

Index

a

- ab initio* methods 67–71, 91, 94
- *ab initio* molecular dynamics (AIMD) 253
- absolute tautomerism 116
- absorption UV–Vis spectroscopy 25–46, *See also* Quantitative analysis of tautomeric equilibria
- activation energy 216
- acylamidines, $\Delta(\text{NMe})$ in 313–315
- adenine, gas-phase spectroscopy of 187
- adenosine triphosphate (ATP) 2
- adiabatic reactive molecular dynamics (ARMD) 256
- alicyclic ketones and amides, tautomerism in 3
- amidines 308–309
- amidine correction factors, conformational effects on 309–310
- 4-((4-Aminophenyl)diazanyl)-N,N-dimethylaniline 43–45
- ammonium–azonium tautomerism 43–45
- in 4-((4-aminophenyl)diazanyl)-N,N-dimethylaniline 43–45
- annular tautomerism in tetrazole 363
- aromatic ketones and amides, tautomerism in 3
- aromatic resonance 3–4
- Arrhenius theory 17
- azaindole 17
- azo–hydrazone tautomerism 133

b

- ballistic wavepacket motion 88–90
- bands decomposition, quantitative analysis by using 29–33
- barrier frequency 222
- base pairs 189–191
- base-strengthening effect 329

- ‘basicity method’ for tautomer ratio estimation 5, 299, 305–333
- complicating factors in use of 326–330
- – caused by hydrogen bonding 327–328
- – caused by protonation at the ‘wrong site’ 328
- – caused by steric and stereoelectronic factors 326–327
- correction factors 308–320, *See also individual entry*
- experimental protocol 307–308
- tautomeric problems to which basicity method is inapplicable 330–332
- using model compounds 306
- Beer’s law 26
- benzofusion
- to give benzenoid structures in six-membered ring oxoheterocycles 321–324
- to give quinonoid structures in a variety of compounds 324–325
- bifunctional NH/N azaaromatics, tautomerism in 56–67
- intramolecular excited-state NH tautomerization in 2,9-(di-2′-pyridyl)-4,7-di(*tert*-butyl)carbazole 59
- intramolecular NH/N tautomerization 56–59
- biophysics, NH Tautomerism as a tool in 72–74
- Boltzmann distributions 184–185
- bond energy bond order (BEBO) potential 255
- Born–Oppenheimer approximation 145
- Brownian motion 98, 223

