

Contents

Foreword	xi
Jonathan TENNYSON	
 Introduction	 xv
Iwona GULACZYK, Michaël REY and Ha TRAN	
 Chapter 1. Quantities and Units in Spectroscopy	 1
Vincent BOUDON and Cyril RICHARD	
1.1. Introduction.	1
1.2. Energy and associated quantities	2
1.3. Intensity	3
1.4. Line shape quantities	7
1.5. Other quantities	8
1.6. References	8
 Chapter 2. Accounting for the Anomalous Centrifugal Distortion of the Water Molecule.	 11
Laurent H. COUDERT	
2.1. The bending-rotation approach	13
2.1.1. The bending-rotation Hamiltonian	15
2.1.2. Bending energies and wavefunctions	16
2.1.3. Accounting for $ \Delta k > 0$ matrix elements	20

2.2. The fitting bending-rotation approach	21
2.2.1. The fitting bending-rotation Hamiltonian	22
2.3. Extended version of the fitting bending-rotation approach	24
2.4. References	24
 Chapter 3. Hindered Torsion of Asymmetrical Groups	 27
Laurent H. COUDERT	
3.1. Torsion of an asymmetrical top	29
3.1.1. Rotation–torsion Hamiltonian	29
3.1.2. Torsional Hamiltonian and energy levels	32
3.1.3. Rotation–torsion energy levels	35
3.2. The fitting Hamiltonians	36
3.2.1. The fitting torsional Hamiltonian	38
3.2.2. The fitting rotation–torsion Hamiltonian	39
3.3. References	41
 Chapter 4. Coupled Large Amplitude Motions	 45
Isabelle KLEINER, Iwona GULACZYK and Marek KRĘGLEWSKI	
4.1. Introduction	45
4.2. Theory for one LAM	46
4.3. Theory for coupled LAMs	47
4.3.1. Coupling two internal methyl group rotors	48
4.3.2. Coupling the internal rotation with a wagging motion	58
4.4. Fitting examples	74
4.4.1. Coupling hydrogen transfer motion to internal rotation: the methylmalonaldehyde case	74
4.4.2. A molecule with astrophysical importance: methylamine CH_3NH_2	75
4.5. Conclusion and future work	77
4.6. References	78
 Chapter 5. Simplified yet Full Theory of Microwave Three-Wave Mixing (M3WM)	 87
Denis S. TIKHONOV, Wenhao SUN and Melanie SCHNELL	
5.1. Introduction	87
5.2. Basic concepts	89
5.2.1. Rotations of molecules	89

5.2.2. Interactions with electromagnetic waves	93
5.3. Semi-classical description of polarization in a molecular ensemble.	108
5.3.1. What is polarization, and why is it absent by default?	108
5.3.2. Polarization of the molecular ensemble with a single-frequency pulse.	110
5.3.3. Classical averaging over the molecular frame distribution.	112
5.4. M3WM in sequential fashion	116
5.4.1. Rotational level scheme	116
5.4.2. M3WM signal in the perturbative regime.	117
5.4.3. Conditions for the pulse durations	124
5.4.4. Where will the signal go?	127
5.5. M3WM driven by simultaneous pulses	129
5.5.1. General solution.	129
5.5.2. Initial state for M3WM being $ 0\rangle$	131
5.5.3. Initial state being $ 1\rangle$	132
5.5.4. Initial state being $ 2\rangle$	133
5.5.5. Summary of the simultaneous M3WM scheme	133
5.6. Decoherence of the M3WM signal	133
5.6.1. Mechanisms of decoherence	133
5.6.2. De-excitation of excited molecules	134
5.6.3. Doppler effect	137
5.7. Conclusion	139
5.8. Appendix	139
5.8.1. Calculation of the classical selection rules using the wxMaxima	139
5.8.2. Calculation of the simultaneous excitation using the wxMaxima	140
5.8.3. Dephasing integration using the wxMaxima	140
5.9. References	140

Chapter 6. A Network Approach to High-Resolution and Precision Spectroscopy 143

Attila G. CSÁSZÁR, Roland TÓBIÁS, Péter ÁRENDÁS and
Tibor FURTENBACHER

6.1. Introduction.	143
6.2. Measured line positions and related issues	146
6.3. Spectroscopic networks.	149
6.3.1. Basic definitions.	149

6.3.2. Wavenumber uncertainties	151
6.3.3. Further network properties	154
6.4. MARVEL	156
6.4.1. The algorithm	157
6.4.2. Outlier analysis	158
6.4.3. Energy uncertainties and confidence intervals	160
6.4.4. Prediction of lines based on empirical (MARVEL) energies.	161
6.4.5. MARVEL datasets	163
6.5. Network-based design of spectroscopic experiments	164
6.5.1. General workflow.	164
6.5.2. Strategies for line selection	166
6.5.3. SNAPS	168
6.6. Acknowledgments.	169
6.7. References	169

**Chapter 7. Using Internal Coordinates and Iterative
Eigensolvers to Compute (Ro-)Vibrational Energy Levels 179**

Tucker CARRINGTON JR.

7.1. Introduction.	179
7.2. Deriving the kinetic energy operator	180
7.3. Basis functions.	184
7.3.1. Vibrational basis functions	184
7.3.2. Ro-vibrational basis functions	185
7.4. Eigensolvers	186
7.4.1. Direct methods	186
7.4.2. Iterative methods	186
7.5. Using iterative methods with a product basis set.	187
7.6. Using contracted bases with the Lanczos method	189
7.6.1. Matrix-vector products for ΔV	191
7.7. Conclusion	192
7.8. Acknowledgments.	193
7.9. References	193

**Chapter 8. Adiabatic and Diabatic Representations
in Diatomic Molecules: A Rovibronic Context 199**

Ryan P. BRADY and Sergei N. YURCHENKO

8.1. Introduction.	199
8.2. The BO approximation	201

8.3. Beyond BO: NACs	205
8.3.1. Hellmann–Feynman formalism of the NAC	208
8.4. Conditions for a strictly diabatic representation	210
8.5. Computing the AtDT	214
8.5.1. The two-state problem	215
8.5.2. The multi-state problem	220
8.5.3. Ansatz/block-diagonalization diabatization.	222
8.6. Conclusion	225
8.7. References	226

Chapter 9. From Ab Initio, to Variational Methods, Effective Models and High-Resolution Spectra Analyses 231

Oleg EGOROV, Andrei NIKITIN and Vladimir TYUTEREV

9.1. Introduction.	231
9.2. Born–Oppenheimer approximation.	232
9.2.1. Analytical model of ab initio PES and DMS	234
9.2.2. Single- and multi-reference ab initio approaches	236
9.2.3. Contributions from highly excited Slater determinants	238
9.2.4. Scalar-relativistic correction	238
9.2.5. Diagonal Born–Oppenheimer correction	239
9.2.6. Examples	240
9.3. Derivation of the KEO for the nuclear motion	244
9.3.1. Transformation to internal coordinates	244
9.3.2. Basis functions, matrix elements and truncation schemes	246
9.4. Dipole-allowed transitions	247
9.4.1. Line intensities	250
9.4.2. Metastable states, dissociation and molecular dynamics	251
9.5. Contact transformations to effective Hamiltonians	252
9.5.1. Separation of molecular variables	253
9.5.2. H^{eff} for ro-vibrational polyads.	254
9.6. Application to high-resolution spectra analyses	258
9.7. References	260

Conclusion	267
Iwona GULACZYK, Michaël REY and Ha TRAN	
List of Authors	269
Index	273
Summary of Volume 1B	277