

---

# INDEX

---

- Ab initio calculations  
carbocation chemistry, 29–32  
cyclopropylmethyl cations, Cram's phenonium ions, 82–83  
hydrogen/deuterium exchange, methane-ethane complexes, solid acids, 317–319  
protonated cyclopropane intermediates, 1,3-hydride shifts, 219  
zwitterionic viability, neutral carbocationic analogs, 50–51
- Acenaphthylenium ion, nonarenium carbocation structure and reactivity, 143–145
- Activation free energies, long-lived carbocations, nonarenium carbocation structure and reactivity, 143–148
- 2-(Adamantylidenemethyl)-2-admantyl cation, steric hindrance, 76–77
- Adamantyl cations,  $\text{CH}^+$  carbocation, isoelectronic BH substitution, 56–57
- Alkyl groups, polyfluorinated carbocations, 162–163
- Alcoholysis, polyfluorinated carbocations, electrophile properties, 201–208
- Alkaloids, organic synthesis in superacids  
electrophilic hydroxylation, 367–370  
fluorination and ionic hydrogenation, 370–373
- Alkanes  
hypercoordinate carbocations, 32–38  
organic synthesis in superacids, nonactivated carbon-hydrogen bond functionalization, 360–363  
superacid proton exchange reactions  
methane-ethane, 311–319  
hydrogen/deuterium exchange, liquid acids, 311–317  
FSO<sub>3</sub>H-based superacids, 313  
HF-based superacids, 313–317  
sulfuric acid, 311–313  
hydrogen/deuterium exchange, solid acids, 317–319  
research background, 309–311  
small alkanes, two-plus carbon atoms, 319–328  
hydrogen/deuterium exchange  
liquid acids, 319–325  
DF-SbF<sub>5</sub>, 323–325  
DSO<sub>3</sub>F-SbF<sub>5</sub>, 323  
fluorosulfonic acid, 321–323  
sulfuric acid, 319–320  
triflic acid, 320–321  
solid acids, 326–328
- “Alkplane” cages, neutral carbocationic analogs, formation strategies, 49–50
- Alkenes, alkylation of isoalkanes, 35
- Alkyl cations, long-lived structures, 10–15
- Alkyl fluoride ionization, long-lived alkyl cations, 10–13
- Allyl alcohols, 2-(adamantylidenemethyl)-2-admantyl cation, steric hindrance, 76–77
- Allyl cations, fast rearrangement reactions, 220–221
- Alternant polycyclic aromatic hydrocarbons, future research applications, 274–275
- $\gamma$ -Aluminas, hydrogen/deuterium exchange, methane-ethane complexes, solid acids, 317–319
- Aluminum chloride, Lewis acids like, “neutral” carbocationic analogs, 45–48

- AMI-derived changes in charges, polycyclic aromatic hydrocarbons  
 benzannelation, 257–260  
 chrysenium ions, 257
- AMI-derived relative energies, 256
- Amides, organic synthesis in superacids  
 nonactivated carbon-hydrogen bond  
 functionalization, 360–364  
 hydroxylation, 367
- tert*-Amyl cation, 217–218
- Anionic carbocation analogs, 64–67  
 early examples, 48  
 examples, 64–67  
 overall negative charge, 44
- Anthracene substituted carbocations, polycyclic aromatic hydrocarbons, chrysenium ions, 255–256
- Antiaromaticity  
 bisfluorenyl dications, 114–115  
 cyclopentadienyl cation, 255–256  
 cyclopentadienyl radicals, aromaticity and antiaromaticity, 115–120  
 indenyl and fluorenyl cations, 111–113
- Anti*-diol epoxides, polycyclic aromatic hydrocarbons, 259–260  
*cyclopenta[a]*phenanthrenium cations, 246–251
- Anti*-metal complexes, 2-benzonorbornenyl cation, 285–286
- Antimony fluorides  
 fast rearrangement reactions, protonated cyclopropane intermediates, 217–218  
 hydrogen/deuterium exchange  
 methane-ethane, HF-based superacids, 315–317  
 small alkanes  
 DF-SbF<sub>5</sub>, 323–325  
 DSO<sub>3</sub>F-SbF<sub>5</sub>, 323  
 fluorsulfonic acid, 321–323  
 long-lived alkyl cations, 11–15  
 polyfluorinated carbocations, 164–177  
 electrophile properties, 201–208  
 isomeric transformations, 197–201
- Anti-van't Hoff structure, polyaurated carbocations, quantum chemical calculations, 301
- Aqueous acids, pH, 16
- Arenium ions  
 dihydrocyclobuta[e]pyrenium ions, 269  
 methylene-bridged PAH-arenium ions, 269–272  
 persistent ArC<sup>+</sup>(R)CF<sub>3</sub> carbocations, 264–265  
 phenonium cation, 285  
 polycyclic aromatic hydrocarbons, 241–242  
 polyfluorinated carbocations, 165–177  
 electrophile properties, 202–208  
 isomeric transformations, 195–201  
 structure and reactivity, 128–140
- Aromaticity studies  
 arenium ion structure and reactivity, 129–140  
 binuclear gold carbocations, 301–302  
 cyclopentadienyl carbocations  
 free radical aromaticity and antiaromaticity, 115–120  
 historical perspective, 104–111  
 long-lived carbocations, arenium ion structure and reactivity, 138–140  
 organic synthesis in superacids, amine hydroxylation, 367
- Arrhenius parameters, long-lived carbocations, arenium ion structure and reactivity, 136–140
- Aryl complexes, gold carbocations, 303–304
- Aryl group migration, long-lived carbocations, arenium ion structure and reactivity, 137–140
- Arylmethyl cations, polyfluorinated carbocations, 162–163
- Aurophilicity, basic principles, 292
- Azide clock method, electrophilicity scales, carbocations, 334, 344–345
- Backdonation order, polyfluorinated carbocations, 183–185
- Baldwin rules, cationic  $\pi$ -cyclization reactions, 150–152
- Bay-region-methoxy derivative, polycyclic aromatic hydrocarbons  
 benzannelation, 257–260  
*cyclopenta[a]*phenanthrenium cations, 246–251
- Benzene rings, polyfluorinated carbocations, 166–177  
 isomeric transformations, 197–201  
 stability parameters, 187–192
- Benzenium ions, stability parameters, 188–192
- Benzhydryl cations, electrophilicity scales, rate constants, 337–345
- Benzo[c]phenanthrenium cations, polycyclic aromatic hydrocarbons, 257–260
- Benzo[g]chrysenium cations, polycyclic aromatic hydrocarbons, 257–260
- 2-Benzonorbornenyl cation, structure and properties, 285–286
- 7-Benzonorbornenyl cation, structure and properties, 286–287

