

Inclusion of thermal motion in laser fluorescence lifetime measurement using $^{80}\text{Se}_2$ as an example

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The effect of thermal motion of particles through the excitation zone of a laser beam with a Gaussian power density distribution profile on the determination of the relaxation time by the kinetics of excited laser fluorescence is considered. Investigation is performed in a polarization moment apparatus, taking into account both the spatial configuration of the excitation zone, the width of which is much smaller than the size of the cell with the vapor, and the effect of finite width of the entrance slit of the spectral instrument. The effect of the flight through the beam on the determined time of radiative decay of the vibrational–rotational levels of the electronically excited $B 0_u^+$ and $B 1_u^+$ states of the $^{80}\text{Se}_2$ molecule is estimated when excited by the 488.0, 496.5, and 514.5-nm lines of an argon laser. Measured lifetimes equal to 39 ± 2 nsec for $B 0_u^+$ and 63 ± 4 nsec for $B 1_u^+$ states of $^{80}\text{Se}_2$ are given.

INTRODUCTION

Among the reasons that stimulate interest in the lifetimes and other relaxation constants of diatomic molecules of heavy elements of the 6A group, we should note their participation in processes affecting lasing in the vapor lasers of these elements. This is also attributed to the selenium Se_2 molecule, for which there is insufficient data on these questions. Thus, there are no data in Refs. 1–4 on the lifetimes τ_{sp} of the spectroscopically best studied state $B 0_u^+$ of the Se_2 molecule, while for the $B 1_u^+$, only the value for one vibrational–rotational (VR) level is given;¹ this does not allow us to determine the absolute values of the transition strength.⁵ To increase existing information, measurement is made in this paper on the τ_{sp} of a series of VR states of Se_2 ($B 0_u^+$, $B 1_u^+$) using direct and detailed methods of the kinetics of laser induced fluorescence (LIF) under pulsed excitation.^{6,7}

With sufficient temporal resolution and sensitivity of the recording system the actual degree of matching of the proposed (single-exponential in the simplest case) functional dependence of the LIF can affect the reliability of the determination of the relaxation time. Thus, when exciting by narrow laser beam, whose action zone is much smaller than the size of the cell with vapor at low concentrations (this is required for transition to the spontaneous lifetime τ_{sp}), we should also analyze the possibility of distortion of the result due to the effect of thermal motion of the excited particles, which has already been considered in Ref. 8 and also in Ref. 9. The essence of the phenomenon lies in the fact that drift of particles in the excited state out of the observation region and arrival of particles in other states take place. The practically important case of a Gaussian profile of the exciting and probe beams is considered in Ref. 10, where the joint appearance of relaxation and diffusion of particles under collision

conditions was included, using the NO molecule ($v' = 5$) as an example. However, the situation can exist in τ_{sp} measurement when this time is significantly shorter than the period between collisions, i.e., the case can be realized of free flight through a beam whose diameter is less than the mean free path. The effect of relaxation during flight through a beam with a different profile on the kinetics of the process of nonlinear optical depopulation of the ground state of the molecules was considered in Refs. 11 and 12; a similar approach is also contained in Ref. 13, devoted to light-induced drift. The effect of flight of excited particles through a beam is considered in this paper, taking into account not only the spatial configuration of the excitation zone, but also the fact that light is collected by the recording instrument from every region of space, i.e., the effect of the finite width of the entrance slit of the spectral instrument.

