Systematic errors in the frequency of transitions among excited states of atoms determined by analyzing recorded fluorescence pulses

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Using a 5-level model of an atom, I have identified the nature and determined the magnitude of the systematic errors in the frequencies of inelastic transitions among excited states measured by a fluorescence method. The errors arise because of describing the dynamics of the energy level population by use of models involving fewer number of the energy states (2, 3, and 4). It is shown that these errors may lead to reduction of the determined frequency by an order of magnitude in the region of high pressures. Two criteria for selection of an adequate model are given.

At excitation of atoms by short laser pulses, it is possible to measure rates of inelastic transitions among sufficiently close energy states, from which the fluorescence takes place, since the duration and shape of the fluorescence pulses essentially depend on the time of population redistribution due to collisions with the buffer gas particles. The simplest variant of such measurements is realized in the case when only two levels exchange by energy, one of which is populated by laser pulse while the other loses it due to emission. However, such a situation is quite seldom. As a rule, population migrates among several states. It is obvious that use of atomic models in treatment of the observed pulses that allow for fewer than actual number of states leads to a systematic error in measured frequency of inelastic collisions. Namely, in that case, one should expect its essential reduction, as the rate of a level population from which re-emission occurs, actually decreases because the atom resides, for some time, in the states that are not accounted for.

The aim of this study was to improve understanding of how an incomplete modeling of the atom (unclosed quantum system) influences, and to what degree, the frequency of inelastic collisions retrieved from the fluorescence pulse parameters.

Let us consider that five levels (Fig. 1) take part in the energy exchange while the population spread due to collisions occurs only between two adjacent levels. For simplicity of description, we assume the frequencies of all the inelastic collisions being the same. Let the population of the "−1" level at zero time be equal to unity and the rest levels be not populated at this moment at all. The measurable quantity is the pulse shape of the spectrally integrated fluorescence from the "0" level to the underlying one (not shown in Fig. 1), including the ground one. In the case of an optically thin medium, radiation reabsorption can be ignored and the

fluorescence intensity is proportional to the population of the "0" level. Since the energy states near the level from which the fluorescence occurs are, as a rule, not the upper levels of resonance transitions, we shall not take into account their radiation relaxation.
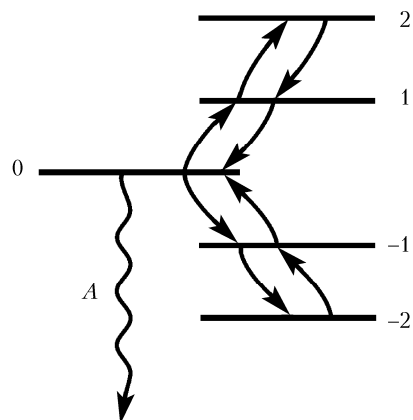

Fig. 1. Diagram of the atomic energy levels.

The accepted model of an atom is rather conditional, but can be easily generalized in the case of particular atoms while allows one to trace the basic features of the population dynamics influence on the shape and duration of the fluorescence pulse. We shall test the description completeness by the least squares fitting of the fluorescence pulse shape (population of the "0" level) calculated for systems with fewer number of levels (2, 3, and 4) to the shape of the "experimental" pulse, computed for the five-level system at different frequencies ν (buffer gas pressures). Thus, the Einstein coefficient A is considered known, frequency of the inelastic collisions ν and the amplitude factor appear as the fitting parameters. We normalize ν by A and time by

A^{-1}. Equations for the state populations in 2-, 3-, 4-, and 5-level atomic models within the limits of the accepted approximations take the form

$$a\dot\rho_0 = -(1+a)\rho_0 + \rho_{-1}, \quad a\dot\rho_{-1} = \rho_0 - \rho_{-1}, \qquad (1)$$

$$a\dot\rho_1 = -\rho_1 + \rho_0, \quad a\dot\rho_0 = \rho_1 - (2+a)\rho_0 + \rho_{-1},$$
$$a\dot\rho_{-1} = \rho_0 - \rho_{-1}, \qquad (2)$$

$$a\dot\rho_1 = -\rho_1 + \rho_0, \quad a\dot\rho_0 = \rho_1 - (2+a)\rho_0 + \rho_{-1},$$
$$a\dot\rho_{-1} = \rho_0 - 2\rho_{-1} + \rho_{-2}, \quad a\dot\rho_{-2} = \rho_{-1} - \rho_{-2}, \qquad (3)$$

$$a\dot\rho_2 = -\rho_2 + \rho_1, \quad a\dot\rho_1 = \rho_2 - 2\rho_1 + \rho_0,$$

$$a\dot\rho_0 = \rho_1 - (2+a)\rho_0 + \rho_{-1}, \quad a\dot\rho_{-1} = \rho_0 - 2\rho_{-1} + \rho_{-2}, \qquad (4)$$