- Benzylic cations  
 chromium tricarbonyl carbocations, stable ion chemistry, 281–282  
 structure and properties, 283–284
- Bicyclic carbocation  
 isotopic perturbation, 227–230  
 nonclassical ion structure, 19–25
- Bicyclobutanoid resonance structure, polyfluorinated carbocations, 183–185
- Binuclear gold cations, aromatic systems, 301–302
- Biological applications  
 carbocation chemistry, 239–241  
 electrophilicity scales, carbocations, 345–352
- Biscarboxonium dications, formation mechanisms, 267–268
- 1,6- and 1,8-Bis(diphenylmethylenium)pyrene dications, polycyclic aromatic hydrocarbons, 263
- Bisfluorenyl dications, antiaromaticity, 114–115
- B3LYP/6-13G\* geometry  
 cyclopentadienyl free radical from fulvenone, 117
- 2,6-dimethylmethylene-2,6-diyl dication characterization, 88–89
- isotopic perturbation, carbocations, 232–234
- neutral carbocationic analogs, Lewis acid complexes, 62–64
- “neutral” carbocationic analogs  
 carbene-Lewis acid complexes, 59–62  
 CH<sup>+</sup> carbocation, isoelectronic BH substitution, 54–57  
 delocalized carbanion stabilization, 52–53  
 early examples, 45–48  
 positive/negative organic fragment stabilization, 53–54  
 remote H replacement, delocalized anions, 51–52  
 unusually long carbon-carbon bonds, 48–49  
 zwitterionic viability, 50–51
- 1,1,1,3,3-tetracyclopropyl-1,3-propanediyl dication, 96
- triaxane-2-methyl cation, 79
- Bond dissociation energy (BDE)  
 cyclopentadienyl free radical aromaticity and antiaromaticity, 115–120  
 “neutral” carbocationic analogs, unusually long carbon-carbon bonds, 49
- Boradiadamantyl, CH<sup>+</sup> carbocation, isoelectronic BH substitution, 55–56
- Borane  
 carbocation chemistry, 27–29
- CH<sup>+</sup> carbocation, isoelectronic BH substitution, 54–57
- high-coordinate carbocations, 30–38
- Boron cages, “neutral” carbocationic analogs, early examples, 45–48
- Bridgehead-bridgehead separations, “neutral” carbocationic analogs, unusually long carbon-carbon bonds, 48–49
- Brønsted acids, carbocation chemistry, superacids, 16–17
- Brown-Winstein nonclassical ion controversy, carbocation structure, 20–25
- 2-Butyl cation, protonated cyclopropane intermediates, fast rearrangement reactions, 216–217
- tert*-Butyl cations  
 electrophilicity scales, research background, 331–334  
 historical perspective on, 11–15  
 hydrogen/deuterium exchange, small alkanes, sulfuric acid, 320  
 superacids, 15–17
- Calculated nucleus independent chemical shifts (NICS), 116
- Carbene-Lewis acid complexes, neutral carbocation analogs, 59–62
- Carbenium ions, basic concepts, 26–29
- Carbocations  
 general concepts, 25–29  
 electrophilicity scales  
 applications, 345–352  
 equilibrium and reactivity parameters, 335–345  
 experimental protocols, 334–335  
 stability properties, 331–334  
 fast rearrangement reactions  
 allyl cations, 220–221  
 1,3-hydride shifts, 218–219  
 protonated cyclopropane intermediates, 215–218  
 research background, 215  
 five- and higher-coordinate chemistry, 29–38  
 historical perspective on, 1–6  
 isotopic perturbation, 222–234  
 kinetic and stereochemical studies, early research, 8–10  
 nonclassical ion controversy, 19–25  
 stable ion conditions, 18–19
- Carbocations  
 research background, 74–75  
 structure and classification, 86–98

- Carbocations (*Continued*)
- trans*-cyclopropane-1,2-diylobis(dicyclopropylmethylium) dication, 91–93
  - 2,6-dimethylmesitylene-2,6-diyl dication, 87–90
  - (hexaaryltrimethylene)methane dications, 97–98
  - 2,10-*para*[3<sup>2</sup>.5<sup>6</sup>]octahedrane dication, 90–91
  - 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication, 93–96
- Carbon, high-coordinate carbocations, 30–38
- Carbon atoms, small alkanes, hydrogen/deuterium exchange
- liquid acids, 319–325
    - DF-SbF<sub>5</sub>, 323–325
    - DSO<sub>3</sub>F-SbF<sub>5</sub>, 323
    - fluorosulfonic acid, 321–323
    - sulfuric acid, 319–320
    - triflic acid, 320–321
  - solid acids, 326–328
- Carbon-carbon bonds
- bisfluorenyl dications, 114–115
  - carbocation chemistry, historical perspective, 5–6
  - cationic  $\pi$ -cyclization reactions, 150–152
  - hydrogen/deuterium exchange, small alkanes and solid acids, 326–328
  - neutral carbocationic analogs
    - carbene-Lewis acid complexes, 60–62
    - delocalized carbanion stabilization, 52–53
    - early examples, 45–48
    - Lewis acid complexes, 62–64
    - unusually long structures, 48–49
  - polyfluorinated carbocations, 184–185
- <sup>13</sup>C NMR spectroscopy
- arenium ion structure and reactivity, 128–140
  - bisfluorenyl dications, 114–115
  - carbocation structures, 74–75
  - carboxonium-substituted pyrenium ion, 267–268
  - cyclobutylmethyl cations, 84–86
  - cyclopentadienyl carbocations, 109–111
  - trans*-cyclopropane-1,2-diylobis(dicyclopropylmethylium) dication, 91–93
  - cyclopropylmethyl cations, 78
    - Cram's phenonium ions, 82–83
    - 3-spirocyclopropyl-2-bicyclo[2.2.2]octyl cation, 81–82
    - 3-spirocyclopropyl-2-norbornyl cations, 80–81
  - triaxane-2-methyl cations, 79
  - 2,6-dimethylmesitylene-2,6-diyl dication, 87–90
  - hydrogen/deuterium exchange, methane-ethane, HF-based superacids, 314–317
  - isotopic perturbation, carbocations, 223–234
  - long-lived alkyl cations, 12–15
  - long-lived carbocations
    - nonarenium carbocation structure and reactivity, 145–148
    - phenol/Lewis acid complexes, 141
  - 2,10-*para*[3<sup>2</sup>.5<sup>6</sup>]octahedrane dication characterization, 90–91
  - polyaurated carbocations, 297–300
  - polycyclic aromatic hydrocarbons
    - cyclopenta[*a*]phenanthrenium cations, 248–251
    - methylene-bridged PAH-arenium ions, 269–272
    - phenanthrenium ion model, 242–244
    - sterically crowded carbocations, 75–77
    - 1,1'-diadamantylbenzyl cations, 76
    - tris(1-naphthyl)- and tris(2-naphthyl)methyl cations, 77
    - 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication, 94–96
- Carbon-hydrogen (C-H) bonds
- carbocation chemistry, historical perspective, 5–6
  - gold carbocation reference compounds, 296–297
  - hydrogen/deuterium exchange, small alkanes and solid acids, 326–328
  - organic synthesis in superacids
    - nonactivated bond functionalization, 360–367
      - acyclic ketones, imines, and amides, 360–363
      - cyclic ketone carbonylation (carboxylation), 363–364
      - polycyclic ketone dehydrogenation to dienones, 364–367
      - polycyclic ketone dehydrogenation to dienones, 365–367
- Carbonium ions
- basic concepts, 26–29
  - cyclopentadienyl carbocations, basic properties, 104
  - hypercoordinate structures, 34–38
- Carbon scrambling
- hydrogen/deuterium exchange, small alkanes and solid acids, 326–328
  - protonated cyclopropane intermediates, fast rearrangement reactions, 216–218

