laser with a wavelength of 532 nm with a pulse repetition rate of 10 MHz and pulse duration of 70 ps was also used to excite the luminescence of F_2 centers. The signal accumulation time was 0.1 s.

Experimental Results and Their Discussion

Fig. 1(a, b) [2, 3] shows fragments of the luminescence intensity trajectories of a single F_2 center. The term “intensity trajectory” is understood as the time dependence of the luminescence intensity of a single-color center at constant excitation. The authors of [1–4] call these trajectories quantum trajectories of the photoluminescence of the F_2 center.



A



b

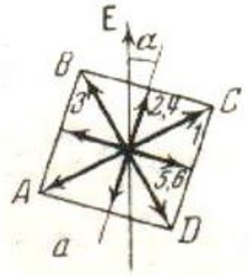
Figure1a. *Experimental time dependences of the luminescence intensity of single F_2 centers for the 0° sample orientation with luminescence intensity ratios (a) $I_1 : I_2 = 1 : 1$, (b) $I_1 : I_2 = 1 : 2$ and for the 45° sample orientation with luminescence intensity ratios (e) $I_1 : I_2 = 1 : 1$, and (f) $I_1 : I_2 = 1 : 8$ [2].*

Figure1b. *Experimentally recorded intensity trajectories of F_2 center in a LiF crystal subjected to excitation by the second harmonic of a neodymium laser [3].*

The F_2 center has a three-level scheme of main energy states, including triplet level. The repetitive transitions between the ground singlet state S_0 and the lowest excited singlet state S_1 give rise to fluorescence. The molecule can be undergoing intersystem crossing from S_1 to the lowest excited triplet state T_1. In T_1 the fluorescence is absent. Fluorescence time trajectory of a single center will have periods of a continuous fluorescence signal ("on" state) spaced by periods with no signal ("off" state). From the analysis of the given four trajectories (Fig. 1a) it follows that the durations "off" states are measured in tens of seconds. For example, in Fig. 1a the duration "off" state is 42 seconds (fragment (a) of the figure). However, there is no such information in scientific literature on the lifetime of the triplet state of the F_2 center in LiF at room temperature [12–15]. In these papers, the lifetime of the triplet state of the F_2 center in LiF at room temperature was estimated from 5–10 ms [12–14] to 72 ms [15]. In other alkali halide crystals, the lifetimes of the triplet states of the F_2 center measured in seconds only at low temperatures [16].

The Fig. 1a [2] shows the ratio of the luminescence intensities of a single F_2 center in four out of six possible orientations, based on the model of a linear oscillator oriented along one of six possible C_2 axes. The authors of [1] assume that, as a result of two-photon absorption, the center passes into a metastable mobile state (possibly a triplet state) with the center reorientation during the experiment under laser excitation (470 nm). The luminescence intensity changes for a reoriented single center. In [2], the authors reject two-photon absorption and suggest that after the ordinary single photon absorption and relaxes into a long-lived nonluminescent triplet state, a transition (due to absorption) occurs from a triplet state of the same orientation into metastable mobile nonluminescent state A, in which the center is reoriented. The nature of this state A is not specified. However, it is clear that this is neither S_0, nor S_1, nor T_1 state. In [2], only four of the six possible orientations of the presumed single F_2 center are considered. The authors do not discuss why on time trajectory of luminescence two time intervals are not denoted at which the luminescence intensity of F_2 center is equal to zero. The luminescence intensity of F_2 centers is zero in orientations when F_2 center dipole axis is perpendicular to the direction of the exciting radiation vector **E**. All time intervals in which $I_{\text{lum}} = 0$, the authors of [1, 2] ascribe only to the existing of F_2 center in the triplet state.

