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diode thermometry, and to V. Wang for technical assistance.

¹ A discussion of thermal conductivity is given in NBS Monograph 131 and references cited therein (G. E. Childs, L. J. Ericks, and R. L. Powell, *Thermal conductivity of solids at room temperature and below* (Cryogenics Div., NBS, Sept. 1973).

² For a discussion of diode thermometry, see D. L. Swartz and J. M. Swartz, *Proc. of ISA-76 Int'l Cont. and Exhibit*, Houston, Oct. 1976 (Instrum. Soc. Am. New York, 1976), pp. 1-15.

³ The diodes used are Model DT-500FP-HRC, Lake Shore Cryotronics, Inc.

⁴ At this current level the diode self-heating is more than three orders of magnitude smaller than the heater power.

⁵ Ref. 1, Fig. 64a.

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^{1,2} have been used for fluorescence lifetime measurements. In these experiments the fluorescence is measured in the time domain, this has the advantage that no *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.³⁻⁵ To achieve picosecond resolution, picosecond light pulses have been used.^{6,7}

On the other hand, it is well known⁸ 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

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

where ϕ is the phase shift, ν_0 the excitation frequency, τ the excited state lifetime, M_E 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^{9,10} or even picosecond resolution is possible.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 ν_0 , amplitude A , and constant width 2Δ . It has recently been shown that the shape is wavelength independent.¹² The intensity of the SR can be described by the time series

$$f(t) = [1/\Delta(2\pi)^{1/2}] \times \exp[-(t - nT_0)^2/2\Delta^2], \quad n = 0, 1, 2, \dots,$$

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

$$G(\omega) = \delta(\omega - \omega_0 n) \exp[-(\Delta\omega)^2/2], \quad n = 1, 2, 3, \dots,$$

where ω_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 Δ is small. Using presently available techniques, we can measure phases with an accuracy of 10^{-1} degrees and amplitude ratios with an accuracy of 10^{-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-

TABLE I. Electron storage ring, ESR; repetition frequency, ν_0 ; width of the Gaussian pulse, 2Δ ; frequency of the harmonic whose intensity is 10% of the fundamental, ν_h ; maximum resolution possible for a 10^{-1} degree phase measurement, $\Delta\tau_\phi$; maximum resolution possible for a 10^{-3} modulation ratio measurement, $\Delta\tau_M$; ν_h , $\Delta\tau_\phi$, $\Delta\tau_M$ have the same meaning as ν_h , $\Delta\tau_\phi$, and $\Delta\tau_M$, respectively, but a frequency cutoff of 500 MHz is assumed for the photomultiplier.

ESR	ν_0 (MHz)	2Δ (ns)	ν_h (MHz)	$\Delta\tau_\phi$ (ps)	$\Delta\tau_M$ (ps)	ν_h (MHz)	$\Delta\tau_\phi$ (ps)	$\Delta\tau_M$ (ps)
ACO	13.7	1	685	0.4	10	~600	0.5	15
SPEARS	1.3	0.25	2731	0.1	2.5	~1500	0.2	5
DORIS	1.0	0.14	4879	0.05	1.5	~1500	0.2	5

multiplier, and (d) the maximum resolution for single lifetime measurements for the three ESR in operation. It appears that subpicosecond resolution can be achieved and relatively high intensities compared to the fundamental are available.

It is clear that the proposed experiment can be performed with any pulsed light source if the pulse shape and the period fulfill some requirements. The most important parameter is the rise and fall time of the pulse since this determines the high-frequency harmonic content. The repetition rate determines the total intensity and the spacing between harmonics. Very impressive time resolution can be attained using 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 con-

tent 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.⁹ 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.

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Simple partial pressure measurement of SF₆ in mixtures with nitrogen

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A simple but accurate method for the measurement of the partial pressure of SF₆ gas in mixtures with nitrogen is described. It is based on the ease with which the gases can be separated by freezing the SF₆.

SF₆ 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.¹ These mixtures can be made by slowly admitting SF₆ 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 SF₆ 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 SF₆