- Carbonylation, superacid organic synthesis, cyclic ketones, 363–364
- Carboxonium ions, polycyclic aromatic hydrocarbons, 244–246  
 benzannulation, 258–260  
 chrysenium ions, 252–254  
 pyrenium ion substitution, 265–268
- Carboxylation, organic synthesis in superacids, cyclic ketones, 363–364
- Carcinogenesis  
 carbocation chemistry, 239–241  
 polycyclic aromatic hydrocarbons  
 chrysenium ions, 252–254  
 $\alpha$ -pyrenyl-substituted carbocations, 262–263
- Cationic  $\pi$ -cyclization reactions, long-lived carbocations, 148–152
- Charge compensation strategies, neutral carbocationic analogs, 49–50  
 delocalized carbanion stabilization, 52–53
- Charge delocalization, polycyclic aromatic hydrocarbons  
 benzannulation, 259–260  
 carboxonium-substituted pyrenium ion, 267–268  
 chrysenium ions, 256  
 dihydropyrenium(ethanophenanthrenium) cations, 260–261  
 future research, 275  
 methylene-bridged PAH-arenium ions, 269–272  
 persistent  $\text{ArC}^+(\text{R})\text{CF}_3$  carbocations, 264–265  
 phenanthrenium ion model, 242–244
- $\text{CH}^+$  carbocation, isoelectronic BH substitution, 54–57
- Chemical shift additivity criterion  
 cyclobutylmethyl cations, 84–86  
*trans*-cyclopropane-1,2-diyldis(dicyclopropylmethyl) dication, 92–93  
 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication, 96
- Chlorination, polyfluorinated carbocations, 170–177
- Chromacycle structure, phenonium cation, 284–285
- Chromium tricarbonyl carbocations  
 basic properties, 280–282  
 2-benzonorbornenyl cation, 285–286  
 7-benzonorbornenyl cation, 286–287  
 benzylic cations, 283–284  
 phenonium cation, 284–285
- Chrysenium ions, polycyclic aromatic hydrocarbons, 252–254
- Cis* isomers, allyl cations, fast rearrangement reactions, 220–221
- Classical carbocations, “neutral” carbocationic analogs, 46–48
- Cold Siberia, long-lived carbocations  
 arenium ion structure and reactivity, 128–140  
 cationic  $\pi$ -cyclization reactions, 148–152  
 nonarenium carbocation structure and reactivity, 142–148  
 phenol-Lewis acid complexes, 140–141  
 research background, 125–128
- Computational criteria  
 cyclopentadienyl free radical aromaticity and antiaromaticity, 116–120  
 zwitterionic viability, neutral carbocationic analogs, 50–51
- Counterions, neutral carbocationic analogs, formation strategies, 49–50
- Covalent bonds, nonclassical ion controversy, 26–29
- C60-pyrene adduct, dihydrocyclobuta[*e*]pyrenium ions, 269
- Cram’s phenonium ions, structure and properties, 82–83
- Croconate, zwitter anionic carbocation analogs, 65–67
- Crystalline state, acceleration of carbocation rearrangements in a partially ordered medium, 136
- Cumyl-type carbocations, steric hindrance, 75–77
- Cyclization reactions, long-lived carbocations, cationic  $\pi$ -cyclization reactions, 148–152
- Cycloaddition reactions, electrophilicity scales, carbocations, 351–352
- Cyclobutenyl cations, long-lived structures, nonarenium carbocation structure and reactivity, 146–148
- Cyclobutylmethyl cations, 83–86  
 long-lived structure, 83–86
- Cyclohexadienones, polyfluorinated carbocations, electrophile properties, 202–208
- Cyclohexyl cations, fast rearrangement reactions, 218
- Cyclopenta[*a*]phenanthrenium cations, polycyclic aromatic hydrocarbons, 246–251
- Cyclopentadienyl carbocations  
 aromaticity and antiaromaticity, 115–120  
 basic properties, 103–111  
 bisfluorenyl dications, 114–115  
 free radical aromaticity and antiaromaticity, 115–120  
 indenyl and fluorenyl cation comparisons, 113  
 indenyl and fluorenyl cations, 111–113

- Cyclopentadienyl carbon center, gold carbocations, 303
- Cyclopropenium fragment, neutral carbocationic analogs, positive/negative organic fragment stabilization, 54
- Cyclopropenyl cations, polyfluorinated carbocations, 163–177  
stability parameters, 186–192
- trans*-Cyclopropane-1,2-diylbis(dicyclopropylmethyl) dication, structure and classification, 91–93
- Cyclopropylmethyl cations, 78–83  
Cram's phenonium ions, 82–83  
3-spirocyclopropyl-2-bicyclo[2.2.2]octyl cation, 81–82  
3-spirocyclopropyl-2-norbornyl cations, 80–81  
trixane-2-methyl cation, 79–80
- Degenerate rearrangements, long-lived carbocations  
arenium ion structure and reactivity, 130–140  
nonarenium carbocation structure and reactivity, 143–148
- Dehydrogenation, organic synthesis in superacids, polycyclic ketone dehydrogenation to dienones, 364–367
- Delocalized anions  
neutral carbocationic analogs  
formation strategies, 49–50  
remote H replacement, 51–52  
polycyclic aromatic hydrocarbons,  
phenanthrenium ion model, 242–244
- Delocalized carbanions, neutral carbocationic analogs, stabilization, 52–53
- Density functional theory (DFT)  
2,6-dimethylmesitylene-2,6-diyl dication  
characterization, 88–90  
hydrogen/deuterium exchange, methane-ethane  
HF-based superacids, 315–317  
sulfuric acid, 312–313  
polycyclic aromatic hydrocarbons, 274–275  
trixane-2-methyl cation geometry, 80  
zwitterionic viability, neutral carbocationic analogs, 50–51
- Destabilization properties  
cyclopentadienyl carbocations, antiaromaticity, 105–111  
neutral carbocationic analogs, carbene-Lewis acid complexes, 61–62  
polyfluorinated carbocations, stability parameters, 186–192
- Deuterium labeling. *See also* Hydrogen/deuterium exchange  
isotopic perturbation, carbocations, 222–234  
long-lived carbocations, 127–128  
nonarenium carbocation structure and reactivity, 148  
superacid-alkane proton exchange reactions, research background, 311
- 1,1'-Diadamantylbenzyl cations, steric hindrance, 75–76
- Diarylmethyl cations, electrophile properties, 202–208
- Dienones, organic synthesis in superacids, polycyclic ketone dehydrogenation to, 364–367
- Dihydrocyclobuta[e]pyrenium ions, polycyclic aromatic hydrocarbons, 269
- Dihydropyrenium(ethanophenanthrenium) cations, polycyclic aromatic hydrocarbons, 260–261
- 2,6-Dimethylmesitylene-2,6-diyl dication, structure and classification, 87–90
- Dimethyl sulfoxide (DMSO), electrophilicity scales, carbocations, 338–345
- Diol-epoxide reactivity, polycyclic aromatic hydrocarbons  
benzannulation, 257–260  
chrysenium ions, 254–256  
 $\alpha$ -pyrenyl-substituted carbocations, 262–263
- Disfavored 5-endo-trig processes, cationic  $\pi$ -cyclization reactions, 150–152
- Dithiocarbenium ions, electrophilicity scales, 347–352
- DNA adducts  
carbocation chemistry, 239–241  
polycyclic aromatic hydrocarbons,  
benzannulation, 259–260
- Doublet structures, isotopic perturbation, 222–234
- Electron donation  
benzylic cations, 283–284  
phenonium cation, 284–285
- Electron pair acceptors  
arenium ion structure and reactivity, 128–140  
carbocation chemistry, superacids, 16–17
- Electron spectroscopy for chemical analysis (ESCA)  
five-coordinate carbocations, 30  
nonclassical ion controversy, 22–25
- Electron spin resonance spectroscopy, cyclopentadienyl carbocations, 105–111  
free radical aromaticity and antiaromaticity, 115–120
- Electron-withdrawing substituents  
chromium tricarbonyl carbocations, 280–282  
cyclopentadienyl carbocations, 108–111