The calculations of the ratios of the luminescence intensities of a reorienting single F_2 center presented by the authors of [1, 2] were already performed earlier by P. P. Feofilov for groups of oscillators of F_2 centers [17]. An image of the orientations of oscillators groups and the calculation equations are shown in Fig. 2.



a

$$I_1 = \cos^2(\pi/4 + \alpha) = \tfrac{1}{2}(1 - \sin 2\alpha),$$

$$I_2 = I_4 = \tfrac{1}{4}\cos^2\alpha,$$

$$I_3 = \tfrac{1}{2}(1 + \sin 2\alpha),$$

$$I_5 = I_6 = \tfrac{1}{4}\sin^2\alpha,$$

$$\sum I = 3/2 = \text{const}(\alpha).$$

b

Figure2(a). *Image of six oscillators groups of F_2 centers on the (100) plane [17]; (b) – calculation formulas for the luminescence intensities of six oscillators groups [17].*

In the first case, the angle α = 0º. Substitution of α = 0º into the calculation formulas (Fig. 2 b) gives the ratio: $I_1=I_3=1/2$; $I_{2,4}=1/4$; $I_{5,6}=0$. Thus, the ratio of the three values of the luminescence intensities for the groups of oscillators is equal to $I_{1,3}$: $I_{2,4}$:$I_{5,6}$= 2:1:0, i.e. is the same as for the single center [1, 2].In the second case, the crystal plate had been rotated at an angle α = 45º around the beam exciting the luminescence. Substitution of α = 45º into the calculation formulas gives the following ratios: $I_1=0$; $I_3=1$; $I_{2,4}= I_{5,6}=1/8$. Thus, the ratio of the three values of the luminescence intensities for the groups of oscillators is I_3: $I_{2,4,5,6}$: I_1=8:1:0, i.e. is the same as in [1, 2] for the single center. Thus, the authors of [1, 2] have no reason to ascribe the ratio of the luminescence intensities shown in Fig. 1a, to a single reorienting F2 center.

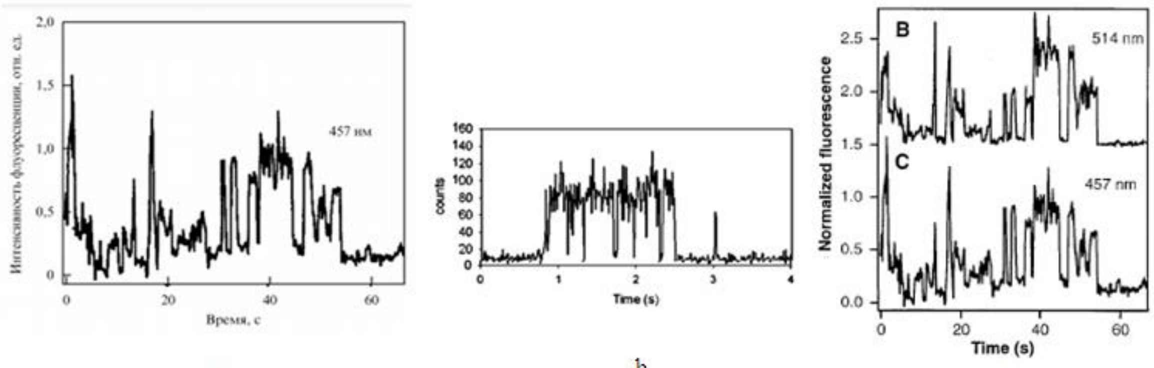
The authors of [3] do not explain why the luminescence intensity is the same at all "on" intervals (Fig. 1b [3]), although, according to the concepts developed in [1, 2], the intensity ratio should be 2: 1: 0. Since the luminescence intensity is the same at all "on" intervals, this means, within the framework of the theory of [1, 2], that a single F_2 center, for unknown reasons, does not reorient, although the luminescence intensity under the conditions of this experiment is 10–20 times higher(from a comparison of Fig. 1a and Fig. 1b).

The authors of [3] try to determine the lifetime of the triplet state of F_2 centers in LiF by analyzing the statistics of “off” intervals. For this purpose, in [3], data about the lifetime of the triplet state of F_2 centers in LiFτ_{ST} = 10 s were used for the calculation, referring to the [18], where such data are absent. Developing these ideas [4], it was found that with increase in intensity of the exciting radiation observed decrease in the average time of the F_2 center stay in a non-emitting state T_1. This fact contradicts the concept known in the literature that the lifetime of the triplet state of a single molecule remains constant regardless of an increase in the intensity of the exciting light.