c

- carbohydrate tautomerism 132–133
- cation salvation 306

- chemical shifts in tautomeric equilibria study 145–173, *See also* Isotope effects
 - chemometrics 25–46, *See also* Quantitative analysis of tautomeric equilibria
 - citrinin 169
 - classical Liouville equation 235, 241
 - classical proton transfer reaction 236–238
 - coherences 238
 - coherently excited vibrations in product modes 90–92
 - *ab initio* calculations 91
 - common cation 307, 331–333
 - complete active space perturbation theory (CASPT2) calculations 68
 - complete active space self-consistent field (CASSCF) 68
 - computational approaches to proton transfer 254–256
 - concentration effect on equilibrium 36
 - concentric tubes 149
 - concerted mechanism 67
 - condensed-phase proton transfer 263–264
 - conductor-like screening model (COSMO) 354
 - configuration
 - integrationsingles–second-order Møller–Plesset (CIS-MP2) studies 67
 - configuration interaction (CI) 340
 - contiguous nitrogen atoms, compounds with, $\Delta(\text{NMe})$ for 315–317
 - continuum solvation models 353–355
 - contracted basis function 348
 - coordinate covalency term 278
 - correction factors 307–325
 - derivation of 308–320
 - – acylamidines, $\Delta(\text{NMe})$ in 313–315
 - – amidines and related compounds 308–309
 - – imides, $\Delta(\text{NMe})$ in 313–315
 - – lactams 310–312
 - – thiolactams, $\Delta(\text{NMe})$ for 317–320
 - – vinylogous lactams 312–313
 - regularities revealed by 320–325
 - – six-membered ring oxoheterocycles 321–324
 - correlated treatments 340–342
 - coupled cluster (CC) calculations 340
 - coupling quantum and classical motion 242–246
 - couplings 149
 - critical micelle concentration (CMC) 73–74
 - cyclic anhydride-enol tautomerism 114
 - cytosine, gas-phase spectroscopy of 187–188
 - lowest energy structures of hydrogen-bonded cytosine dimmers 190
- d**
- Debye relaxation time 225
 - definition of tautomerism 1–3
 - practicalities 1–3
 - principles 1–3
 - density functional theory (DFT) methods 60, 67–71, 166, 189, 254–255, 338, 342–347
 - double (doubly) hybrid functionals 344–345
 - generalized gradient approximation (GGA) 343
 - Hybrid Functionals 344
 - Kohn–Sham formulation of 343
 - Lee, Yang, and Parr (LYP) 343
 - local density approximation (LDA) 343
 - meta-GGA functionals 344
 - OPTimized eXchange (OPTX) 343
 - orbital-free DFT procedures 342
 - unconventional' approaches to 345–346
 - – dispersion corrections 345
 - – local hybrids 345
 - validation of density functionals 346–347
 - density matrix 236
 - density operator 236
 - deuterium isotope effects 153–154, *See also* Intrinsic isotope effects
 - diatomics in molecules (DIM) 255
 - diffraction methods 197–211, *See also under* Solid state; X-ray diffraction
 - diffuse functions 348
 - dipolar repulsion 4–5
 - dipyridocarbazole, ESDPT in 64
 - direct evidence of solid-state tautomerism by diffraction methods 197–211
 - direct intramolecular proton transfer reactions 50–51
 - disorder 198
 - dispersion corrections 345
 - double (doubly) hybrid functionals 344–345
 - double ESIPT, reaction-path-specific wavepacket dynamics in 96–97
 - double hybrid density functionals (DHDfFs) 347
 - double zeta, DZ 348
 - double-resonant spectroscopy 178, 185
 - dynamic electron correlation 339
- e**
- electrical effect substituent constants 7
 - electronegative substituents, changes in tautomeric form brought about by 7–8

electronic rearrangement 233–234
 environmental changes affecting equilibrium
 33–37
 – concentration effect 36–37
 – mathematical expression 33–37
 – optimization procedure 35
 – physical meaning 33–37
 – salt addition effect 34
 – solvent effect 33–34
 – temperature change effect 35
 exchange of isotopes 149
 excited state protontransfer reaction (ESIPT)
 13–15
 excited-state intramolecular proton transfer
 (ESIPT) reactions 57, 79–80, 213–250, *See also* Transition state theory (TST)
 – quantum and classical 236–238
 – ‘self-assisted’ intermolecular ESIPT 59
 – solvent friction and solvent dynamics
 224–226
 – ultrafast transient absorption signatures of
 85–87
 experimental and theoretical methods in
 tautomerism 1–20
 – history 1–20
 – introduction 1–20
 – recent developments in 1–20
 explicit solvent models 355–357

f

femtochemistry 247–249
 femtosecond photoelectron 84
 femtosecond pump–probe spectroscopy
 79–100
 – double ESIPT, reaction-path-specific
 wavepacket dynamics in 96–97
 – internal conversion 97–99
 – of photoinduced tautomerism 79–100, *See also* Pump–probe spectroscopy dynamics;
 Ultrafast pump–probe spectroscopy
 – reaction mechanism 93–96
 five- or six-membered heterocyclic
 compounds, annular tautomerism of
 126–128
 flavones 17
 fluorescence anisotropy 54–55
 fluorescence correlation spectroscopy (FCS)
 55–56
 fluorescence microscopy 55–56
 fluorescence sensing 72
 fluorescence techniques for studying
 tautomerism 52–56
 – advanced techniques in 54–56
 – – fluorescence anisotropy 54–55