- polyfluorinated carbocations, stability parameters, 190–192
- Electrophilicity scales, carbocations applications, 345–352 equilibrium and reactivity parameters, 335–345 experimental protocols, 334–335 stability properties, 331–334
- Electrophilic reactions arenium ion structure and reactivity, 129–140 aromatic systems, binuclear gold cations, 301–302 hypercoordinate carbocations, 35–38 organic synthesis in superacids, hydroxylation aromatic amines, 367 indoles and alkaloids, 367–370 polycyclic aromatic hydrocarbon stability benzo[*a*]anthracenium BA cations, 254–256 benzo[*c*]phenanthrenium/ benzo[*g*]chrysenium cations, 257–260 biological applications, 239–241 1,6- and 1,8-bis(diphenylmethylene)pyrene dications, 263–265 carboxonium-substituted pyrenium ion, 265–268 chrysenium ions, 252–254 cyclopenta[*a*]phenanthrenium cations, 246–251 dihydrocyclobuta[3]pyrenium ions, 269 dihydropyrenium(ethanophenanthrenium) cations, 260–261 fluoranthrene carbocations, 272–274 future research issues, 274–275 methylene-bridged PAH-arenium ions, 269–272 phenanthrenium ions, 242–244 protocols, 241–242 protonation, 241 (1-pyrenyl)diphenylmethyl cation, 263–265 regioisomeric  $\alpha$ -phenanthrenyl-substituted carbocations and carboxonium ions, 244–246 regioisomeric  $\alpha$ -pyrenyl-substituted carbocations, 261–263 research background, 238–239 polyfluorinated carbocations, 201–208
- Endo* isomers cationic  $\pi$ -cyclization reactions, 149–152 isotopic perturbation, carbocations, 230–234
- Equilibrium constants, electrophilicity scales, carbocations, 335–345
- Ethane hydrogen/deuterium exchange liquid acids, 311–317 FSO<sub>3</sub>H-based superacids, 313 HF-based superacids, 313–317 sulfuric acid, 311–313 solid acids, 317–319 superacid proton exchange reactions, 311
- Evans neutral nonclassical model,  $\alpha$ -ketol rearrangements, symmetric geometry, 58–59
- Exo* isomers, isotopic perturbation, carbocations, 230–234
- Extended Hückel MO theory (EHT) neutral carbocationic analogs, carbene-Lewis acid complexes, 59–62 polyaurated carbocations, quantum chemical studies, 300–301
- Extended X-ray absorption fine structure (EXSAFS) spectroscopy, gold carbocations, aryl complexes, 303–304
- Fast rearrangement reactions, carbocations 1,3-hydride shifts, 218–219 protonated cyclopropane intermediates, 215–218 research background, 215 to allyl cations, 220
- Ferrocenyl derivatives, gold carbocations, 301–302
- Fjord*-region diol epoxides, polycyclic aromatic hydrocarbons, benzannulation, 257–260
- Five-coordinate carbocations, chemical properties, 29–38
- Five-membered ring structures indenyl and fluorenyl cations, 113 isotopic perturbation, carbocations, 232–234 polyfluorinated carbocations, stability parameters, 186–192 zwitter anionic carbocation analogs, 64–67
- Flash photolysis, indenyl and fluorenyl cations, 113
- Fluoranthrene polycyclic aromatic hydrocarbons, carbocation formation, 272–274
- Fluorenyl cations, antiaromaticity, 111–113
- Fluoride anion addition-elimination mechanism, polyfluorinated carbocations, isomeric transformations, 197–201
- <sup>19</sup>F NMR spectra, polyfluorinated carbocations, 178–185
- Fluorination, organic synthesis in superacids alkaloids, 370–373 electrophilic hydroxylation aromatic amines, 367 indoles and alkaloids, 367–370 nonactivated carbon-hydrogen bond functionalization, 362–363

- Fluorosulfuric acid, carbocation chemistry, 15–17
- Fluorosulfonic acid, hydrogen/deuterium exchange, small alkanes, 321–323
- Fourier transform infrared (FTIR) spectroscopy  
long-lived alkyl cations, 12–15  
long-lived carbocations, nonarenium carbocation structure and reactivity, 148
- Free-energy profiles, hydrogen/deuterium exchange, methane-ethane, HF-based superacids, 316–317
- Free radicals, cyclopentadienyl aromaticity and antiaromaticity, 115–120
- Friedel-Crafts alkylation, intramolecular analog in a saturated system, 32
- Friedel-Crafts reaction  
carbocation chemistry  
historical perspective, 4–6  
superacids, 16–17  
long-lived alkyl cations, 10–15  
long-lived carbocations, phenol/Lewis acid complexes, 141  
polyfluorinated carbocations, electrophile properties, 207–208
- $\text{FSO}_3\text{H}$ -based superacids, hydrogen/deuterium exchange, methane-ethane, 313
- Fulvenones, cyclopentadienyl free radical aromaticity and antiaromaticity, 117–120
- Gas chromatography mass spectroscopy (GS-MS), hydrogen/deuterium exchange, methane-ethane, liquid superacids, 313
- Gas-phase hydride ion affinity, polyfluorinated carbocations, 186
- Gas-phase ionization potentials, cyclopentadienyl carbocations, 105–111
- Gauge-invariant atomic orbital (GIAO) calculations  
2,6-dimethylmesitylene-2,6-diyl dication characterization, 89  
nonclassical ion controversy, 23  
polycyclic aromatic hydrocarbons  
benzannelation, 260  
future research applications, 274  
ion chemistry, 242
- Generalized diffusion clock technique, electrophilicity scales, carbocations, 344
- Gold chemistry, carbocation structures  
aryl complexes, 303–304  
aurophilicity, 292  
binuclear cations, aromatic systems, 301–302  
heteroaryl complexes, 304–305  
metallocene complexes, 301–302  
methane carbon atom auration, 293–295  
polyaurated structural data, 296–298  
heteroleptic tri- and tetranuclear cations, 297  
homoleptic penta- and hexanuclear carbocations, 297  
NMR and Mössbauer spectroscopy, 298–300  
quantum-chemical calculations, 300–301  
reference compounds, 296–297  
research background, 292
- Ground-state triplets, cyclopentadienyl carbocations, 105
- Halogen interaction  
long-lived carbocations, nonarenium carbocation structure and reactivity, 145  
polyfluorinated carbocations, 180–185  
isomeric transformations, 194–201  
stability parameters, 189–192
- Heavy anions, polyfluorinated carbocations, stability parameters, 200–201
- Heptamethylbenzenium cation, 135, 214
- Heteroaryl complexes, gold carbocations, 304–305
- Heteroleptic complexes  
gold carbocations, 297  
polyaurated carbocations, quantum chemical calculations, 300–301
- (Hexaaryltrimethylene)methane dications, structure and classification, 97–98
- Hexafluoroisopropanol (HFIP), cyclopentadienyl carbocations, 108–111
- Hexanuclear carbocations, homoleptic gold carbocations, 297
- HF-based superacids, hydrogen/deuterium exchange, methane-ethane, 313–317
- $^1\text{H}$  NMR  
allyl cations, fast rearrangement reactions, 221  
bisfluorenyl dications, 114–115  
cyclopentadienyl free radical aromaticity and antiaromaticity, 118–120  
cyclopropylmethyl cations, 78  
2,6-dimethylmesitylene-2,6-diyl dication, 87–90  
(hexaaryltrimethylene)methane dications, 97–98  
hydrogen/deuterium exchange, methane-ethane HF-based superacids, 314–317  
sulfuric acid, 312–313  
sterically crowded carbocations, tris(1-naphthyl)- and tris(2-naphthyl)methyl cations, 77
- Homodesmotic equation  
7-benzonorbornenyl cation, 286–287

- phenonium cations, 285
- Homoleptic compounds
- gold carbocations, penta- and hexanuclear carbocations, 297
  - polyaurated carbocations, spectroscopic data, 298–300
  - tetragoldmethane, 293–294
- HOMO-LUMO energy gaps
- neutral carbocationic analogs, Lewis acid complexes, 63–64
  - “neutral” carbocationic analogs
    - CH<sup>+</sup> carbocation, isoelectronic BH substitution, 56–57
    - remote H replacement, delocalized anions, 51–52
    - zwitterionic viability, 50–51
- 1,3-Hydride shifts
- fast rearrangement reactions, 218–219
  - isotopic perturbation, 222–234
- Hydrides
- electrophilicity scales, carbocations, 341–345
  - organic synthesis in superacids
    - alkaloid ionic hydrogenation and fluorination, 372–373
    - nonactivated carbon-hydrogen bond functionalization, 361–363
- Hydrocarbon chemistry
- carbocations, 27–29
  - hypercoordinate carbocations, 32–38
- Hydrogenation, organic synthesis in superacids, alkaloid ions, 370–373
- Hydrogen/deuterium exchange
- methane-ethane complexes
    - liquid acids, 311–317
      - FSO<sub>3</sub>H-based superacids, 313
      - HF-based superacids, 313–317
      - sulfuric acid, 311–313
    - solid acids, 317–319
  - small alkanes with two carbon atoms
    - liquid acids, 319–325
      - DF-SbF<sub>5</sub>, 323–325
      - DSO<sub>3</sub>F-SbF<sub>5</sub>, 323
      - flurosulfonic acid, 321–323
      - sulfuric acid, 319–320
      - triflic acid, 320–321
    - solid acids, 326–328
- Hydrogen substitution
- polyfluorinated carbocations, 179–185
  - protonated cyclopropane intermediates, fast rearrangement reactions, 216–218
- Hydrolysis, polyfluorinated carbocations, electrophile properties, 201–208
- Hydroxy derivatives, organic synthesis in superacids
- aromatic amines, 367
  - indoles and alkaloids, 367–370
  - nonactivated carbon-hydrogen bond functionalization, 362–363
- Hyperconjugation
- carbocation chemistry, 29
  - isotopic perturbation, carbocations, 222–234
  - long-lived carbocations, nonarenium carbocation structure and reactivity, 142–148
  - polyfluorinated carbocations, 173–177
- Hypercoordinate carbocations, basic chemistry, 31–38
- Imines, organic synthesis in superacids, nonactivated carbon-hydrogen bond functionalization, 360–362
- Indenyl cation
- antiaromaticity, 111–113
  - polyfluorinated carbocations, 165–177
- Individual gauge for localized orbitals (IGLO)
- cyclopentadienyl carbocations, 106–111
  - cyclopropylmethyl cations, triaxane-2-methyl cation, 80
  - 2,6-dimethylmesitylene-2,6-diyl dication characterization, 88–90
  - nonclassical ion controversy, 23
  - 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication, 96
- Indoles, organic synthesis in superacids, electrophilic hydroxylation, 367–370
- Infrared (IR) spectroscopy
- arenium ion structure and reactivity, 128–140
  - long-lived alkyl cations, 13–14
  - polyfluorinated carbocations, 162
- Internuclear double resonance (INDOR), long-lived alkyl cations, 12
- Intramolecular reactions
- hydrogen/deuterium exchange, small alkanes, DF-SbF<sub>5</sub>, 324–325
  - polyfluorinated carbocations, 165–177, 172–177
- Ionic hydrogenation, organic synthesis in superacids, alkaloid ions, 370–373
- Ips*o substitutions
- polycyclic aromatic hydrocarbons, cyclopenta[*a*]phenanthrenium cations, 247–251
  - polyfluorinated carbocations, 167–177
  - electrophile properties, 206–208
  - isomeric transformations, 193–201