EXPERIMENT

The selenium isotope ^{80}Se (no lower than 95% purity) was placed in a section of a fluorescence cell made of fused quartz. The cell was connected to a vacuum station that provided a vacuum of $<10^{-6}$ Torr through a dry valve. The temperature of the section with the selenium was maintained close to 550–590 K, and the part of the cell, from which LIF was observed, was at a significantly higher temperature (close to 950 K) to suppress the formation of Se_6 , Se_7 , and Se_8 polymers.¹⁴ The LIF was observed perpendicular to the vertically directed exciting beam; then the fluorescence column was focused using a lens onto the entrance slit of a DFS-12 monochromator (reciprocal dispersion of 0.5 nm/mm), situated parallel to the direction of excitation. The 488.0, 496.5-nm lines of an LG-69 type Ar^+ laser, lasing in multi-longitudinal TEM_{00q} modes (0.5 W at the 514.5-nm line), were used as the light source. The laser radiation was modulated using an ML-102 Pockels electrooptic modulator, controlled by a G5-54 pulse generator. The total duration of the light pulse was close to 100 nsec with the duration of the trailing edge of the order of 20 nsec and repetition rate close to 10 kHz. The LIF kinetics was recorded by the method of delayed coincidences, counting single-electron pulses with an FEU-79 in the start-stop mode (the method is also called single-photon statistical analysis)^{6,9} with time-amplitude conversion and storage on an AI-256-6 pulse analyzer.

Noise and also correction of over-filling of initial channels of the pulse analyzer with respect to the higher-number channels¹⁵ were included in the processing. This is due to the fact that if two or more single-electron pulses enter over the period of measurement (equal to 1 μsec in our case), then only the first enters the pulse analyzer channels (since it triggers the stop pulse). According to Ref. 15, we can correct readily the number of pulses n_i in the i th channel by

$$n_i = -M \ln \left[1 - n'_i \left(M - \sum_{j=1}^{i-1} n'_j \right) \right], \quad (1)$$

where n'_i and n'_j are number of pulses recorded (without correction) in channels with numbers i and j ; M is the total number of pulses (i.e., periods of measurements). We note that due to proximity to unity, the expressions under the ln sign are unsuitable for computation by standard computer programs (1), so that the following expansion into a series was used (the first six terms were included):

$$\ln(1-x) = -\left[x + \frac{x^2}{2} + \frac{x^3}{3} + \frac{x^4}{4} + \dots \right], \quad -1 \leq x < 1. \quad (2)$$

DESCRIPTION OF THE KINETICS SIGNAL

To describe the relaxation processes in the afterglow, we use the polarization moment (PM) tool,¹⁶ convenient for calculation of depolarizing and quenching collisions.¹⁷ The LIF intensity is expressed in terms of the PM of the excited state f_Q^K (K is the rank of the tensor, Q is its projection)

$$I(t) \sim (-1)^{J'+J''} \sum_K (2K+1) \left\{ \begin{matrix} 1 & 1 & K \\ J' & J' & J'' \end{matrix} \right\} \sum_Q (-1)^Q f_Q^K(t) \Phi_{-Q}^{\pi}(\theta), \quad (3)$$

where J' , and J'' are angular momenta of the excited and ground levels; the quantity in the curly brackets are $6j$ symbols; Φ_{-Q}^{π} is the observation tensor,¹⁶ depending on the component of the light polarization ϵ recorded. From the properties of the $6j$ symbols, $K \leq 2$. If power density distribution of excitation in the TEM_{00q} mode directed along the z axis is described by a Gaussian function, then immediately after termination of excitation (at time $t = 0$), the spatial PM density distribution in the xy plane will be

$$f_Q^K(t=0) = \frac{\sigma f_Q^K}{\pi \sigma^2} \exp[-(x^2 + y^2)/\sigma^2], \quad (4)$$

where σ is the typical radius of the laser beam. Let us track the group of excited particles moving along x with velocity v_x . Decay of the PM describing this group in the coordinate system x_1, y_1, z_1 associated with it, takes place exponentially with rate Γ_K . We have by transforming to the laboratory coordinate system

$$f_Q^K(t) = \frac{\sigma f_Q^K}{\pi \sigma^2} \exp\{-[(x - uv)t + y^2]/\sigma^2 - \Gamma_K t\}, \quad (5)$$

