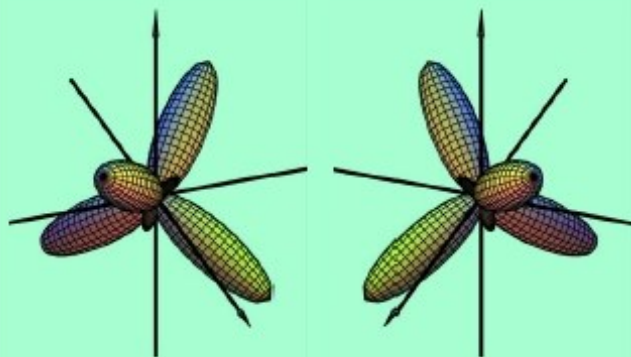


INSTITUTE OF PHYSICS
SERIES IN CHEMICAL PHYSICS



FUNDAMENTALS OF MOLECULAR SYMMETRY

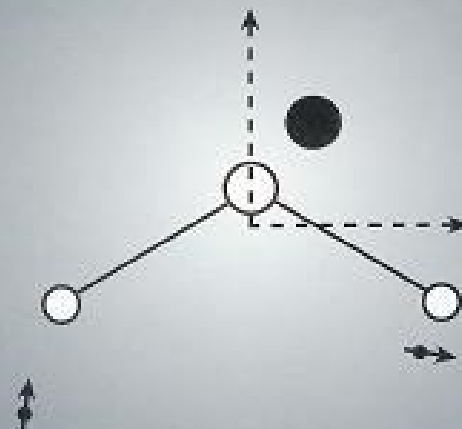
P R BUNKER
P JENSEN

IoP

ARC-CARC

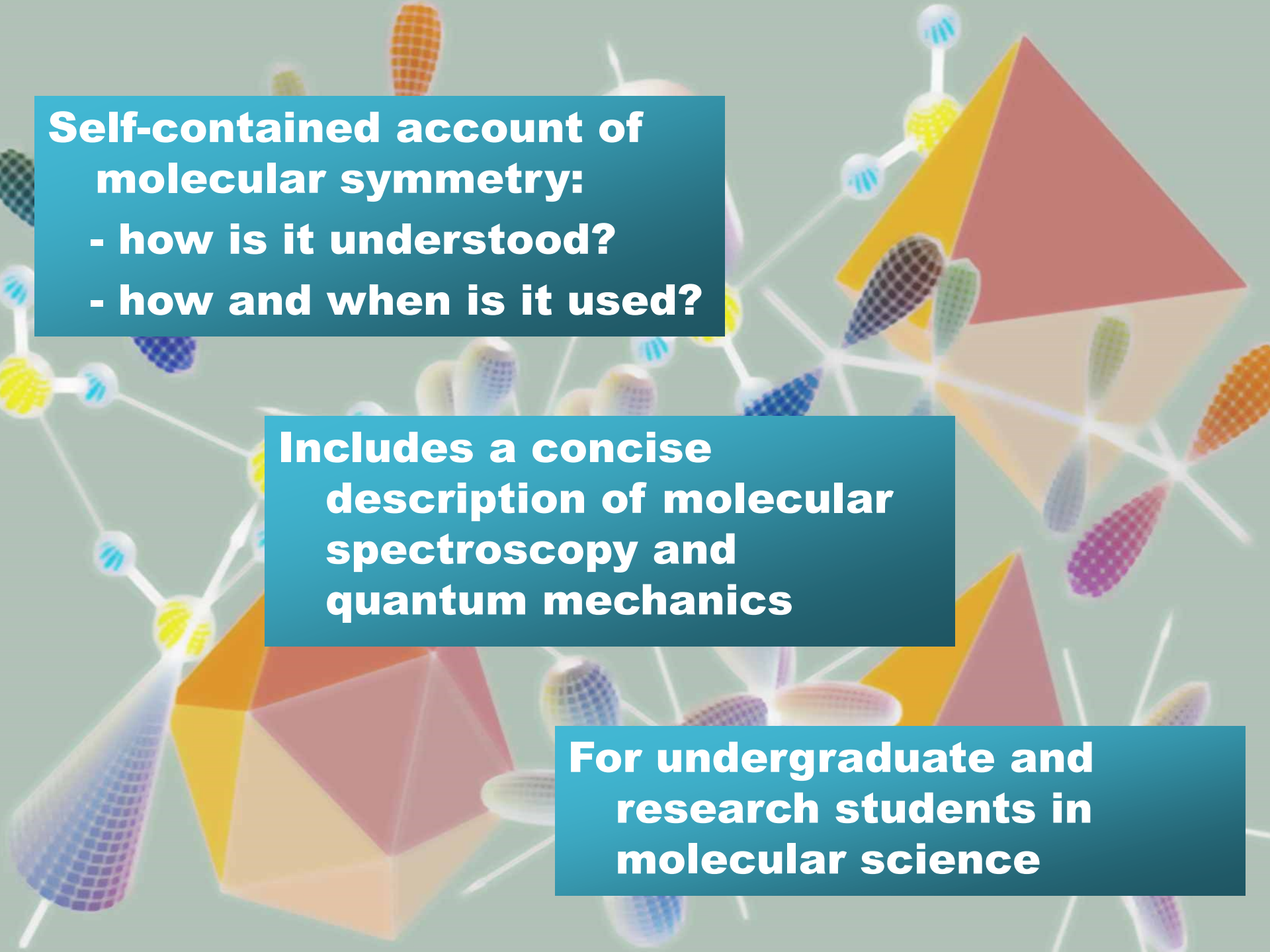
MOLECULAR SYMMETRY AND SPECTROSCOPY

SECOND EDITION



The prequel to

Phillip R. Bunker
and Per Jensen

The background of the slide is a light green-grey color. It is decorated with various 3D molecular models and polyhedral shapes. On the left, there are ball-and-stick models of molecules with yellow, blue, and white spheres. In the center and right, there