- Isobutane, hydrogen/deuterium exchange, small alkanes, DF-SbF<sub>5</sub>, 323–325
- Isodesmic equation, neutral carbocationic analogs, carbene-Lewis acid complexes, 60–62
- Isomeric structures
- long-lived carbocations, 126–128
    - arenium ion structure and reactivity, 130–140
    - phenol/Lewis acid complexes, 140–141
  - polyfluorinated carbocations, 167–177
    - chemical properties and synthetic applications, 193–201
- Isopentane, hydrogen/deuterium exchange, small alkanes, DF-SbF<sub>5</sub>, 324
- Isotopic perturbation, carbocations, 222–234
- $J_{\text{FF}}$  values, polyfluorinated carbocations, 183–184
- Ketenes, cyclopentadienyl free radical aromaticity and antiaromaticity, 116–120
- $\alpha$ -Ketol rearrangements, symmetric geometry, 57–59
- Ketone formation, long-lived carbocations, phenol/Lewis acid complexes, 141
- Ketones, organic synthesis in superacids
- acyclic, nonactivated carbon-hydrogen bond functionalization, 360–363
  - cyclic carbonylation (carboxylation), 363–364
  - polycyclic dehydrogenation to dienones, 364–367
- Kinetic isotope effects, hydrogen/deuterium exchange, small alkanes, fluorsulfonic acid, 322–323
- Kinetic studies
- carbocations, early research, 8–10
  - cyclopentadienyl carbocations, 106–111
    - free radical aromaticity and antiaromaticity, 116–120
  - electrophilicity scales, carbocations, 334–335
  - isotopic perturbation, carbocations, 232–234
  - long-lived carbocations
    - arenium ion structure and reactivity, 138–140
    - nonarenium carbocation structure and reactivity, 147–148
- Koch–Haaf reactions, 36
- Laser flash photolysis, carbocations, 334–335
- Lewis acids
- carbocation chemistry
    - historical perspective, 4–6
    - superacids, 16–17
  - electrophilicity scales, carbocations, 333–334
  - equilibrium constants, 335–345
  - long-lived carbocations, phenol complexes, 140–141
  - neutral carbocationic analogs
    - carbene-Lewis acid complexes, 59–62
    - formation strategies, 50
    - x-ray structural analysis, 62–64
  - polyfluorinated carbocations, stability parameters, 186–192
- Linear combination of atomic orbitals–molecular orbital (LCAO–MO) method, polyaurated carbocations, quantum chemical calculations, 300–301
- Liquid acids
- hydrogen/deuterium exchange, small alkanes with two carbon atoms, 319–325
    - DF-SbF<sub>5</sub>, 323–325
    - DSO<sub>3</sub>F-SbF<sub>5</sub>, 323
    - fluorosulfonic acid, 321–323
    - sulfuric acid, 319–320
    - triflic acid, 320–321
  - hydrogen/deuterium exchange, methane-ethane, 311–317
    - HF-based superacids, 313–317
    - SO<sub>3</sub>-based superacids, 313
    - sulfuric acid, 311–313
- Long-lived alkyl cations
- early research on, 10–15
  - polyfluorinated carbocations, 163–177
- Long-lived carbocations
- carbocations, 86–98
    - trans*-cyclopropane-1,2-diylbis(dicyclopropylmethylium) dication, 91–93
    - 2,6-dimethylmesitylene-2,6-diyl dication, 87–90
    - (hexaaryltrimethylene)methane dications, 97–98
    - 2,10-*para*[3<sup>2</sup>.5<sup>6</sup>]octahedrane dication, 90–91
    - 1,1,3,3-tetracyclopropyl-1,3-propanediyl dication, 93–96
  - cyclobutylmethyl cations, 83–86
  - cyclopropylmethyl cations, 78–83
    - Cram's phenonium ions, 82–83
    - 3-spirocyclopropyl-2-bicyclo[2.2.2]octyl cation, 81–82
    - 3-spirocyclopropyl-2-norbornyl cations, 80–81
    - triaxane-2-methyl cation, 79–80
  - polyfluorinated carbocations, 163–177
  - research background, 74–75
  - sterically crowded carbocations, 75–77
    - 2-(adamantylidenemethyl)-2-adamantyl cation, 76–77

- 1,1'-diadamantylbenzyl cations, 75–76  
 tris(1-naphthyl)- and tris(2-naphthyl)methyl cations, 77
- Löwdin bond orders, 2,6-dimethylmesitylene-2,6-diyl dication characterization, 89–90
- Madelung potential, hydrogen/deuterium exchange, methane-ethane complexes, solid acids, 317
- Magic acid  
 carbocation chemistry, 15–17  
 hydrogen/deuterium exchange  
 methane-ethane, 313  
 small alkanes,  $\text{DSO}_3\text{F-SbF}_5$ , 323
- Magnetic susceptibility exaltations  
 bisfluorenyl dications, 114  
 cyclopentadienyl carbocations, 106
- Markovnikov's rule, hydrogen/deuterium exchange, small alkanes, sulfuric acid, 319
- Medium variations, long-lived carbocations  
 arenium ion structure and reactivity, 135–140  
 nonarenium carbocation structure and reactivity, 143–148
- Meso* structures, polycyclic aromatic hydrocarbons, regioisomeric  $\alpha$ -phenanthrenyl-substituted cations and carboxonium ions, 246
- Metallic carbocations, electrophilicity scales, 347–352
- Metalloocene complexes, gold carbocations, 301–302
- Meta* structures  
 (hexaaryltrimethylene)methane dications, 97–98  
 “neutral” carbocationic analogs, early examples, 45–48  
 polyfluorinated carbocations, 178–185  
 electrophile properties, 202–208  
 isomeric transformations, 194–201  
 stability parameters, 187–192
- Methane  
 carbon atom auration, 293–295  
 hydrogen/deuterium exchange  
 liquid acids, 311–317  
 $\text{FSO}_3\text{H}$ -based superacids, 313  
 HF-based superacids, 313–317  
 sulfuric acid, 311–313  
 solid acids, 317–319  
 superacid proton exchange reactions, 311
- Methylene-bridged PAH-arenium ions, 269–272
- Migration mechanisms  
 long-lived carbocations, arenium ion structure and reactivity, 131–140  
 polyfluorinated carbocations, isomeric transformations, 193–201
- Mixed multiple fluorinated carbocations, structure and properties, 164–177
- Molecular rearrangement, organic synthesis in superacids, quinine, 373–374
- Mössbauer spectroscopy, polyaurated carbocations, 298–300
- Nafion H, 34
- Naphthalenium ions, polyfluorinated carbocations, isomeric transformations, 197–201
- Natural bond orbital (NBO) analysis  
 2,6-dimethylmesitylene-2,6-diyl dication characterization, 89–90  
 neutral carbocationic analogs  
 delocalized carbanion stabilization, 52–53  
 formation strategies, 49–50  
 positive/negative organic fragment stabilization, 54
- Neutral carbocationic analogs  
 carbene-Lewis acid complexes, 59–62  
 delocalized carbanion stabilization, 52–53  
 formation strategies, 49–50  
 isoelectric BH substitution of  $\text{CH}^+$ , 54–57  
 $\alpha$ -ketol rearrangement symmetric geometry, 57–59
- Lewis acid complexes, 62–64  
 negative anion delocalization, remote H replacement, 51–52  
 nonclassical analogs, 45–48  
 research background, 44  
 stabilized positive/negative organic fragment links, 53–54  
 structure and properties, 45–51  
 long carbon-carbon bonds, 48–49  
 zwitterionic analogs, 49–50  
 zwitterionic viability, computational criteria, 50–51
- Nitronium compounds, long-lived carbocations, arenium ion structure and reactivity, 131–140
- Nonalternant carbocations  
 fluoranthrene PAHs, 272–274  
 methylene-bridge PAHs, 269–272  
 polycyclic aromatic hydrocarbons, future research applications, 274–275
- Nonarenium carbocations, structure and reactivity, 142–148
- Nonclassical ions  
 carbocation chemistry, 19–25  
 hypercoordinate carbocations, 30–38