DISCUSSION

In [1–4] are used for studies not the initial crystal irradiated with ionizing radiation but a γ-irradiated and then annealed crystal. It is widely known that annealing of a crystal with color centers (starting from 450 K and above) leads to clustering of color centers, their integration to ~ a thousand F centers in one nanoscale region, in which a lithium nanoparticle is subsequently formed [9, 10, 19-21]. In this region, the crystal lattice is distorted, and this place becomes a place for the sink of point defects, including hole and electron color centers. The authors of [1-4] directed the radiation of a picosecond laser into this nanoscale region of a crystal, which appeared as a result of thermal annealing, and thus continued to initiate the process of aggregation and transformation of color centers under photo-irradiation.

The third aspect that must be taken into account when considered the luminescence of a single center is the presence of an on/off “blinking” behavior in the intensity of a wide fluorescence band. The fundamental difference between the fluorescence of a single molecule and the fluorescence of an ensemble manifests itself in the behavior of fluorescence over time (Fig. 3). The fluorescence intensity of an ensemble of polymer molecules does not depend on time for tens of seconds, and the fluorescence intensity of a single polymer molecule fluctuates (Fig. 3).



a b c

Figure3(a). – *The behavior of fluorescence over time (quantum trajectory of intensity) of a single polymer PPV-PPyV molecule excited by continuous light with λ = 457 nm (from Ref. [12]). The fluorescence signal was accumulated for 0.1 s [22]; (b) – Time trajectory of the emission from a single copy of the GFP mutant 10C in PAA using a confocal microscope, with 10 ms integration time and 514 nm pumping with an excitation intensity of 1.6 kW/cm^2 (from Ref. 109, used by permission) [23]; (c) – (**B** and **C**) Portions of two simultaneous fluorescence transients recorded at two excitation wavelengths, 457 nm (blue edge) and 514 nm (red edge). The two transients are virtually identical [24].*

One more aspect concerns the identity of the species of time trajectory of the emission of a single molecule at different wavelengths of fluorescence excitation. In [24] time trajectory of the emission of a single molecule were taken at three wavelengths (457, 488, and 514 nm) (Fig. 3 c present wavelengths 457 and 514 nm) to ensure that the single molecule had similar time trajectories. In contrast, in [1-4] time trajectories of F_2 center emission have a various form.

The explanation of fluorescence intensity time trajectories (Fig. 1 b [3]) can be done from the point of view of [25-27]. F_2 centers can be efficiently excited on the long-wavelength side of the absorption band by the second harmonic of a neodymium laser. A radiation quantum of 532 nm transfers one electron from the excited level of the neutral F_2 center to the conduction band, creating an ionized F_2^+ center by two-step photoionization of F_2 centers:

$$F_2 + h\nu_{532} \rightarrow F_2^* + h\nu_{532} \rightarrow F_2^+ + e^- \qquad (1)$$

During the LiF:F_2 lasing the laser-active F_2 centers are destroyed and F_2^+ centers are produced. The same action is performed and under the 441.6 nm He-Cd laser pumping [27]. The almost complete ionization of F_2 centers can occur on fluorescence intensity time trajectories (Fig. 1b [3]). As a result, an “off” time interval appears at which F_2 centers do not emit, since they are destroyed, and F_2^+ centers are created. Then the photophysical processes of restoring the concentration of F_2 centers take place. There is a balance between the destruction of F_2 and the creation of F_2^+ centers. The abrupt drops to zero seen on the intensity trajectories (Fig. 1) are explained by the impossibility of fixing a very low concentration of the remaining F_2 centers, perhaps due to the low signal-to-noise ratio.

