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# Time-Resolved Fluorescence from Ba and Ca Excited by a Pulsed Tunable Dye Laser

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We have observed the oscillatory magnetic-field and time dependence of the fluorescence from the $^1P_1$ levels of Ba and Ca excited by a pulsed tunable dye laser. We have observed level-crossing signals narrowed by the technique of time-delayed observation.

We report the use of a pulsed tunable dye laser to study the lifetimes, $g$ factors, and hfs of the lowest-lying $^1P_1$ states of Ba and Ca. Ba and Ca were chosen for the convenience of the wavelength of the resonance light and because of the relatively simple structure of the excited states.

In our experiments, atoms in a thermal beam of Ca or Ba are excited by a $\leq 5$-nsec pulse of $x$- or $z$-polarized light traveling in the $y$ direction from the $N_2$-laser–pumped dye laser,[1] tuned to the atomic resonance line (4227 Å for Ca, 5535 Å for Ba) and pulsed at a rate of about 25 per sec. The incident optical power is attenuated by 20 dB to about 10 W. The spectrum of the dye laser output is broad enough ($\simeq 0.4$ Å) to excite all the magnetic and hyperfine sublevels of a given state. An external magnetic field is applied in the $z$ direction and the $y$- or $z$-polarized light in the $x$ direction is detected by a 1P21 photomultiplier wired for fast response. The output of the 1P21 is fed to a sampling scope which is triggered by the laser pulse (using an auxiliary detector). The sampling scope can be used either in its time-sweep mode to observe the rapid decay and modulation of fluorescence or in a fixed-delay mode where samples are taken a fixed time after the trigger pulse (Fig. 1). In either case the analog output of the sampling scope is stored and averaged in a multichannel signal averager. We present data below which illustrate both the time-sweep and fixed-delay observation modes, to show the power of both methods in allowing the extraction of excited-state parameters.

Many authors[2-4] have laid the groundwork for calculating the fluorescence of atoms excited by pulsed light. We present here an amalgam of that work, which provides a suitable description of our data. We assume that the atom is in some initial state $u_m$ before the laser pulse. If the atom is excited by a $\delta$-function pulse at $t=0$, the atom can be described, in the low-light-intensity limit, by a superposition of states,

$$\psi = u_m + \sum a_\mu u_\mu, \quad a_\mu(t) \propto f_{\mu m} \exp[-(i\omega_\mu + \Gamma/2)t];$$

$u_\mu$ is an excited state with energy $\omega_\mu$ and decay rate $\Gamma$; $f_{\mu m}$ is the excitation transition matrix element. If the atom is instead subjected to a laser pulse whose electric field varies as $E(t_e)$,

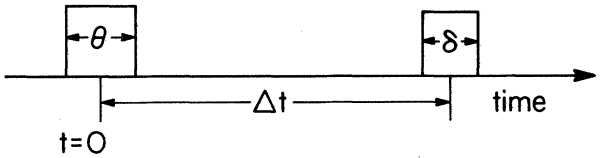


FIG. 1. Definition of time variables. $t_e$, variable around $t=0$ (excitation); $t'$, variable around $t=\Delta t$ (detection). Equation (4) is based on a rectangular excitation pulse and rectangular detection window as shown here.

the excited-state amplitude is given by

$$a_\mu(t') \propto f_{\mu m}\int_{-\infty}^{t'} E(t_e)\exp[-(i\omega_\mu + \Gamma/2)(t'-t_e)]\,dt_e \equiv f_{\mu m} I_\mu(t') \tag{1}$$

(since the time between laser pulses is very long compared to $1/\Gamma$, the pulses are independent).

Following Ref. 2, we calculate the rate of fluorescence as a function of time by summing over all initial, excited, and final states. We find

$$R(t') \propto \sum f_{\mu m} f_{m\mu'} g_{\mu' m'} g_{m'\mu} I_\mu(t') I_{\mu'}{}^*(t'), \tag{2}$$

where the $g$'s are the transition matrix elements for fluorescence from the excited states to a final state $u_{m'}$. We can now use the arguments of Dodd, Corney, and Series[3,4] to show that in the limit of laser bandwidth broad compared to the differences in excited-state energies, the product of the integrals in Eq. (2) can be written as an integral whose kernel is $P(t_e)\exp[-(i\omega+\Gamma)(t'-t_e)]$, where $\omega = \omega_\mu - \omega_{\mu'}$ and $P(t_e)$ is the intensity of the laser pulse. If we assume for simplicity that the laser pulse is a rectangular pulse of length $\theta$ and that we observe the fluorescence for time $\delta$ centered around $t = \Delta t$ after the laser pulse (see Fig. 1), we can evaluate the integrals

$$R(\Delta t, \theta, \delta) \propto \sum f_{\mu m} f_{m\mu'} g_{\mu' m'} g_{m'\mu} \int_{\Delta t - \delta/2}^{\Delta t + \delta/2}\int_{-\theta/2}^{\theta/2} P(t_e)\exp[-(i\omega+\Gamma)(t'-t_e)]\,dt_e\,dt' \tag{3}$$