- Nonclassical ions (*Continued*)
- $\alpha$ -ketol rearrangements, symmetric geometry, 58–59
  - neutral carbocationic analogs
    - carbene-Lewis acid complexes, 59–62
    - formation strategies, 50
    - zwitterionic viability, computational criteria, 50–51
  - zwitterionic carbocations, basic properties, 44
- Nondegenerate rearrangements, long-lived carbocations
- arenium ion structure and reactivity, 133–140
  - nonarenium carbocation structure and reactivity, 144–148
- Nonresonance positions, polyfluorinated carbocations, 160–161, 163–177
- 7-Norbornadienyl cation
- CH<sup>+</sup> carbocation, isoelectronic BH substitution, 54–57
  - delocalized carbanion stabilization, 52–53
- Norbornyl cation
- carbocations, nonclassical ion structure, 19–25
  - hypercoordinate carbocations, 32–38
  - isotopic perturbation, 227–234
- Nuclear magnetic resonance (NMR)
- arenium ion structure and reactivity, 128–140
  - carbocation chemistry
    - historical perspective, 4–6
    - nonclassical ion controversy, 22–25
  - cationic  $\pi$ -cyclization reactions, 150–152
  - cyclopentadienyl carbocations, 109–111
  - cyclopropylmethyl cations, 78
  - gold carbocations
    - aryl complexes, 303–304
    - heteroaryl complexes, 304–305
  - isotopic perturbation, carbocations, 223–234
  - long-lived alkyl cations, 11–15
  - long-lived carbocations, 126–128
  - neutral carbocationic analogs, carbene-Lewis acid complexes, 61–62
  - polyaurated carbocations, 298–300
  - polycyclic aromatic hydrocarbons, ion chemistry, 241–242
  - polyfluorinated carbocations
    - linear parameter correlation, 176–177
    - resonance position, 161–162
    - structural data, 178–185
- Nucleophilic agents, long-lived carbocations, arenium ion structure and reactivity, 138–140
- Nucleophilicity, electrophilicity scales, carbocations, 333–334
- biological applications, 345–352
  - rate constants, 336–345
- Nucleus-independent chemical shift (NICS) values
- bisfluorenyl dication, 114–115
  - cyclopentadienyl carbocations, 106–111
    - free radical aromaticity and antiaromaticity, 116–120
  - indenyl and fluorenyl cations, 113
  - neutral carbocationic analogs, carbene-Lewis acid complexes, 61–62
  - polycyclic aromatic hydrocarbons, benzannulation, 259–260
  - zwitter anionic carbocation analogs, 65–67
- 2,10-*para*[3<sup>2</sup>.5<sup>6</sup>]Octahedrane dication, structure and classification, 90–91
- Octanuclear cations, heteroleptic gold carbocations, 297
- Organic fragments
- electrophilicity scales, carbocations, 345–352
  - neutral carbocationic analogs, positive/negative stabilization, 53–54
- Organic synthesis, superacids
- electrophilic hydroxylation
    - aromatic amines, 367
    - indoles and alkaloids, 367–370
  - fluorination and ionic hydrogenation, alkaloids, 370–373
  - nonactivated carbon-hydrogen bond
    - functionalization, 360–67
    - acyclic ketones, imines, and amides, 360–363
    - cyclic ketone carbonylation (carboxylation), 363–364
    - polycyclic ketone dehydrogenation to dienones, 364–367
  - quinine rearrangement, 373–374
- Ortho* isomers
- arenium ion structure and reactivity, 129–140
  - (hexaaryltrimethylene)methane dication, 97–98
  - “neutral” carbocationic analogs, early examples, 45–48
  - polycyclic aromatic hydrocarbons
    - chrysenium ions, 252–254
    - cyclopenta[*a*]phenanthrenium cations, 247–251
  - polyfluorinated carbocations, 171–177
    - isomeric transformations, 194–201
    - stability parameters, 187–192
    - structural characteristics, 183–185
- Oxo derivatives, organic synthesis in superacids, nonactivated carbon-hydrogen bond functionalization, 360–363

- Oxygen backdonation, polyfluorinated carbocations, 164–177
- <sup>18</sup>O-isotope shift  
 cyclopentadienyl carbocations, 109–111  
 indenyl and fluorenyl cations, 111–113
- Ozone reactions, hypercoordinate carbocations, 36–37
- Para* substitutions  
 arenium ion structure and reactivity, 129–140  
 1,1'-diadamantylbenzyl cations, 75–76  
 (hexaaryltrimethylene)methane dications, 97–98  
 polycyclic aromatic hydrocarbons,  
 cyclopenta[*a*]phenanthrenium cations, 247–251  
 polyfluorinated carbocations, 167–177  
 isomeric transformations, 193–201  
 stability parameters, 187–192
- Partially ordered mediums, long-lived carbocations, arenium ion structure and reactivity, 136
- Pentacoordinate carbocations  
 methane carbon auration, 293–295  
 polyaurated carbocations, quantum chemical calculations, 300–301
- Pentanuclear carbocations, homoleptic gold carbocations, 297
- Perchloric acid, carbocation chemistry, 16–17
- Perfluorinated cyclopropenyl cation, structure and properties, 162
- Pericyclic reactions, long-lived carbocations, nonarenium carbocation structure and reactivity, 146–148
- Peri*-located fluorines, polyfluorinated carbocations, 184–185  
 stability parameters, 198–201
- $\alpha$ -Phenanthrenyl-substituted carbocations, regioisomeric properties, 244–246
- Phenanthrenium ion model  
 long-lived carbocations, arenium ion structure and reactivity, 133–140  
 polycyclic aromatic hydrocarbons, 242–244
- Phenol complexes, long-lived carbocations, Lewis acids and, 140–141
- Phenonium cation, structure and properties, 284–285
- Phenyl rings, “neutral” carbocationic analogs, early examples, 46–48
- Phosphines  
 gold carbocation reference compounds, 296–297  
 methane auration, 293–295
- <sup>31</sup>P NMR spectroscopy, gold carbocations, metal-locene complexes, 301–302
- $\pi$ -electronic charge distribution  
 carboxonium-substituted ions, 265–268  
 persistent ArC<sup>+</sup>(R)CF<sub>3</sub> carbocations, 264–265  
 polyfluorinated carbocations, 178–185
- Polyaurated structural data, gold carbocations, 296–298  
 heteroleptic tri- and tetranuclear cations, 297  
 homoleptic penta- and hexanuclear carbocations, 297
- NMR and Mössbauer spectroscopy, 298–300  
 quantum-chemical calculations, 300–301  
 reference compounds, 296–297
- Polycyclic aromatic hydrocarbons (PAHs), stable ion chemistry  
 benzo[*a*]anthracenium BA cations, 254–256  
 benzo[*c*]phenanthrenium/benzo[*g*]chrysenium cations, 256–260  
 biological applications, 239–241  
 1,6- and 1,8-bis(diphenylmethylenium)pyrene dications, 263–265  
 carboxonium-substituted pyrenium ion, 265–268  
 chrysenium ions, 252–254  
 cyclopenta[*a*]phenanthrenium cations, 246–251  
 dihydrocyclobuta[3]pyrenium ions, 269  
 dihydropyrenium(ethanophenanthrenium) cations, 260–261  
 fluoranthrene carbocations, 272–274  
 future research issues, 274–275  
 methylene-bridged PAH-arenium ions, 269–272  
 phenanthrenium ions, 242–244  
 protocols, 241–242  
 protonation, 241  
 (1-pyrenyl)diphenylmethyl cation, 263–265  
 regioisomeric  $\alpha$ -pyrenyl-substituted carbocations, 261–263  
 regioisomeric carbocations,  $\alpha$ -phenanthrenyl-substituted carbocations and carboxonium ions, 244–246  
 research background, 238–239
- Polyfluorinated carbocations  
 chemical properties and synthetic applications, 193–208  
 electrophiles, 201–208  
 isomeric transformations, 193–201  
 NMR data, 178–185  
 research perspective, 159–160  
 stability properties, 185–192  
 structure and generation, 160–177