where $u = v_x/\bar{v}$, \bar{v} is the most probable velocity of the particles. Let LIF be recorded along the y axis, and photons from the region bounded by the values of x from $-l/2$ to $l/2$ pass through the entrance slit of the monochromator (assuming magnification of the illuminating lens is equal to unity, we will call l the width of the entrance slit). In order to find the observed kinetics signal, it is necessary to average Eq. (5) over the spatial region of fluorescence observation and over velocity projections v_x , since the depth of definition along y is usually quite large and in our experimental geometry, only motion along the x axis can lead a particle out of the zone, from which the light flux is collected. The mean value of PM sought is

$$\begin{aligned} \bar{f}_Q^K(t) &= \int_{-\infty}^{\infty} du \int_{-l/2}^{l/2} dx \int_{-\infty}^{\infty} dy f_Q^K(t) \sqrt{\pi} \exp(-u^2) \\ &= \sigma f_Q^K \exp(-\Gamma_K t) \operatorname{erf}(l/2 \sqrt{\sigma^2 + \sigma^2 t^2}). \end{aligned} \quad (6)$$

A Maxwellian velocity distribution of the particles is assumed in Eq. (6). Let the laser beam be linearly polarized along x . Then, for molecular rotational levels with $J' \gg 1$, typical for the experiments considered, nonzero PM σf_Q^K in Eq. (3) in the case of Q type transitions ($J' = J''$) assume values:¹⁸ $\sigma f_0^0 = G/3$, $\sigma f_2^0 = 2G/15$; G is the probability of photon absorption over the time of action of the pulse, which is assumed to be infinitely short. PM assume values

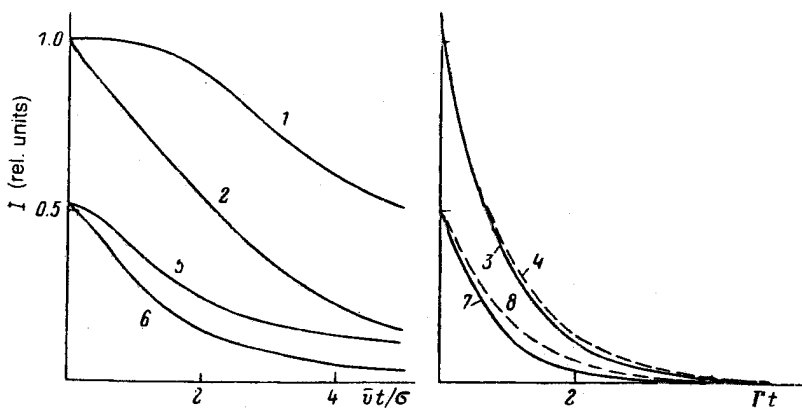


FIG. 1. Signals of fluorescence kinetics, computed by Eq. (8) for $l/\sigma = 5$ (curves 1-4) and $l/\sigma = 1$ (curves 5-8) for relations of parameters: $\Gamma = 0$ (1 and 5), $\Gamma = 0.25\bar{v}/\sigma$ (2 and 6), $\Gamma = \bar{v}/\sigma$ (3 and 7); the case of exponential decay with rate Γ , when $\bar{v}/\sigma = 0$ is shown by dashed curves 4 and 8:

$\sigma f_0^0 = G/3$, $\sigma f_0^2 = -G/15$ for P, R types of transitions ($J' = J'' \pm 1$), taking place in the transitions studied in Se_2 molecules, and the LIF intensity, for instance, polarized along the x axis, is

$$I(t) \sim (5e^{-\Gamma_0 t} + e^{-\Gamma_2 t}) \text{erf}(l/2 \sqrt{\sigma^2 + \bar{v}^2 t^2}). \quad (7)$$