are larger, semi-transparent polyhedral structures in shades of orange, red, and yellow. Interspersed among these are several molecular orbital visualizations, which appear as colored, grid-like lobes in blue, purple, green, and orange, representing the probability density of electrons in a molecule.

Self-contained account of molecular symmetry:

- how is it understood?**
- how and when is it used?**

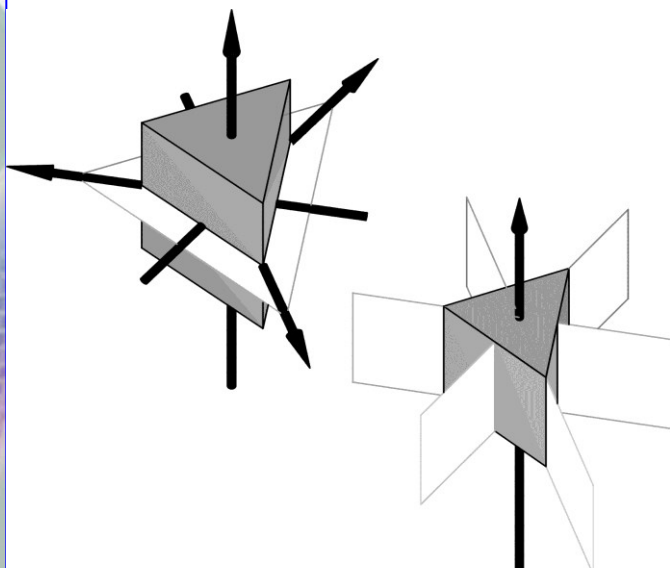
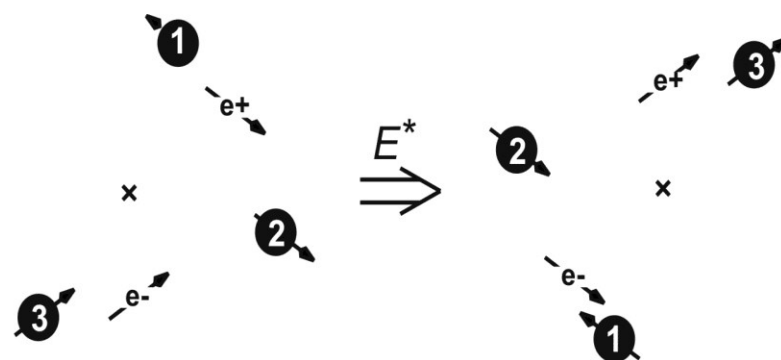
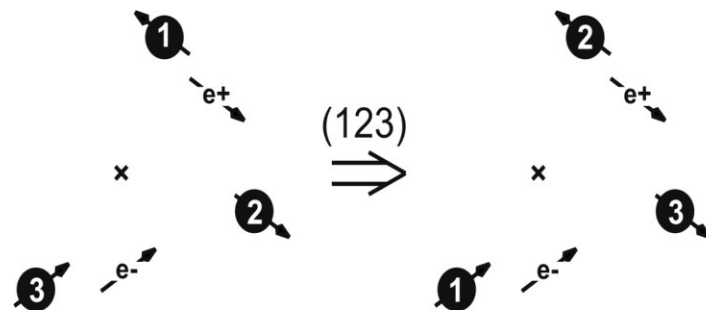
Includes a concise description of molecular spectroscopy and quantum mechanics