- Potential energy surfaces  
 cationic  $\pi$ -cyclization reactions, 151–152  
 hydrogen/deuterium exchange, small alkanes, DF-SbF<sub>5</sub>, 324–325  
 neutral carbocationic analogs, zwitterionic viability, 51
- Protonated cyclopropane intermediates, fast rearrangement reactions, 215–218
- Proton exchange reactions, strong acids and alkanes  
 methane-ethane, 311–319  
 hydrogen/deuterium exchange, liquid acids, 311–317  
 FSO<sub>3</sub>H-based superacids, 313  
 HF-based superacids, 313–317  
 sulfuric acid, 311–313  
 hydrogen/deuterium exchange, solid acids, 317–319
- research background, 309–311
- small alkanes, two-plus carbon atoms, 319–328  
 hydrogen/deuterium exchange  
 liquid acids, 319–325  
 solid acids, 326–328  
 hydrogen/deuterium exchange liquid acids  
 DF-SbF<sub>5</sub>, 323–325  
 DSO<sub>3</sub>F-SbF<sub>5</sub>, 323  
 fluorosulfonic acid, 321–323  
 sulfuric acid, 319–320  
 triflic acid, 320–321
- Proton exchange transition state, hydrogen/deuterium exchange, methane-ethane, sulfuric acid, 312
- Pyramidane, neutral carbocationic analogs, carbene-Lewis acid complexes, 61–62
- Pyrenium ions  
 carboxonium-substituted ions, 265–268  
 dihydrocyclobuta[e]pyrenium ions, 269  
 (1-Pyrenyl)diphenylmethyl cation, polycyclic aromatic hydrocarbons, 263  
 $\alpha$ -Pyrenyl-substituted carbocations, polycyclic aromatic hydrocarbons, 261–263
- Quantum chemical studies  
 aurophilicity principles, 293  
 isotopic perturbation, carbocations, 232–234  
 polyaurated carbocations, 300–301  
 polyfluorinated carbocations, stability parameters, 186–192
- Quenching mechanisms  
 long-lived carbocations, arenium ion structure and reactivity, 138–140  
 polycyclic aromatic hydrocarbons  
 cyclopenta[a]phenanthrenium cations, 251  
 future research, 274–275
- Quinine, superacid-catalyzed rearrangement, 373–374
- QUIVER program, isotopic perturbation, carbocations, 224–234
- Radialene derivatives, zwitter anionic carbocation analogs, 64–67
- Raman spectroscopy, arenium ion structure and reactivity, 128–140
- Rate constants, electrophilicity scales, carbocations, 336–345
- Reactivity parameters, electrophilicity scales, carbocations, 339–345
- Reactivity-selectivity principle, long-lived carbocations, arenium ion structure and reactivity, 131–140
- Reference compounds, gold carbocations, 296–297
- Regioisomeric carbocations  
 carboxonium-substituted pyrenium ion, 265–268  
 persistent ArC<sup>+</sup>(R)CF<sub>3</sub> carbocations, 264–265  
 polycyclic aromatic hydrocarbons,  
 $\alpha$ -phenanthrenyl-substituted carbocations, 244–246  
 $\alpha$ -pyrenyl-substituted carbocations, 261–263
- Regioselective chlorination, polyfluorinated carbocations, 170–177
- Resonance position  
 polycyclic aromatic hydrocarbons,  
 cyclopenta[a]phenanthrenium cations, 251  
 polyfluorinated carbocations, 160–161, 183–185  
 stability parameters, 186–192
- Resonance stabilization energies (RSE), cyclopentadienyl free radical aromaticity and antiaromaticity, 115–120
- RF-BF<sub>3</sub> complexes, long-lived alkyl cations, 10–15
- Rhodizonate, zwitter anionic carbocation analogs, 65–67
- Ring expansion  
 7-benzonorbornenyl cation, 286–287  
 cyclobutylmethyl cations, long-lived structure, 83–86  
 polycyclic aromatic hydrocarbons, chrysenium ions, 255–256
- “Rule of eight” valence electrons, carbocation chemistry, 28–29
- Salt effect, solvolytic studies of indenyl and fluorenyl cations, 112–113

- Secondary isotope effect, cyclopentadienyl carbocations, 108–111
- Secondary kinetic isotope effects (SKIEs), hydrogen/deuterium exchange, methane-ethane, HF-based superacids, 313–317
- Seven-coordinate carbocations, chemical properties, 30–38
- $\sigma$  basicity  
hydrogen/deuterium exchange, small alkanes, DF-SbF<sub>5</sub>, 323–325  
superacid-alkane proton exchange reactions, 310–311
- $\sigma$  C-C bonds  
cyclopropylmethyl cations, 78  
3-spirocyclopropyl-2-norbornyl cations, 81  
zwitterionic carbocations, basic properties, 44
- Sigmatropic rearrangements, long-lived carbocations  
arenium ion structure and reactivity, 136–140  
nonarenium carbocation structure and reactivity, 145–148
- [1,5]-sigmatropic rearrangement, cyclopentadienyl carbocations, 109–110
- [3,3]-sigmatropic rearrangement, cyclopentadienyl carbocations, 109–110
- Six-coordinate carbocations, chemical properties, 30–38
- Six-membered ring structures, indenyl and fluorenyl cations, 113
- Skeletal rearrangements, carbocations, nonclassical ion structure, 19–25
- Solid acids  
carbocation chemistry, superacids, 17  
hydrogen/deuterium exchange  
methane-ethane complexes, 317–319  
small alkanes, 326–328
- Solvent effect, indenyl and fluorenyl cations, 112–113
- Solvolysis  
allyl cations, fast rearrangement reactions, 220–221  
2-benzonorbornenyl cation, 285–286  
cyclopentadienyl carbocations, 106–111  
electrophilicity scales, carbocations, 334–335  
indenyl and fluorenyl cations, 111–113  
polycyclic aromatic hydrocarbons,  
cyclopenta[*a*]phenanthrenium cations, 251
- Spin saturation transfer, long-lived carbocations, 127–128
- arenium ion structure and reactivity, 130–140
- 3-Spirocyclopropyl-2-bicyclo[2.2.2]octyl cation, structure and properties, 81–82
- 3-Spirocyclopropyl-2-norbornyl cations, structure and properties, 80–81
- Splitting effects, isotopic perturbation, carbocations, 224–234
- Square pyramidal structures, cyclopentadienyl carbocations, 105–111
- Stable ion chemistry  
2-benzonorbornenyl cation, 285–286  
chromium tricarbonyl carbocations, 281–282  
electrophilicity scales, carbocations, 331–334  
polycyclic aromatic hydrocarbons (PAHs)  
benzo[*a*]anthracenium BA cations, 254–256  
benzo[*c*]phenanthrenium/  
benzo[*g*]chrysenium cations, 256–260  
biological applications, 239–241  
1,6- and 1,8-  
bis(diphenylmethylenium)pyrene  
dications, 263–265  
carboxonium-substituted pyrenium ion, 265–268  
chrysenium ions, 252–254  
cyclopenta[*a*]phenanthrenium cations, 246–251  
dihydrocyclobuta[3]pyrenium ions, 269  
dihydropyrenium(ethanophenanthrenium)  
cations, 260–261  
fluoranthrene carbocations, 272–274  
future research issues, 274–275  
methylene-bridged PAH-arenium ions, 269–272  
phenanthrenium ions, 242–244  
protocols, 241–242  
protonation, 241  
(1-pyrenyl)diphenylmethyl cation, 263–265  
regioisomeric  $\alpha$ -phenanthrenyl-substituted carbocations and carboxonium ions, 244–246  
regioisomeric  $\alpha$ -pyrenyl-substituted carbocations, 261–263  
research background, 238–239  
polyfluorinated carbocations, 185–192
- Stable ion conditions, carbocation chemistry, 18–19
- Stereochemical studies, carbocations, early research, 8–10
- Sterically crowded carbocations, 75–77  
2-(adamantylidenemethyl)-2-adamantyl cation, 76–77  
1,1'-diadamantylbenzyl cations, 75–76  
tris(1-naphthyl)- and tris(2-naphthyl)methyl cations, 77