The expression obtained allows us to take into account the flight of particles through a beam of Gaussian profile, and also include in the treatment collisions with different rates of relaxation of the population (Γ_0) and alignment (Γ_2).¹⁷ The last difference is usually negligibly small for molecules with $J' \gg 1$, and in this case Eq. (7) acquires a rather simple form ($\Gamma_2 = \Gamma_0 \equiv \Gamma$)

$$I(t) \sim e^{-\Gamma t} \text{erf}(l/2 \sqrt{\sigma^2 + \bar{v}^2 t^2}). \quad (8)$$

The temporal dependence $I(t)$ of the kinetics signal of LIF, computed by Eq. (8) for different values of the parameters, is given in Fig. 1. For curves 1-4, the width of the entrance slit l is five times larger than the beam radius σ , while for 5-8, they are equal, and, naturally, lower intensity is recorded. The cases 1 and 5 describe a purely flight process. Curves 4 and 8 (dashed curves), being exponential with constant Γ demonstrate the other limiting case. Figure 1 shows that with conditions remaining equal (identical l/σ), the role of flight is determined by the relation between Γ and \bar{v}/σ . Thus, the curves presented in Fig. 1 in coordinates, $I, \bar{v}t/\sigma$ pertain to the case of dominance of flight (\bar{v}/σ exceeds Γ). The curves in Fig. 1 in coordinates $I, \Gamma t$ allow us to compare the case of equality of \bar{v}/σ and Γ with a pure exponential. We should note that signals for the cases of $\bar{v}/\sigma < \Gamma$ are situated between curves 3 and 4, 7 and 8, respectively, approximating rather closely the exponential. For example, for $\bar{v}/\sigma = 0.1$, difference from the exponential is no more than 0.5% for $\Gamma t = 1$. Taking into account the effect of the width of the slit, we can estimate the effect of flight by comparing with the identity criterion

$$A_0 = \frac{l\Gamma/\sigma}{[1 + (\sigma\Gamma/\bar{v})^2]^{3/2}} \exp\left\{-\frac{l^2\Gamma^3}{\bar{v}^2} \left[4 + 4\left(\frac{\sigma\Gamma}{\bar{v}}\right)^2\right]\right\}, \quad (9)$$

the smallness of which ensures that exponential decay is well satisfied.

RESULTS AND CONCLUSIONS

The kinetics of LIF is studied for the levels of $^{80}\text{Se}_2$ in the states of $B 0_u^+$, $v' = 0$, $J' = 129$ when excited by laser line

496.5 nm, and also $B 1_u^+$, $v' = 0$, $J' = 95$ and $B 1_u^+$, $v' = 1$, $J' = 39$ when excited by 514.5 and 488.0 nm. Identification of VR numbers was achieved by comparison of the experimentally recorded LIF spectrum with that computed from the data of Ref. 19. The form of kinetics signals is given in Fig. 2. In processing, after inclusion and correction of overfilling by Eq. (1), the recorded LIF kinetics signal $\Phi(t)$ was represented in the form of the convolution of the function describing the excitation pulse $F(\vartheta)$, and the function $I(t - \vartheta)$, describing relaxation of the state under study, i.e.,

$$\Phi(t) = \int_0^t F(\vartheta) I(t - \vartheta) d\vartheta. \quad (10)$$

To estimate the role of flight relaxation, the single-exponential approximation for $I(t - \vartheta)$ was used first, and this led to τ_{sp} values within 40-65 nsec. Estimates show that for such lifetime values, use of a lens-focused laser beam to amplify the signal, requires, in general, the inclusion of flight through the beam. In fact, with an entrance slit width of ~ 0.08 mm necessary for resolution and spectrum identification, and approximately the same radius of the focused beam, we have, at a temperature of 950 K, $\Gamma \approx \bar{v}/\sigma$ by assuming the beam profile to be Gaussian. This is close to the case, described by curve 3 (Fig. 1), and, strictly speaking, it is necessary under these conditions to use approximation of the kinetics, according to Eq. (8). In order to avoid compli-