For undergraduate and research students in molecular science

A balanced account of

MOLECULAR SYMMETRY (MS) GROUPS

and



POINT GROUPS

Contents

Contents	v
Preface	ix
PART 1	
Spectroscopy and the quantum states of molecules	1
1 Molecular spectroscopy	2
1.1 Molecular spectra	2
1.2 The energies of molecules in the gas phase	5
1.3 The positions of spectral lines	9
1.4 The intensities of spectral lines	10
1.5 The shapes of spectral lines	12
1.6 Raman spectra	14
1.7 Problems	15
2 Quantum mechanics	17
2.1 The Schrödinger equation	17
2.2 The postulates of quantum mechanics	18
2.3 Diagonalizing the Hamiltonian matrix	21
2.4 The molecular Schrödinger equation	26
2.5 The separation of translational energy	27
2.6 The rovibronic Schrödinger equation	32
2.7 The angular momentum operator	34
2.8 The dipole moment operator and line strengths	36
2.9 Matrices and matrix algebra	37
2.10 Problems	41
3 Electronic states	43
3.1 The Born-Oppenheimer approximation	43
3.2 Spin and the Pauli exclusion principle	47
3.3 Electronic wavefunctions and energies	49
3.4 Molecular orbital theory	55
3.5 Problems	67

	<i>Contents</i>	vi
4 Vibrational states		70
4.1 Space-fixed and molecule-fixed axes		70
4.2 The vibrational Hamiltonian		72
4.3 Vibrational wavefunctions and energies		74
4.4 Anharmonicity		80
4.5 Tunneling		83
4.6 Problems		90
5 Rotational states		92
5.1 The Euler angles		92
5.2 The principal moments of inertia		93
5.3 The rigid-rotor Hamiltonian		95
5.4 Rovibronic wavefunctions		99
5.5 The Hamiltonian and wavefunctions in detail		100
5.6 Problems		111
PART 2		
Symmetry and symmetry groups		115
6 Geometrical symmetry		116
6.1 Geometrical symmetry operations		116
6.2 Geometrical symmetry groups: Point groups		120
6.3 The point group symmetry of molecules		125
6.4 Problems		129
7 The symmetry of the Hamiltonian		130
7.1 Hamiltonian symmetry operations		130
7.2 Nuclear permutations and the inversion E^*		131
7.3 Symmetry labels		136
7.4 Symmetry groups		138
7.5 The vanishing integral rule		141
7.6 Selection rules		144
7.7 The rovibronic symmetry label J		145
7.8 Diagonalizing the Hamiltonian matrix using symmetry		146
7.9 The Stark effect		147
7.10 The symmetry of H_3^+		148
7.11 Group theory		154
7.12 Problems		161
8 The symmetry groups of rigid molecules		164
8.1 The CNPI group		164
8.2 The molecular symmetry (MS) group		168
8.3 The MS group and the point group		170
8.4 Problems		182

PART 3	
Applications of symmetry	184
9 Nuclear spin, statistical weights and hyperfine structure	185
9.1 The fifth postulate of quantum mechanics	185
9.2 Statistical weights	186
9.3 Missing levels	190
9.4 Statistical weights for CH ₃ F	193
9.5 Nuclear spin hyperfine structure	194
9.6 Problems	198
10 The symmetry of electronic wavefunctions	199
10.1 The water molecule	199
10.2 The benzene molecule	203
10.3 The butadiene molecule	212
10.4 Conservation of orbital symmetry	213
10.5 The noncrossing rule	224
10.6 The C_6 and σ_v operations for benzene	225
10.7 Problems	227
11 The symmetry of rotation-vibration wavefunctions	229
11.1 The transformation properties of the Euler angles	229
11.2 The symmetry of rotational wavefunctions	233
11.3 The symmetry of normal coordinates	238
11.4 The symmetry of vibrational wavefunctions	243
11.5 Rotation-vibration coupling	245
11.6 Problems	251
12 Symmetry selection rules for optical transitions	253
12.1 Forbidden and allowed transitions	253
12.2 Zero order transition moment integrals	255
12.3 Transitions within an electronic state	257
12.4 Transitions between electronic states	273
12.5 Raman transitions	275
12.6 Problems	281
13 The symmetry groups of nonrigid molecules	283
13.1 The MS group of a nonrigid molecule	283
13.2 The ammonia molecule	284
13.3 Torsionally tunneling ethylene	286
13.4 Intensity alternations for HSSH and DSSD	289
13.5 The water dimer and the water trimer	292
13.6 Ethylene and its Raman spectrum	298
13.7 Problems	300

PART 4	
Other symmetries and symmetry violation	301
14 Other symmetries	302
14.1 The fourth postulate of quantum mechanics	302
14.2 Conservation laws	303
14.3 Electron permutation symmetry	304
14.4 Translational symmetry	305
14.5 Rotational symmetry	310
14.6 Charge conjugation	313
14.7 Parity	315
14.8 Time reversal	318
15 Symmetry violation	320
15.1 The electroweak Hamiltonian	320
15.2 Parity (P) violation	321
15.3 CP violation	323
15.4 T violation	325
15.5 Testing for CPT violation	326
15.6 Testing for permutation symmetry violation	327
A Answers to selected problems	330
B Character tables	341
C Books for further reading	363



Publisher:
IOP Publishing, Bristol, UK

Expected publication date:
December 2004

Expected price (paperback, 378 pages):
US\$ 65

See

<http://bookmark.iop.org/bookpge.htm?&isbn=0750309415>

(or see our homepages)