– – fluorescence correlation spectroscopy
 55–56
 – – fluorescence microscopy 55–56
 – phase-modulation fluorimetry 54
 – pulse fluorimetry 54
 – steady-state fluorescence methods 52–53
 – time-resolved fluorescence approaches 54
 fluorescence upconversion 84
 Fokker–Planck equation 214, 222, 234–236,
 239, 241
 force-field-based reactive MD 255
 Fourier grid Hamiltonian method 247
 Fourier transform microwave spectroscopy
 178
 Franck–Condon principle 91, 93–95, 278
 frequency domain 54
 fully polarizable continuum model (FPCM)
 354

g

gas phase, classical and quantum proton
 transfer in 261–263
 gas-phase experiments 177–192, *See also*
under Tautomer-selective spectroscopy
 Gaussian-type orbitals (GTOs) 348
 general Amber force field (GAFF) 359
 generalized gradient approximation (GGA)
 343
 geometric isotope effect 151
 ground-state intramolecular proton transfer
 reactions 213–250, *See also* Transition
 state theory (TST)
 – quantum and classical 236–238
 – solvent friction and solvent dynamics
 224–226
 guanine 179–187
 – gas-phase spectroscopy of 179–187
 – – IR absorption spectra 182
 – – IR–UV hole burning 181–182, 185–186
 – – keto guanine 184
 – – REMPI 181–187
 – – UV–UV hole burning 181

h

halochromism 43
 Hamiltonian (\mathcal{H}) operator 235–238
 Hartree–Fock (HF) theory 254–255, 339
 Hilbert space 214
 Hildebrand solubility parameter 278, 301
 Hohenberg–Kohn theorem 342
 hole-burning 178
 hybrid functionals 344
 – double (doubly) hybrid functionals
 344–345

- hybrid functionals (*contd.*)
 - local hybrids 345
 - random phase approximation (RPA) 345–346
 - range-separated hybrids 345
- hydrogen-bonded dimers, intermolecular
 - NH/N tautomerization in 59–60
- hydrogen bonding 327–328
- hydrogen transfer (HT) in molecular systems 253–268
 - force field treatment of 253–268
- 2-(2-Hydroxyphenyl)benzothiazole (HBT) 80
- i**
 - imides, $\Delta(\text{NMe})$ in 313–315
 - imine–amine tautomerism 116–124
 - independent particle methods 339–340
 - infrared (IR) absorption 178
 - infrared spectroscopy 259–261
 - instrument response function (IRF) 73
 - integral intensities 38
 - inter alia 279, 326
 - interactive non-linear least-squares (I-NoLLS) 267
 - internal conversion, in femtosecond pump–probe spectroscopy 97–99
 - intramolecular hydrogen bonding 5–6
 - selective stabilization through 5–6
 - with a side chain group 6
 - intramolecular NH/N tautomerization 56–59
 - π -conjugation role in 58
 - in 2,9-(di-2-pyridyl)-4,7-di(*tert*-butyl)carbazole 59
 - in hydrogen-bonded dimers 59–60
 - intramolecular proton transfer reactions 50–51
 - intrinsic isotope effects 151–156
 - intrinsic deuterium isotope effects 153–154
 - on ^{13}C CS 153–154
 - on ^{19}F CS 154–155
 - on ^{15}N chemical shifts 154
 - on ^{17}O chemical shifts 154–155
 - on ^{18}O isotope effects on ^{13}C chemical shifts 155–156
 - intrinsic splitting width 106
 - ionization techniques 84
 - isotope effects on chemical shifts as a tool in tautomeric equilibria study 145–173, *See also* Intrinsic isotope effects; Secondary isotope effects
 - experimental requirements 148–151
 - concentric tubes 149
 - couplings 149
 - exchange of isotopes 149
 - isotope labeling 151
 - one-tube experiments 148
 - solvent variation 150
 - temperature 150
 - potential energy wells 147
 - primary effects 146–147, 149–150, 161–163
 - secondary effects 146–147
 - solid state 164–165
 - theoretical calculations 165–166
 - isotope labeling 151
 - isotopic perturbation of equilibrium 160–161
- k**
 - Kamlet–Abboud–Taft (KAT) 283
 - keto–enol tautomerism 15, 112–116
 - of monosubstituted phenylpyruvic acid 114
 - in 4-(phenyldiazenyl)naphthalen-1-ol 37–40
 - keto-hydrazone–azo enol tautomeric equilibrium 203
 - ketopyridine–enolpyridine–ketoenamine tautomerization 203–204
 - kinetic isotope effect (KIE) 262
 - Kirkwood function 301
 - Kohn–Sham formulation of DFT 343
- l**
 - lactam–lactim tautomerism 124–126
 - of 2-hydroxypyridine 360–362
 - lactams 310–312
 - vinylogous lactams 312–313
 - lactim–lactam phototautomerization 93
 - Langevin equation 222–223
 - laser-induced fluorescence (LIF) 178
 - Lee, Yang, and Parr (LYP) density function 343
 - Legendre polynomials 257
 - Lennard–Jones parameters 356
 - linear combination of atomic orbitals (LCAO) 339
 - linear solvation energy relationship (LSER) methods 2, 277–302
 - case histories 287–298
 - enol formation from β -diketones and related compounds 288
 - pyrazolone 25, 295–298
 - Schiff bases and related azo compounds 292–295
 - disadvantages 298–300

