## **Subject Index**

Data analysis; see also Specific

impurities, effect on, 163

numerical integration in, 175

multiple exponential decay, 11, 181

techniques

Amplifiers, see also Specific types rising edge effects on, 178, 179, 186 arrangement of, 136 smoothing in, 179 Anisotropy, 23, 252–283; see also standard errors, 173 Polarization, Time-dependent wavelength effect on; see Zero-time fluorescence anisotropy construction of from  $I_{//}$ ,  $I_{\perp}$ , 270 Decay associated spectra, 226–228 deconvolution procedures, 269-274 Decay of excited states difference function, 270 bimolecular processes, 6–21 fitting by Lagrange multipliers, 273 chemical reaction, 3 in liquid crystal, 25 concentration quenching, 7 magic angle viewing, 258, 268 excimer formation, 8–11 measurement of time-dependence, exciplex formation, 11–12 261-263 impurity quenching, 11 measured by up-conversion, 36 internal conversion, 3, 4 origin of time-dependence of, 253, intersystem crossing, 3 274-282 Deconvolution; see Data analysis polarized excitation, 255, 257, 258 Delay lines, 138, 156  $r_0$  values, 265 Depolarization; see Polarization theory for restricted motion, 279-282 Diffusion-controlled reactions, 13–14, unpolarized emission, 260 216 Diffusional motion unpolarized excitation, 259 weighting factors, 270 of oblate ellipsoid, 278 of prolate ellipsoid, 278 Background noise, 46–47, 158 of spherical molecule, 277–278 Biased amplifier, 138, 145 Diffusion coefficient sphere, prolate and oblate ellipsoids, Chemical timing, 13, 218 278 Chi-square; see Statistical tests wobbling, 279 Connectors, 148, 157 Discriminators, 133, 152 Convolution constant fraction timing, 135–136 definition, 43-45 leading edge timing, 134 Cone angle, 279 level timing, 134 Curve fitting; see Least squares curve setting discriminator levels in, 152 fitting snap-off timing, 136

Electron beams, 55

Energy migration

Electric dipole transition, 1

Excimers; see Decay of excited states, excimer formation Exciplexes; see Decay of excited states, exciplex formation, TRES Exponential series deconvolution techniques, 176	1-cyanonaphthalene, 52 1-cyanonaphthalene-triethylamine exciplex system, 12 definition of, 2, 5 1, 2-dimethyl indole, 52 N,N-dimethyl-1-naphthylamine, 52 2,5-diphenyloxazole, 52
Flash lamps, 100 arc gap in, 60, 77 electrode materials, 58 filling gas, 65, 68, 70, 74 gas leakage in, 61 high pressure, 63–65, 76	lower limit of measurement of, 41–42 9-methyl anthracene, 19 1-methyl indole, 52 3-methyl indole, 52 modulation methods, 25–29 pulse sampling methods 29–31 pump and probe techniques, 31–34
high voltage in, 76 housings, 62, 66 pressure, operating, 76–77 pulse frequency, 64, 73, 77 pulse intensities, 77–78, 94 pulse shape, 63, 67, 74–75, 96–97 pulse stability, 96	quinine bisulphate, 45 rhodamine B., 28 standards 51–52 synthesis from $I_{\parallel}$ , $I_{\perp}$ , 266 up-conversion 32–34 Fourier transforms, 170
r.f. generation in; see Radio-frequency noise spectral range, 66, 69-70, 95 thyratrons for, 71-73 windows in, 58	Gated spectra; see TRES G-factor, correction by leading-edge matching, 265
Fluorescence; see also Anisotropy, Decay of excited states, Polarization competing processes, 3-4 diffusion-controlled quenching, 13 environmental effects, 15-20	correction by tail-matching 263 measurement using free rotor probe, 266  Instrument response function measurement of, 45–46
intensity, 1–6 Jablonskii diagram, 4 mean radiative lifetime, 2 quantum yield, 5 radiative rate-constant, 2 refractive index effects, 2, 3	Lagrange multipliers, 273 Laplace transforms, 168 Lasers, 101 cavity dumping, 84–87 frequency doubling, 92–94
solvent relaxation and 15, 16 specific solvent effects, 8 static quenching, 12 Stern-Volmer quenching, 8 Stokes loss, 16, 46 Fluorescence decay time; see also Data	mode-locking, 86–87 Pockels cell pulse selection, 90 pulse intensity, 94 pulse stability, 96 pulse widths, 96–97 spectral range, 91–92, 95
analysis acid-base equilibria and, 19 anthracene, 19, 53 benzene vapour, 5, 6 9,10 bis(phenylacetyleno) anthracene, 3	synchronously pumped, 87–89 Leading-edge matching; see G-factor Least squares curve fitting; see also Statistical tests, 171 Fortran routine for, 192 global analysis, 176
$\beta$ -carboline 19	Marquardt algorithm, 174–175

weighting factors in, 172
Lifetimes; see Fluorescence decay time
Magic-angle viewing; see Anisotropy
Method of moments, 166–168
Mirrors, rotating, 55
Modulating functions, 169–170
Multichannel analyser, 146–147, 156
channel width effect of on
deconvolution, 159
multi-channel mode, 211