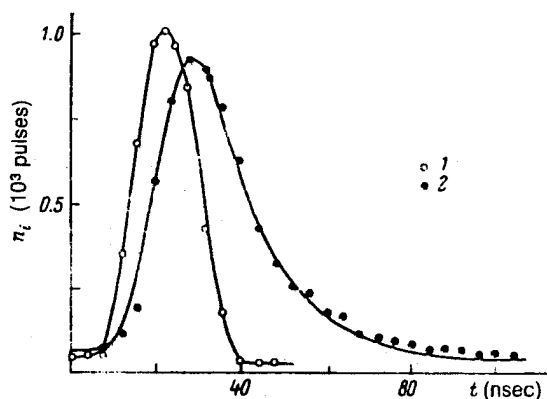


FIG. 2. Experimentally recorded exciting ($\lambda = 514.5$ nm) laser pulse (1) and response pulse of the afterglow from $^{80}\text{Se}_2$ level $B 1_u^+$, $v' = 0$, $J' = 95$ in the R_{11} line (2). The solid curve shows the fluorescence-kinetics signal calculated from Eq. (10); the number of pulses n_i in the channel is plotted in the graph.

cation in the calculations, a significantly broader exciting beam with a diameter close to 1 mm was used in lifetime measurement, and a choice of a suitable line from the LIF series allowed us to widen the entrance slit of the monochromator up to the same size. This leads to $\bar{v}/\sigma \approx 0.05\Gamma$, and this, according to the comments to Fig. 1, eliminates completely the effect of flight through the beam on the measured kinetics signal.

We should say that since for atoms and small molecules, $\bar{v} \approx 10^2-10^3$ m/sec are the typical values of the most probable velocities in the gaseous phase in experiments, then the effect of flight through the beam begins to appear for decay rates of the state studied $\Gamma \lesssim 10^6$ sec⁻¹ for typical unfocused laser beam diameter of 2-3 mm and entrance slit width of $\lesssim 1$ mm.

Processing data according to the above procedure leads to the following lifetime values of ⁸⁰Se₂: 39 ± 2 nsec for $B 0_u^+$, 0.129; 63 ± 3 nsec for $B 1_u^+$, 0.95; and 63 ± 4 nsec for $B 1_u^+$, 1.39. The error value given is obtained from spread of the results and corresponds to one standard deviation.

The values obtained for the $B 1_u$ state coincide within errors with the single lifetime value given in Ref. 1 of 58 ± 6 nsec for ⁸⁰Se₂ ($B 1_u^+$, 0.105). Measurements by the authors of Ref. 1 were performed by the Hanle effect¹⁷ method. The data given in Ref. 1 on the dependence of the halfwidth of the Hanle profile on selenium vapor pressure allow us to assume that collisional quenching leads to a reduction in the decay by no more than 1% at the temperature of the section with the selenium $T < 590$ K in our measurements, and this corresponds to a pressure $p < 0.5$ Torr.²⁰ A slightly lower value of τ_{sp} is obtained for the $B 0_u^+$ state, since judging from the data of Ref. 21, the level with $v' = 0, J' = 129$ is unperturbed and can be typical for the state as a whole. A value of 85 ± 10 nsec is given in Ref. 4 for a natural mixture of selenium isotopes, attributable to the $B^3\Sigma_u^-$ state (without resolution according to v', J' , and also according to $\Omega = 0$ or 1) by exciting the transition $X_3\Sigma_g^- - B^3\Sigma_u^-$ in the range of 26 000

cm⁻¹ by a pulsed dye laser. We note that the lifetime of the $B 0_u^+$ and $B 1_u^+$ states is more than an order shorter than the lifetime of the Se₂ ($A 0_u^+$) state, equal approximately to 700-780 nsec, according to the data of Refs. 3 and 4. A similar relation is typical for such molecules of the 6A group, as Te₂, and also molecules of the 7A group of ICl and Br₂.

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