- earlier approaches 301–302
- Taft–Kamlet LSER methodology 277–287,
 See also individual entry
- in tautomer ratio study 277–302
- linearized coupled cluster theory with single
 and double excitations (LCCSD) 340
- Liouville equation 214
- classical 214
- quantum 215
- Liouville space 238
- local density approximation (LDA) 343
- local hybrids 345
- lone-pair repulsion 4–5
- low-barrier hydrogen bond (LBHB) systems
 203
- lumichrome 66

m

- many-body perturbation theory (MBPT) 340
- Marcus's theory 215
- Maxwell–Boltzmann distribution 216
- meta-GGA functionals 344
- microwave spectroscopy 178
- Miertus–Scrocco–Tomasi model (MST) 354
- minimal augmentation 349
- minimum basis set 348
- mixed states 238
- model compounds 306
- molecular dynamics free-energy perturbation
 simulations (MD-FEP) 355
- molecular mechanics (MM) dynamics 71
- molecular mechanics with proton transfer
 (MMPT) 254
- applications of 259–267
- – classical and quantum proton transfer in
 gas phase 261–263
- – infrared spectroscopy 259–261
- for NMR properties 264–267
- proton transfer reactions with 256–259
- Moller–Plesset perturbation theory (MP2)
 253
- Monte Carlo free-energy perturbation
 (MC-FEP) 355
- multireference configuration interaction with
 singles (MR-CIS) level 184

n

- N zeta 348
- negative-charge-assisted hydrogen bonding
 202
- NH tautomerism as a tool in biophysics
 72–74
- nitroso (n-oxide)–oxime tautomerism
 128–129

NMR spectroscopy, tautomerism types studied
 by 109–137

- azo–hydrazone tautomerism 133
- carbohydrate tautomerism 132–133
- five- or six-membered heterocyclic
 compounds, annular tautomerism of
 126–128
- imine–amine tautomerism 116–124
- keto–enol tautomerism 112–116
- lactam–lactim tautomerism 124–126
- methodologies 104–108
- MMPT for 264–267
- nitroso (n-oxide)–oxime tautomerism
 128–129
- nucleosides 129–131
- nucleotides 129–131
- phosphorus compounds 134–136
- porphyrins 131–132
- proteins 129–131
- ring–chain tautomerism 109–111
- tetrazole–azide tautomerism 111
- transannular tautomerism 111–112
- nonlinear optics 246–247
- nucleobases 177–192, *See also under*
 Tautomer-selective spectroscopy
- nucleosides, tautomeric structures in
 129–131
- nucleotides, tautomeric structures in
 129–131