and find the following expression for the observed fluorescent intensity:

$$\begin{aligned} R(\Delta t, \theta, \delta) \propto{}& \sum f_{\mu m} f_{m\mu'} g_{\mu' m} g_{m'\mu}[e^{-\Gamma T}/(\Gamma^2+\omega^2)^2] \\ &\times\{[\omega^2 - \Gamma^2 + 2i\omega\Gamma][\cos\omega T + e^{-\Gamma\tau}\cos\omega(T+\tau) - e^{-\Gamma\theta}\cos\omega(T+\theta) - e^{-\Gamma\delta}\cos\omega(T+\delta)] \\ &+ [2\omega\Gamma - i(\omega^2-\Gamma^2)][\sin\omega T + e^{-\Gamma\tau}\sin\omega(T+\tau) - e^{-\Gamma\theta}\sin\omega(T+\theta) - e^{-\Gamma\delta}\sin\omega(T+\delta)]\}, \end{aligned} \tag{4}$$

where $\tau = \theta + \delta$ and $T = \Delta t - \tau/2$.

Equation (4) is plotted in Fig. 2 for the particular case of the $^1P_1$ levels of Ba and our experimental geometry. Figure 2(a) shows intensity versus magnetic field for several values of $\Delta t$, and Fig. 2(b) shows the intensity versus time for a 60-G magnetic field for our experimental conditions. We have used the hyperfine structure constants determined by Lurio[5] to calculate exactly the magnetic field dependence of the transition matrix elements ($f$'s and $g$'s) in Eq. (4) for the two odd isotopes of Ba (nuclear spin $\frac{3}{2}$, 17% abundance). In levels with no hyperfine structure, such as the $^1P_1$ level in calcium, the curves are the same as those calculated by a simple, classical model.[6]

It is clear from Fig. 2(a) that for delay times considerably shorter than the excited-state lifetime, the signal is very much broader than the signal obtained for continuous excitation and observation [which is shown at the bottom of 2(a) for reference], but for delays which are longer than the lifetime, the central part of the signal is considerably narrower. More importantly, because these signals have high-frequency information far into the wings, they will be much more useful in a level-crossing experiment where one attempts to find the center of the signal in order to determine a fine or hfs interval. The improvement in precision of determination of the location of the center of the signal in this kind of experiment is comparable to that achieved by the separated oscillating-field technique in atomic and molecular beam resonance spectroscopy.[7] It should be mentioned that similar oscillations caused by pulsed excitation and delayed detection develop in the signal shape for other related experimental techniques such as optical double resonance and Mossbauer spectroscopy.[8]

Figure 3 presents the experimental results on Ba. Both magnetic field dependence [Fig. 3(a)] and time dependence [Fig. 3(b)] are shown. The excellent agreement with the predictions of Fig. 2 is apparent. Similar data for Ca (not shown) are described well by Eq. (4) with no magnetic field dependence in the matrix elements. Table I presents the results of fitting Eq. (4) to the data for Ba and Ca.

zu Putlitz[9] has reviewed the general technique of time-delayed narrowing, and Ref. 6 contains a brief review of more recent related experiments. The fundamental basis for these experiments, as well as the observation of quantum beats in beam-foil spectroscopy[10] or pulsed-dye-laser experiments,[11] is the same, namely, the apparatus selects for observation only those atoms whose lifetime is within $\pm(\theta+\delta)/2$ of the delay time $\Delta t$. If $\Delta t$, and therefore $T$, is made very long, the intensity oscillates rapidly with

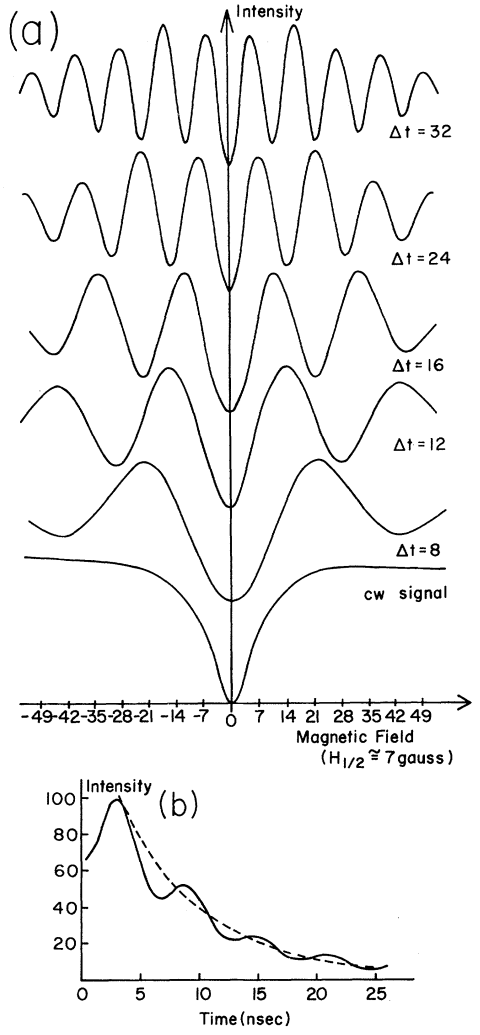


FIG. 2. (a) Equation (4) plotted for Ba ($^1S_0 \leftrightarrow {}^1P_1$) for various values of $\Delta t$ (in nsec) assuming incoming beam, outgoing beam, and magnetic field are mutually perpendicular and the light is polarized perpendicular to the field. The slight deviation from damped sine waves arises from the hf contributions. (b) Equation (4) plotted for barium at 60 G for the case of both polarizations perpendicular to the field. Broken line, exponential with $1/\Gamma \cong 8$ nsec.

