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Use of synchrotron radiation for the measurement of fluorescence lifetimes with subpicosecond resolution

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A method for the measurement of fluorescence lifetimes with subpicosecond resolution is described. The temporal resolution is achieved by using the high harmonic content of the synchrotron radiation produced by an electron storage ring.

The importance of relaxation process in the nanosecond and subnanosecond time scale in organic biological molecules is now quite clear. One technique available for the study of fast relaxation processes is the measurement of the lifetime of the excited states.

Pulsed light sources together with delayed coincidence or with single photon counting\textsuperscript{1}\textsuperscript{2} have been used for fluorescence lifetime measurements. In these experiments the fluorescence is measured in the time domain, this has the advantage that no \textit{a priori} assumptions need to be made about the shape of the decay. However, the time resolution is limited by the width of the light pulse and by the photomultiplier response. Elaborate computational techniques have been used to deconvolve the instrumental response.\textsuperscript{3}\textsuperscript{4}\textsuperscript{5} To achieve picosecond resolution, picosecond light pulses have been used.\textsuperscript{6}\textsuperscript{7}

On the other hand, it is well known\textsuperscript{8} that a fluorescent probe excited with intensity modulated light fluoresces with a phase-shift and a modulation simply related to incident radiation. In the case of an exponential decay

\[
\tan\phi = 2\pi\nu_0\tau; \quad R = M_M/M_F = [1 + (2\pi\nu_0\tau)^2]^{1/2},
\]

where \(\phi\) is the phase shift, \(\nu_0\) the excitation frequency, \(\tau\) the excited state lifetime, \(M_M\) the modulation of the excitation, and \(M_F\) the modulation of the fluorescence. In general it is relatively easy to measure the phase and subnanosecond\textsuperscript{9}\textsuperscript{10} or even picosecond resolution is possible.\textsuperscript{11} However, the phase shift method presents several inconveniences: (a) Eq. (1) is only valid when the decay is a single exponential—this limitation may be overcome using a set of exciting modulation frequencies; and (b) to obtain picosecond resolution, high modulation frequencies are required.

We want to demonstrate that a high-repetition-rate pulsed light source with narrow pulses can be used to combine the advantages of the pulsed and the phase shift method. Typical examples of such light sources are synchrotron radiation, cw mode-locked, cavity-dumped lasers, and Pockels cell or acousto-optic modulated light. For the present discussion we will use the properties of the synchrotron radiation (SR) from an Electron Storage Ring (ESR) but the argument is easily extended to other light sources. Synchrotron radiation consists of a series of equally spaced, nearly Gaussian, pulses with constant repetition frequency \(v_0\), amplitude \(A\), and constant width \(2\Delta\). It has recently been shown that the shape is wavelength independent.\textsuperscript{12} The intensity of the SR can be described by the time series

\[
f(t) = [1/(2\pi)^{1/2}]
\]

\[
\times \exp\left(-\frac{(t - nT_0)^2}{2\Delta^2}\right), \quad n = 0, 1, 2, \ldots
\]

where \(T_0\) is the repetition period and \(2\Delta\) the width of the Gaussian pulse. The harmonic content is given by the Fourier transform of the time series:

\[
G(\omega) = \delta(\omega - \omega_n) \exp\left[-(\Delta\omega)^2/2\right], \quad n = 1, 2, 3, \ldots
\]

where \(\omega_0\) is the fundamental frequency. Since the power spectrum is proportional to \(G(\omega)^2\), energy is available over a wide range of frequencies if \(\Delta\) is small. Using presently available techniques, we can measure phases with an accuracy of 10\textsuperscript{-1} degrees and amplitude ratios with an accuracy of 10\textsuperscript{-3} over the frequency range 1–1000 MHz. Table I lists (a) some of the timing characteristics for the SR of three presently operating ESR (ACO—Orsay; SPEAR—Stanford; Doris—Hamburg), (b) the frequency of the harmonic whose amplitude is 10\% of the fundamental, (c) the frequency of the harmonic whose amplitude is 10\% of the fundamental available at the output of a 500-MHz bandwidth photo-
and since broad intensity spectrum can be used to separate multicomponent decays. In addition it is advantageous to use cw mode-locked cavity-dumped fast repetition lasers. Since sine-wave modulation has a higher integrated intensity than pulse modulation it is advantageous when possible. To summarize, we have described how the total harmonic content of a light pulse train can be used. This is advantageous since the energy available in the first harmonic is only a small fraction of the total energy and since broad intensity spectrum can be used to separate multicomponent decays. In addition subpicosecond resolution is possible using the available high-frequency sources.

Excitation with light pulses with high harmonic content cannot give rise to interference in the fluorescence intensities unless the single decay obeys nonlinear differential equations; this may be the case with strong laser pulse excitation. The noise of the photomultiplier is essentially flat so that the contribution over a small range of frequency is small and measurement over a narrow bandwidth increases the signal-to-noise ratio. To increase further the sensitivity of the method, heterodyne techniques can be used. Although the phase measurement requires a stable reference signal at each harmonic to be measured, the amplitude measurement does not and the modulation could simply be measured with a spectrum analyzer. It is clear that at this level of time resolution the main limiting factor will be the optical design of the experiment.

We thank L. B. Sorensen for helpful discussion. One of us (RLD) wishes to thank Professor S. Doniach for help and support. Material incorporated in this paper was developed with the financial support of the NSF with the cooperation of the Department of Energy.


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<table>
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<th>Multiplier</th>
<th>$\nu_0$ (MHz)</th>
<th>$2\Delta$ (ns)</th>
<th>$\nu_0$ (MHz)</th>
<th>$\Delta T_1$ (ps)</th>
<th>$\Delta T_2$ (ps)</th>
<th>$\nu_0$ (MHz)</th>
<th>$\Delta T_3$ (ps)</th>
<th>$\Delta T_4$ (ps)</th>
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<td>0.5</td>
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<td>0.25</td>
<td>2731</td>
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<td>2.5</td>
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<td>5</td>
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<tr>
<td>DORIS</td>
<td>1.0</td>
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<td>4879</td>
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<td>1.5</td>
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<td>0.2</td>
<td>5</td>
</tr>
</tbody>
</table>

Simple partial pressure measurement of SF$_6$ in mixtures with nitrogen

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A simple but accurate method for the measurement of the partial pressure of SF$_6$ gas in mixtures with nitrogen is described. It is based on the ease with which the gases can be separated by freezing the SF$_6$. SF$_6$ gas is commonly used in various mixtures with nitrogen as the filling for pressurized gas switches which are employed, for example, in pulsed electron beam accelerators. These mixtures can be made by slowly admitting SF$_6$ to an evacuated gas cylinder until the pressure reaches the required partial pressure appropriate for a mixture whose final pressure is determined by the subsequent filling with nitrogen from a standard cylinder with an initial pressure of, say, 150 atm. Typically SF$_6$ is present in the range 2.5%-10% and the maximum pressure of the mixture is then about 76 atm. It is assumed that by this technique complete mixing of the gases is ensured but it is useful to be able to check independently the composition of a sample, either from the cylinder itself or from the contents of a gas switch.

The method depends on the possibility of freezing SF$_6$