o

- ¹⁸O isotope effects on ¹³C chemical shifts
 155–156
- O-hydroxy Schiff bases 157, 162
- one-tube experiments 148
- Onsager's principle 227, 239
- optical dielectric constant 225
- optimization procedure 35
- OPTimized eXchange (OPTX) density
 function 343
- ortho*-hydroxybenzaldehyde (o-HBA)
 derivatives 18, 80, 218–219
- oscillatory model 14

p

- 1-Palmitoyl-2-oleoyl-*sn*-glycero-3-phos-
 phocholine (POPC) 72
- Pauli principle 339
- phase-modulation fluorimetry 54
- 1-((phenylimino)methyl)naphthalen-2-ol
 40–43
- 1-(phenyldiazenyl)naphthalen-2-ol 41–43
- 4-(phenyldiazenyl)naphthalen-1-ol, keto–enol
 tautomerism in 37–40

- phosphorus compounds 134–136
 - photoinduced NH tautomerism studies
 - 49–74, *See also* Bifunctional NH/N azaaromatics; Fluorescence techniques for studying tautomerism; Solute–solvent hydrogen-bonded complexes
 - NH tautomerism as tool in biophysics 72–74
 - by stationary and time-resolved fluorescence techniques 49–74
 - photoinduced proton/hydrogen atom transfer 50–52
 - amino–imino (NH/N) tautomeric transformations 49–51
 - direct intramolecular proton transfer reactions 50–51
 - solvent-mediated 52
 - photoinduced tautomerism 79–100, 208–210, *See also* Femtosecond pump–probe spectroscopy
 - picosecond dynamics of amino–imino tautomerization 65
 - Poisson bracket 235
 - Poisson–Boltzmann, generalized born 354
 - polarizability correction term 278
 - polarizable continuum model (PCM) 354
 - polarization functions 229–231, 348
 - polyfluoroacylmethylenenaphthalides, ring–chain tautomerism of 109–111
 - populations 238
 - porphyrins 131–132
 - positive-charge-assisted hydrogen bonding 202
 - potential energy surfaces (PESs) 256
 - potential of mean constraint force (PMF) 73
 - primary deuterium isotope effects 150
 - primary isotope effects 146–147, 149–151, 161–163
 - deuterium 150
 - tritium 150
 - primary tritium isotope effects 150
 - primitives 348
 - proteins, tautomeric structures in 129–131
 - proton migrations 67–69
 - reaction mechanisms and cooperativity in 67–69
 - – concerted mechanism 67
 - – stepwise or sequential mechanism 67
 - proton transfer
 - in 5′-deoxyypyridoxal 14
 - in malonaldehyde 16
 - proton transfer (PT) in molecular systems 253–268, *See also* Molecular mechanics with proton transfer (MMPT)
 - computational approaches to 254–256
 - – force-field-based reactive MD 255
 - – quantum methods 254
 - – ReaxFF 255
 - condensed-phase proton transfer 263–264
 - force field treatment of 253–268
 - proton transfer analysis 69–71, 199–210, *See also under* X-ray diffraction
 - molecular dynamics 71
 - QM/MM simulations 71
 - reaction path calculations and energy barriers for 69–71
 - using tautomers 2–3
 - protonation effect on ammonium–azonium tautomerism 43–45
 - prototropic tautomerism 1
 - Pseudomerie/ortisomerie* theory 10–11
 - pulse fluorimetry 54
 - pump–dump–probe 247
 - pump–probe spectroscopy dynamics 85–93
 - ballistic wavepacket motion 88–90
 - coherently excited vibrations in product modes 90–92
 - data analysis 87–88
 - ultrafast IR studies 92
 - ultrafast transient absorption signatures of ES IPT 85–87
 - pure state 238
 - pyrazolone 25, 295–298
 - 2-pyridone-2-hydroxypyridine (2PY2HP) 254
- q**
- QM/MM simulations 71
 - quadratically convergent CISD procedure (QCISD) 340
 - quantitative analysis of tautomeric equilibria 26–37
 - classical spectrophotometric analysis 26–29
 - early attempts to find a solution 26–29
 - environmental changes affecting 33–37
 - limitations 26–29
 - using bands decomposition 29–33
 - quantum chemical calculation of tautomeric equilibria 337–364, *See also* Density functional theory (DFT) methods; Wave-function-based methods (WFT)
 - applications of 357–363
 - – annular tautomerism in tetrazole 363
 - – lactam–lactim tautomerism of 2-hydroxypyridine 360–362
 - – SAMPL2 challenge of predicting tautomer ratios 357–360
 - choice of basis set 347–351