NIM Bin, 132, 156

Oblate ellipsoid; see Diffusional motion Onsager theory, 16–19 Oscilloscope, 149, 157

Perrin equation, 252 Phase plane technique, 165-166 Photomultipliers, 103-104, 130 crossed field type, 124 dark current, 107-108 fast, types of, 104 housings for, 113 gain, 106-107, 130 magnetic field effects, 112-113 microchannel plate, 124-126 pulses, anomalous, 113-114 single photon resolution, 110–112 solar blind, 105 spectral response, 105, 130 transit time, 108-110, 119-124 voltage divider, 114-119 wavelength effect; see Zero-time shift Photon-counting fluorimeter, 211 Poisson noise, 41, 158 simulation of, 190 Polarization; see also Anisotropy correction for G-factor 263-269 degree of, 23, 24 effects on intensity measurements, 254-261 scramblers, use of, 260 viscosity dependence, 24 Preamplifiers, 137–138, 156 Precision, in lifetime measurements, 39 - 42Prolate ellipsoid; see Diffusional motion Pulse pile up, 39 correction for, 142-143, 164

inspection, 112, 141, 150

Quenching; see Fluorescence

Radio-frequency noise effect of on deconvolution, 163 generation of, 73 suppression of, 80-84, 116, 139 Random noise; see Poisson noise Rate meter, 147, 156 Ratio correction technique; see Zerotime shift Reduced chi-square; see Statistical tests Restricted motion in lipid bilayers 279 in liquid crystals, 25 in proteins, 281 in synthetic macromolecules, 281–282 Rotational diffusion coefficient, 23, 275 Rotational relaxation time, 23, 252–253

Scattered light, 98 corrections for, in deconvolution, 160-161, 178 Sensitivity in lifetime measurements, 39-42 Single photon conditions, 39, 165 Solvent relaxation; see Fluorescence, Spherical molecule; see Diffusional motion Statistical tests of quality of fit, 180 autocorrelation function, cr(i), 184 chi-square,  $\chi_{\nu}^2$ , 181 Durbin-Watson parameter, DW, 187 kurtosis, K, 188 mean residual, r, 188 residuals,  $r(t_i)$ , 183 root mean square deviation of residuals, 189 skewness, SK, 188 standard deviation of residuals,  $\sigma_r$ , standard normal variate, Z, 182 support plane confidence intervals, 189 Storage ring radiation, 56 properties of, 56-58

Straight line fitting, 165

Strickler-Berg relationship, 2

Synchrotron radiation; see Storage ring radiation
Synthetic data, 189
computer calculation of, 192
Synthetic polymers
excimer fluorescence, 10
fluorescence anisotropy, 266-272, 282

TAC; see Time-to-amplitude converter Tail-matching, 263
Ten-exponential function cut-off correction with, 226 use of, 224, 225
Time calibration
NIM component for, 150, 157 simple method, 153
Time-correlated single-photon counting; see also Fluorescence decay time basic description, 36, 37 reviews, 31 statistics, 37–39
Time-dependent anisotropy; see Anisotropy

Time-to-amplitude converter, 132, 139 inverted configuration, 47–48 multichannel type, 144 non-linearity in, 141, 179 trigger pulse for, 79 Timing filter amplifier, 137, 156 TRES, 18, 19, 211–251

Time-resolved emission spectra; see

amino-naphthalene, 19 8-anilino-1-naphthalene sulphonate (ANS), 215-216 applications and limitations, 213-218 construction from deconvolved decays, 222-226 definition of zero-time, 221 delay time,  $\Delta t$ , 220 1,4-dicyanonaphthalene-2,5-dimethyl-2,4-hexadiene exciplex, 223, 227 direct recording, 219-222 exciplexes studied with, 222 poly(vinyl naphthalene)-poly(methyl methacrylate) 215-217 time-window,  $\delta t$ , 220 Toluidino naphthalene sulphonate, 18

Up-conversion; see Fluorescence decay time

Wavelength effect; see Zero-time shift Weighting factors; see Anisotropy, Least squares curve fitting

X-ray, as excitation sources, 55

Zero-time shift corrections for, 49-51, 161-163, 173, 178 origin of, 96, 119-124