- Steric hindrance  
 carboxonium-substituted pyrenium ion, 267–268  
 electrophilicity scales, carbocations, 347–352  
 polycyclic aromatic hydrocarbons, benzannulation, 257–260  
 polyfluorinated carbocations, 170–177
- Structure-reactivity relations, long-lived carbocations, nonarenium carbocation structure and reactivity, 142–148
- Sulfur deltaxe oxocarbon analog, zwitter anionic carbocation analogs, 66–67
- Sulfur dioxide, carbocation chemistry, 2–6
- Sulfuric acid, hydrogen/deuterium exchange methane-ethane, 311–313  
 small alkanes, 319–320
- Sulfur ylides, methane carbon auration, 295
- SO<sub>3</sub>, neutral carbocationic analogs, remote H replacement, 51–52
- Superacids  
 alkanes, proton exchange reactions methane-ethane, 311–319  
 hydrogen/deuterium exchange, liquid acids, 311–317  
 FSO<sub>3</sub>H-based superacids, 313  
 HF-based superacids, 313–317  
 sulfuric acid, 311–313  
 hydrogen/deuterium exchange, solid acids, 317–319  
 research background, 309–311  
 small alkanes, two-plus carbon atoms, 319–328  
 hydrogen/deuterium exchange liquid acids, 319–325  
 DF-SbF<sub>5</sub>, 323–325  
 DSO<sub>3</sub>F-SbF<sub>5</sub>, 323  
 fluorosulfonic acid, 321–323  
 sulfuric acid, 319–320  
 triflic acid, 320–321  
 solid acids, 326–328  
 arenium ion structure and reactivity, 128–140  
 carbocation chemistry, 15–17  
 cyclobutylmethyl cations, long-lived structure, 83–86  
 hypercoordinate carbocations, 34–38  
 isotopic perturbation, carbocations, 229–234  
 organic synthesis  
 electrophilic hydroxylation aromatic amines, 367  
 indoles and alkaloids, 367–370  
 fluorination and ionic hydrogenation, alkaloids, 370–373  
 nonactivated carbon-hydrogen bond functionalization, 360–367  
 acyclic ketones, imines, and amides, 360–363  
 cyclic ketone carbonylation (carboxylation), 363–364  
 polycyclic ketone dehydrogenation to dienones, 364–367  
 quinine rearrangement, 373–374  
 polyfluorinated carbocations, 162–163  
 electrophile properties, 207–208  
 isomeric transformations, 194–201
- Superelectrophiles, long-lived carbocations, phenol/Lewis acid complexes, 141
- Symmetric geometry,  $\alpha$ -ketol rearrangements, 57–59
- Syn-diol epoxides, polycyclic aromatic hydrocarbons, cyclopenta[*a*]phenanthrenium cations, 246–251
- Syn-metal complexes, 2-benzonorbornenyl cation, 285–286
- Synthetic processes, polyfluorinated carbocations electrophiles, 201–208  
 isomeric transformations, 193–201
- Synthons, long-lived carbocations, phenol/Lewis acid complexes, 141
- TEMPO reactions, cyclopentadienyl free radical aromaticity and antiaromaticity, 116–120
- Tertiary carbocation, 1,3-hydride shifts, 218–219
- 1,1,3,3-Tetracyclopropyl-1,3-propanediyl dication, structure and classification, 93–96
- Tetragoldmethanes, auration principles, 293–294
- Tetranuclear cations, heteroleptic gold carbocations, 297
- Tetravalent structure, carbocations, 27–29
- Three-membered ring structures, zwitter anionic carbocation analogs, 64–67
- Toponondegenerate rearrangement, long-lived carbocations, 144
- Trans*-isomers  
 allyl cations, fast rearrangement reactions, 220–221  
 polyfluorinated carbocations, 185
- Triarylcarbenium salts, “neutral” carbocationic analogs, 46–48
- Triarylphosphine complexes, polyaurated carbocations, spectroscopic data, 298–299
- Triaxane-2-methyl cation, structure and properties, 79–80
- Tricyclanes, carbocations, nonclassical ion structure, 19–25

- Triflic acid/hydrogen/deuterium exchange, small alkanes, 320–321
- Trinuclear cations, heteroleptic gold carbocations, 297
- Triphenylmethyl cations, early studies, 8
- Tris(1-naphthyl)-methyl cations, steric hindrance, 77
- Tris(2-naphthyl)methyl cations, steric hindrance, 77
- Tritylium ions, electrophilicity scales, carbocations, 344–345
- Trivalent carbocations, Koch-Haaf reactions, 36–38
- Tropylium ions, carbocation analogs, 44
- Van't Hoff structure, polyaurated carbocations, quantum chemical calculations, 300
- Wagner-Meerwein rearrangement  
carbocation chemistry, historical perspective, 2–6  
protonated cyclopropane intermediates, 215–218
- Water reactions, cyclopentadienyl free radical aromaticity and antiaromaticity, 119–120
- Wolff rearrangement, cyclopentadienyl free radical aromaticity and antiaromaticity, 117–120
- Woodward-Hoffmann rules, long-lived carbocations, arenium ion structure and reactivity, 136–140
- X-ray diffraction  
arenium ion structure and reactivity, 128–140  
cyclopentadienyl carbocations, 109–111  
high-coordinate carbocations, 30–38
- isotopic perturbation, carbocations, 229–234
- long-lived carbocations, nonarenium  
carbocation structure and reactivity, 142–148
- neutral carbocationic analogs  
CH<sup>+</sup> carbocation, isoelectronic BH substitution, 54–57  
positive/negative organic fragment stabilization, 53–54
- Zeolites, hydrogen/deuterium exchange, methane-ethane complexes, solid acids, 317–319
- Ziegler-Natta polymerization, hypercoordinate carbocations, 38–39
- Zwitterionic carbocations  
“anionic” carbocation analogs, 64–67  
neutral carbocationic analogs  
carbene-Lewis acid complexes, 59–62  
delocalized carbanion stabilization, 52–53  
formation strategies, 49–50  
isoelectric BH substitution of CH<sup>+</sup>, 54–57  
 $\alpha$ -ketol rearrangement symmetric geometry, 57–59  
Lewis acid complexes, 62–64  
negative anion delocalization, remote H replacement, 51–52  
nonclassical analogs, 45–48  
research background, 44  
stabilized positive/negative organic fragment links, 53–54  
structure and properties, 45–51  
long carbon-carbon bonds, 48–49  
zwitterionic analogs, 49–50  
zwitterionic viability, computational criteria, 50–51  
research background, 44