- computational procedures 338–353
- solvent effects 353–357
- – continuum solvation models 353–355
- spectroscopic properties calculation 351–353
- quantum decay 238–242
- quantum Liouville equation 215, 243
- quantum methods 254
- quantum proton transfer reaction 236–238
- r**
- random phase approximation (RPA) 345–346
- range-separated hybrids 345
- Rayleigh–Brillouin spectrum 239
- reaction surface Hamiltonian (RSH) 261
- reactive frequency 223
- real tautomeric systems analysis 37–45
- keto–enol tautomerism
- – in 4-(phenyldiazenyl)naphthalen-1-ol 37–40
- – in 1-(phenyldiazenyl)naphthalen-2-ol 41–43
- – 1-((phenylimino)methyl)naphthalen-2-ol 40–43
- ReaxFF 255
- redfield theory 214, 241–243
- red-shifted fluorescence found in salicylic acid 16
- reduced density matrix 247
- resonance-assisted hydrogen bond (RAHB) systems 154, 199–203
- restricted Hartree–Fock (RHF) 67
- reversal in tautomeric form 3–5
- causes of 3–4
- – aromatic resonance 3–4
- – dipolar repulsion 4–5
- – lone-pair repulsion 4–5
- – selective stabilization through ‘far’ intramolecular hydrogen bonding 5–6
- ring–chain tautomerism 109–111
- of polyfluoroacetylmethylenenaphthalides 109
- root-mean-square (RMS) deviation 351
- s**
- salt addition effect on equilibrium 34
- α Scale 281–283
- β Scale 279–281
- β value for water 283–286
- π^* Scale 278–279
- Schiff bases 93, 157, 162, 292–295
- Schrödinger equation 237
- scope of tautomerism 1–3
- principles and practicalities 1–3
- secondary isotope effects 146–147
- on CS 156–161
- – isotopic perturbation of equilibrium 160–161
- ‘self-assisted’ intermolecular excited-state proton transfer 59
- self-consistent charged-density functional tight binding (SCC-DFTB) 254
- self-consistent field (SCF) 339
- self-consistent reaction field (SCRF) 354
- short, strong hydrogen bonds (SSHBs) 201
- short, strong, low-barrier (SSLB) hydrogen bonds 200
- six-membered ring oxoheterocycles 321–324
- benzofusion to give benzenoid structures in 321–324
- Slater determinants 340
- Slater-type orbitals (STOs) 347
- solid state 164–165
- NMR spectroscopic study of tautomerism in 103–138, *See also* NMR spectroscopy
- tautomerism evidenced by diffraction methods 197–211, *See also* X-ray diffraction
- – isomers, equilibria, and kinetics 197–211
- solute–solvent hydrogen-bonded complexes 60–67
- solution, NMR spectroscopic study of tautomerism in 103–138, *See also* NMR spectroscopy
- solvatochromic approach 277, 284
- solvent coordinate 226–233
- application 231–233
- basics 226–229
- solvent dependence 34
- intensity 34
- shape 34
- solvent effect
- on ammonium–azonium tautomerism 43–45
- in quantum chemical calculation 353–357
- – continuum solvation models 353–355
- – explicit solvent models 355–357
- solvent frequency 243
- solvent functionality 33–34
- solvent influence on tautomeric form 8–9
- solvent-mediated NH tautomerism 52
- solvent role in intramolecular proton transfer reactions 221–224
- spectral charts 12
- spectral files 12
- spectroscopic properties calculation 351–353