There are three ways to restore the concentration of F_2 centers:

$$F_2^+ + e^- \rightarrow F_2 \qquad (2)$$

$$F_2 + e^- \rightarrow F_2^- \qquad (3)$$

$$F_2^- + F_2^+ \rightarrow 2F \qquad (4)$$

Third, electron capturing by a fluorine atom with the formation of an interstitial fluorine ion:

$$e^- + F_i^0 \rightarrow F_i^- \qquad (5)$$

Further, an F center is formed:

$$F_i^- + F_2^+ \rightarrow F_a^- + F \qquad (6)$$

Also, when there are F_3^+ centers in the laser-irradiating region, they can also capture an electron with the formation of a neutral aggregate color center:

$$F_3^+ + e^- \rightarrow F_3 \qquad (7)$$

Thus, exposure to picosecond laser radiation will finally lead to an increase of neutral F centers number in the irradiated region. Aggregate F centers, including F_2 centers, can be created from neutral F centers. The final stages of bleaching will be the capture of electrons of the F centers by lithium ions, the merge of lithium atoms to form lithium nanoparticles. At this stage, the luminescence of F_2 centers is finishes irreversibly.

CONCLUSIONS

The study of the fluorescence intensity time trajectories of F_2 centers has identified several positions that do not allow unambiguously attributing these fluorescence intensity time trajectories (in the form in which they are written) to a single F_2 center in LiF. These several positions are as follows:

1. For investigations, γ-irradiated LiF crystals were selected (the radiation dose and impurity composition of the crystals are unknown), subjected to gradient annealing. However, upon thermal annealing, clustering and aggregation of F centers occurs; therefore, not only F_2 centers, but also other F centers can be present in the luminous points under study. The luminescence of F_3^+ centers was excluded from observation by using the appropriate light filter. The luminescence of F_3^+ centers is excited at λ_{ex} = 458 nm and occurs at λ_{em} = 538 nm. The use of a light filter made it impossible to observe the emission of the F_3^+ center.
2. Duration of "off" state on fluorescence intensity time trajectory of F_2 center (the lifetime of the triplet state of the F_2 center) is tens of seconds and even a few minutes (on Fig.1time trajectories with minute duration have not shown). However, in the scientific literature, the lifetime of the triplet state of the F_2 center in LiF at room temperature is estimated from 5–10 ms to 72 ms.
3. The model of the supposed reorientations of a single F_2 center does not explain why the center does not reorient to two of the six possible orientations, in which the fluorescence intensity of the F_2 center is zero. A long, up to several minutes, finding of the F_2 center in the triplet state during reorientations is unlikely at room temperature. This model cannot be evidence of the observation of single F_2 center, since the ratio of the luminescence intensities given in [1, 2] when the vector **E** of the electric field rotates relative to the beam that excites the luminescence was developed by P. P. Feofilov for groups of oscillators of F_2 centers in LiF crystals.
4. The fundamental difference between the fluorescence of single molecules and the fluorescence of an ensemble is manifested in the time behavior of fluorescence. The fluorescence intensity of an ensemble of molecules does not depend on time for tens of seconds, and the fluorescence intensity of a single molecule has blinking with generally millisecond periods. The duration of "on" and "off" states on fluorescence intensity time trajectories from tens of seconds to several minutes cannot relate to a single F_2 center.

5. The duration of the "off" states does not depend on the change in the intensity of the exciting radiation for a molecule with a triplet level. In studies [3,4] the duration of "off" states becomes shorter with an increase in the intensity of luminescence excitation.
6. The fluorescence intensity time trajectory of single molecules has similar kind at different wavelengths of excitation. Nevertheless in [1-3] the time trajectories of F_2 center emission have a various form at λ_{ex}=470 and λ_{ex}=532 nm.
7. The time trajectories of the emission recorded at different luminous points should be similar. Since fluorescence intensity time trajectories of F_2 centers are very different, the luminous points are not single F_2 centers.

At the moment, it is probably early to state unambiguously that the fluorescence intensity time trajectories of F_2 centers belong to single F_2 centers, since they have features of ensemble behavior. Physicochemical reactions of destruction and reduction of F_2 centers occur in the luminous points under a laser beam. This process continues until the F_2 color centers are completely bleached.

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