$$a\dot\rho_{-2} = \rho_{-1} - \rho_{-2}, \quad a = 1/\nu, \quad A = 1.$$

Solutions of Eqs. (1) to (4) are, respectively

$$\rho_0 = \frac{2B\nu}{\sqrt{1+4\nu^2}}e^{-(\nu+1/2)t}\sinh(t\sqrt{1+4\nu^2}/2), \qquad (5)$$

$$\rho_0 = \frac{2B\nu}{\sqrt{1+2\nu+9\nu^2}}e^{-(3\nu+1)t/2}\sinh(t\sqrt{1+2\nu+9\nu^2}/2), \quad (6)$$

$$\rho_0 = \frac{Be^{-p\tau}}{8qr_1r_2}\{(1+b+2q)r_1e^{-q\tau}\sinh(r_2\tau) -$$

$$- (1+b-2q)r_2e^{q\tau}\sinh(r_1\tau) +$$

$$+ 2r_1r_2[e^{q\tau}\cosh(r_1\tau) - e^{-q\tau}\cosh(r_2\tau)]\}; \qquad (7)$$

$$\tau = \nu t; \quad p = (3+b)/2; \quad q = \sqrt{1+b^2}/2; \quad b = a/2;$$

$$r_{1,2} = \sqrt{3+b+b^2 \mp (1+b)\sqrt{1+b^2}}/\sqrt{2};$$

$$\rho_0 = -c_1e^{-\lambda_1\tau} + c_2e^{-\lambda_2\tau} + c_3e^{-\lambda_3\tau};$$

$$\lambda_1 = \frac{1}{3}(a-1-2s\cos\beta) + 2,$$

$$\lambda_{2,3} = \frac{1}{3}[a-1+s(\cos\beta \mp \sqrt{3}\sin\beta)] + 2;$$

$$c_1 = \frac{2+a-2s\cos\beta}{s^2(1+2\cos2\beta)}, \qquad (8)$$

$$c_{2,3} = \mp\frac{2+a+s(\cos\beta \pm \sqrt{3}\sin\beta)}{2s^2\sin\beta(\sqrt{3}\cos\beta \pm \sin\beta)};$$

$$s = \sqrt{a^2+a+10};$$

$$\beta = \frac{1}{3}\arctan\frac{3\sqrt{3}\sqrt{5a^4+6a^3+43a^2+50a+125}}{2a^3+3a^2-3a+25}.$$

Here B is the amplitude factor, determined by fitting of expressions (5)–(7) to expression (8).

Figure 2 illustrates the agreement of the pulse shapes (5)–(7) with the calculated pulse (8) at low (a) and high (b) pressures ν. The four-level model (curves 4) is practically indistinguishable from that set by expression (8) at low pressures and gives only slight deviation from it in pulse maximum at high pressures. The two- and three-level models in the case

of low pressures almost coincide with each other, while being essentially different than the "real" pulse. At high pressures, the difference increases because the lower order of the characteristic equations of systems (1) and (2), compared to that in system (4) leads to the pulses with the less steep leading edge and faster fall off of the tail at times, longer than the rise time.
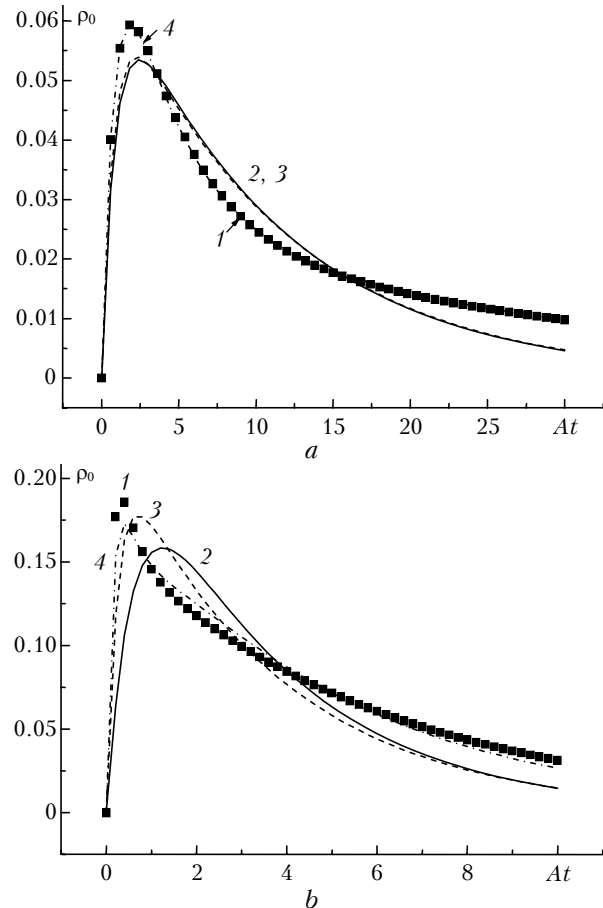

Fig. 2. Results of fitting the fluorescence pulse shapes for two-, three-, and four-level models (curves 2–4, respectively) to the calculated pulse shape for the five-level model (squares 1): (a) $\nu/A = 0.1$; (b) $\nu/A = 2$.