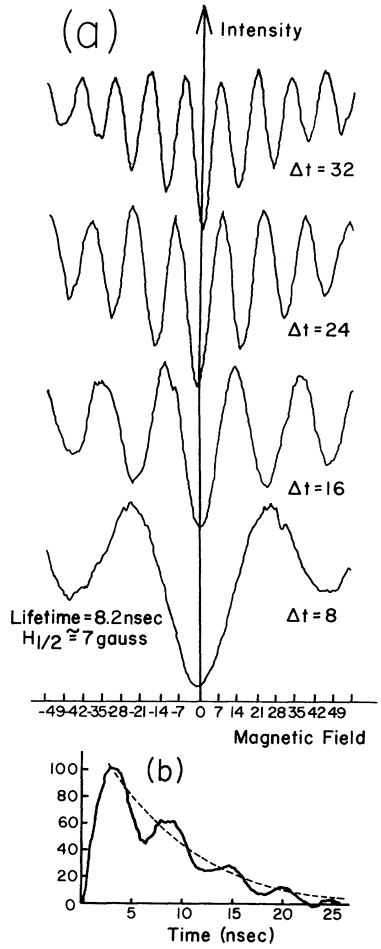


FIG. 3. Ba ($^1S_0 \leftrightarrow {}^1P_1$) data taken under conditions which approximate those of Fig. 2. Averaging time, about 20 min for each run. (a) Field dependence for several values of $\Delta t$ (in nsec). (b) Time dependence at about 60 G. Broken line, exponential with 8-nsec time constant.

magnetic field and one can say that a level-crossing signal has been narrowed as a consequence of selecting particularly long-lived atoms. Naturally, the detected light intensity has been reduced by the factor $\exp(-\Gamma T)$. We have observed these high-frequency oscillations with a signal-to-noise ratio of about 10 for delays as long as 5 lifetimes using about 30 min averaging time.

It is apparent that the idea originally proposed by Hughes[12] and first observed in atoms by Ma and co-workers[13] and by Copley, Kibble, and Series[14] for narrowing resonance signals by selecting longer-lived atoms can be formulated quantitatively and can be routinely observed. Although the results are not as simple as one might naively expect, the presence of the oscillations in the wings should be welcomed as added richness and information in the signal rather than treated as an unwanted nuisance to be eliminated if possible.

The technique described here can be extended to any excited state of an atom or molecule which is accessible from either the ground or other populated state via an optical absorption of wavelength within the broad range of pulsed dye lasers. It would be particularly valuable for stud-

TABLE I. The values of lifetimes and $g$ factors of $^1P_1$ Ba and Ca.

| | $\tau(^1P_1)$ (nsec) | $g_J(^1P_1)$ |
|---|---|---|
| Barium | 8.3(0.5)[a] | 1.00(0.01)[a] |
| | 8.37(0.20)[b] | 1.0039(0.0008)[b] |
| | 8.36(0.25)[c] | |
| Calcium | ...[d] | 1.00(0.01)[a] |
| | 4.48(0.15)[e] | |
| | 4.67(0.11)[c] | |
| | 4.62(0.15)[f] | |

[a]Present work.

[b]M. Swagel and A. Lurio, Phys. Rev. 169, 114 (1968).

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[d]The ≃ 3-nsec width of the pulse response of the 1P21 precludes measurement of such a short time. The effect on the Ba lifetime, however, is small.

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ies of molecular excited states where one could measure the lifetime and $g$ factor of several rotational levels of the same electronic state. In addition, tunable dye lasers with pulse lengths short compared to excited-state lifetimes would be useful tools for the study of radiation trapping in optically dense vapors. Finally, it may be possible to distinguish experimentally between the currently accepted theory of electromagnetic radiation and the recently proposed "neoclassical" theory.[15]

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# Experimental Evidence for New Dissociation Channels in Electron-Impact Ionization of $H_2$

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Proton energy spectra have been obtained from the dissociative ionization of $H_2$ by electrons which reveal the existence of many new states lying between the $1s\sigma_g$ ground state of $H_2^+$ and the $2p\sigma_u$ repulsive state.

Considerable interest is currently being focused on the various possible ionization and dissociation channels in the simplest molecule $H_2$ under electron impact. Considerable evidence is available for the existence of high-lying $H_2^-$ or excited $H_2$ states above the threshold for direct ionization of $H_2$ at 15.4 eV though the relative importance of autoionization and negative-ion forma-