- spin–boson system 242
- spin-component-scaled MP2 method (SCS-MP2) 340
- split valence zeta 348
- static (non-dynamic) electron correlation 339
- stationary fluorescence techniques 49–74, *See also under* Photoinduced NH tautomerism studies
- steady-state fluorescence methods 52–53
- stepwise or sequential mechanism 67
- stereoelectronic hindrance 326–327
- steric hindrance 326–327
- Stokes friction 224
- Stokes shift 80
- structure influence on tautomeric form 9
- surface volume polarization for electrostatics (SVPE) 354
- susceptibility 246
- t**
- Taft–Kamlet LSER methodology 277–287
 - π^* for gas phase 286–287
 - π^* scale 278–279
 - β scale 279–281
 - α scale 281–283
- tautomeric constant (K_T) 26
- tautomeric equilibrium 9–13
 - historical overview 9–13
 - azaindole 17
 - flavones 17
 - *ortho*-hydroxybenzaldehyde derivatives 18
 - *pseudomerie*/*ortisomerie* theory 10–11
 - spectral charts 12
 - spectral files 12
 - tautomerization dynamics 13–19
 - tryptophan 17
- tautomeric shift 177
- tautomer-selective spectroscopy 177–192
 - of nucleobases, isolated in gas phase 177–192, *See also* Guanine
 - adenine 187
 - advantages 178
 - base pairs 189–191
 - challenges in 178
 - cytosine 187–188
 - techniques 177–179
 - thymine 188–189
 - uracil 188–189
- temperature change effect on equilibrium 35
- temperature jump technique 14
- tetrazole, annular tautomerism in 363
- tetrazole–azide tautomerism 111
- thermally induced tautomerism, XRD of 203–208
 - crystal structure 206, 208
 - ketohydrazone-azo enol tautomeric equilibrium 203
 - molecular structure 204
 - viable supramolecular structures and tautomeric states 207
- thiolactams, Δ (NMe) for 317–320
- β -Thioxoketones 156, 166–172
 - multiple equilibria 169–172
- thymine 188–189
- time-dependent density functional theory (TD-DFT) methods 69
- time domain 54
- time-resolved absorption measurements 82–84
- time-resolved fluorescence techniques 54, *See also under* Photoinduced NH tautomerism studies
- time-resolved infrared spectroscopy 84–85
- transannular tautomerism 111–112
- transition state theory (TST) 17, 213, 216–218
 - activation energy 216
 - solvent role 221–224
- triple-zeta, TZ 348
- tryptophan 17
- two-bond isotope effects 153
- u**
- ultrafast IR studies 92
- ultrafast pump–probe spectroscopy 81–85
 - fluorescence upconversion 84
 - ionization techniques 84
 - pump–probe experiment for 82
 - time-resolved absorption measurements 82–84
 - time-resolved infrared spectroscopy 84–85
- ultrafast transient absorption signatures of ESIPT 85–87
- ‘unconventional’ approaches to DFT 345–346
- uracil 188–189
- usnic acid 163
- v**
- valence multiple zeta 348
- vinylous lactams 312–313
- w**
- wave-function-based methods (WFT) 338–342

- correlated treatments 340–342
- independent particle methods 339–340

x

- x-ray diffraction 197–199
 - in proton transfer analysis 199–211
 - – asymmetric hydrogen bonds, proton potentials of 200
 - – photoinduced tautomeric processes 208–210
 - – resonance-assisted hydrogen bonding 199–203

- – tautomerism 199–203
- – thermally induced tautomerism 203–208, *See also individual entry*
- in ratio of tautomers estimation 198
- x-ray photodiffraction 209

z

- zero-point energy (ZPE) 351
- zwitterionic equilibria 330