Thus, the first criterion that the number of levels included into the model of a quantum system is close or equal to the actual number of levels (accurate within percents) is the coincidence of calculated and experimental fluorescence pulse shapes at high pressure of the buffer gas ($\nu > 1 - 2$). Assuming ν equal $Nu\sigma$, where N is the buffer gas density; u is the average thermal velocity; σ is the cross section of inelastic collisions, for $\nu = A$ and $A = 10^8 s^{-1}$, $u \sim 2 \cdot 10^4$ cm/s, $\sigma \sim 10^{-15}$ cm^2 we have $N \sim 2 \cdot 10^{15}$ cm^{-3}, that conforms to the gas pressure ~ 250 Torr at the temperature of 200°C.

Figure 3 presents the results of fitting the pulses (5)–(7) to that given by expression (8). The errors of determination of the fitted frequencies ν_{fit}, are presented by the 95% confidence intervals.
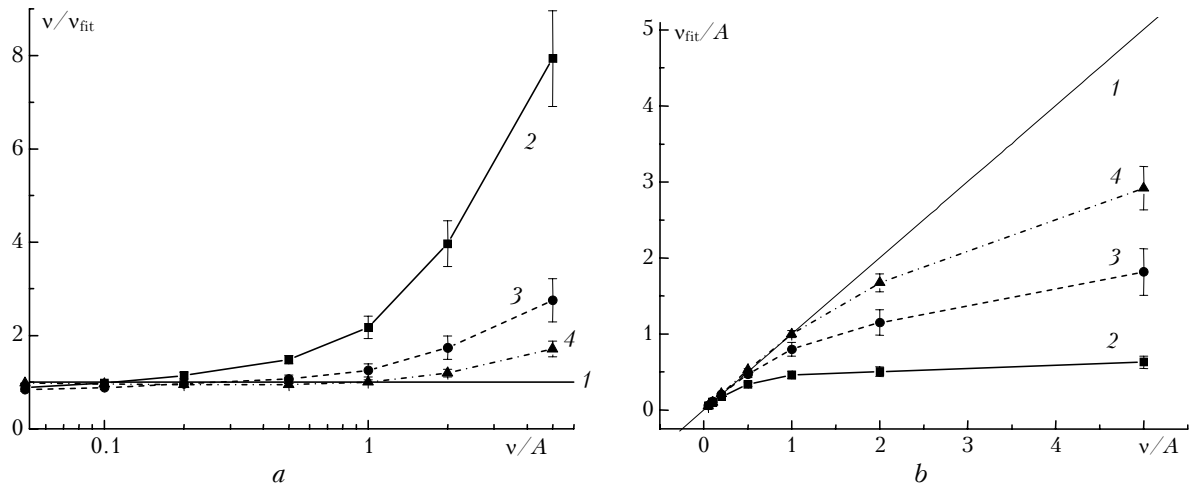
Fig. 3. The ratios of the preset frequency ν for the case of five-level model to the fitted frequencies $ν_{fit}$ as functions of the frequency ν (gas pressure) (*a*); the frequency dependence $ν_{fit}$ on pressure (*b*). Designations of the curves *2–4* are the same as in Fig. 2, the straight lines *1* correspond to the preset frequency ν.

As follows from Fig. 3*a*, model discrepancy with the real quantum system leads to a significant systematic error in the measured frequency ν. For ν ~ 0.5, error is tens percent, attaining orders of magnitude for the two-level model at ν > 5. Thus, the choice of the correct atomic model is the determining factor for quantitative measurements of the rates of inelastic transitions between the excited states by the fluorescence method. The largest error takes place at high pressures of a buffer gas. At the same time, the measurements at high pressures allow one to conclude about the conformity of the model chosen to the experiment. The second criterion, supplemental to the pulse shape, is the dependence of the frequencies retrieved $ν_{fit}$ on pressure (Fig. 3*b*). At full coincidence, this dependence is linear, but significantly differs from linear in the case of incompleteness of the quantum system description. As follows from Fig. 3*b*, this criterion is rather sensitive to the model. Application of two specified criteria will allow one to select the adequate description of the experiment. Since these criteria are connected to the general features of the population dynamics, they should be applied also in a case of more complex models of concrete atoms.

Acknowledgments