

Contents

Preface	vii
1. Basic definitions	1
1.1. Shape and parameters of a spectral line.....	1
1.2. Principle line-broadening mechanisms and model profiles.....	2
1.2.1. Doppler broadening	4
1.2.2. Collisional broadening.....	6
1.2.3. Statistical independence of Doppler and collisional broadening	7
1.2.4. Collisional narrowing due to velocity changes	10
1.2.5. Collisional narrowing due to speed dependence of relaxation rates.....	12
1.2.6. Correlation between velocity changes and speed dependence of relaxation rates	13
1.3. Broadening, shifting and narrowing coefficients.....	15
1.4. Line interference	17
Bibliography	19
2. Semi-classical calculation of pressure-broadened line widths and pressure-induced line shifts	23
2.1. Quantum system of two interacting molecules.....	23
2.2. Spectral function	25
2.3. General expressions for line half-width and shift calculation	30
2.4. Anderson–Tsao–Curnutte theory.....	33
2.5. Interaction potential and irreducible tensors formalism	35
2.5.1. Electrostatic interactions.....	36
2.5.2. Induction and dispersion interactions	37
2.5.3. Atom–atom interactions.....	39
2.5.4. Matrix elements of the tensor operators.....	40
2.6. Interruption function for the long-range intermolecular potential.....	42
2.7. Resonance functions in the straight-line trajectory approximation	45

2.8.	Advanced semi-classical methods for line-broadening calculation.....	48	3.5.	Broadening of water vapour lines by nitrogen, oxygen and carbon dioxide	115
2.8.1.	Murphy and Boggs method	49	3.5.1.	Modelling of H ₂ O line widths broadened by N ₂ , O ₂ , air and CO ₂ ...	124
2.8.2.	Cattani method.....	49	3.6.	Interference of water vapour spectral lines.....	129
2.8.3.	Cherkasov method	49	3.7.	Broadening of water vapour lines by hydrogen and rare gases	134
2.8.4.	Korff and Leavitt method	49	3.7.1.	Broadening of H ₂ O vibrotational lines by hydrogen	135
2.8.5.	Herman and Jarecki method	50	3.7.2.	Broadening of H ₂ O vibrotational lines by rare gases.....	137
2.8.6.	Smith, Giraud and Cooper method	50	3.7.3.	Modelling of calculated and experimental H ₂ O line widths	142
2.8.7.	Davis and Oli method	50	3.7.3.1.	H ₂ O–Ar system	142
2.8.8.	Salesky and Korff method	50	3.7.3.2.	H ₂ O–He, H ₂ O–Ne, and H ₂ O–Kr systems, the v ₂ band	143
2.8.9.	Robert and Bonamy formalism.....	51	3.8.	Tabulation of H ₂ O line-broadening coefficients for high temperatures	147
2.8.10.	Exact trajectory model.....	51	3.8.1.	Surface $\gamma(sur)$	147
2.9.	Parabolic trajectory approximation	55	3.8.2.	Interpolation procedure of Delaye–Hartmann–Taine	148
2.10.	Resonance functions within the exact trajectory model	58	3.8.3.	Exponential representation of Toth	149
2.11.	Approximation for the real parts of exact-trajectory resonance functions	62	3.8.4.	Polynomial representation	150
2.12.	Approximation for the imaginary parts of exact-trajectory resonance functions	66	Bibliography	151	
2.13.	Short-range forces and trajectory effects.....	69	4.	Pressure broadening and shifting of vibrotational lines of atmospheric gases	158
2.14.	Robert and Bonamy formalism with exact trajectories	71	4.1.	Vibrotational lines of asymmetric X ₂ Y molecules	158
	Bibliography	75	4.1.1.	H ₂ S molecule	160
3.	Collisional broadening of water vapour lines	78	4.1.1.1.	Self-broadening case	162
3.1.	Effective operators of physical quantities for X ₂ Y molecule and vibrotational wave functions for water vapour molecule	80	4.1.1.2.	H ₂ O-broadening	168
3.2.	Self-broadening of H ₂ O lines	86	4.1.1.3.	Broadening by N ₂ , O ₂ , H ₂ , D ₂ and CO ₂	168
3.2.1.	Experimental studies.....	86	4.1.2.	SO ₂ molecule	172
3.2.2.	Calculations	90	4.1.2.1.	Self-broadening	173
3.2.3.	Temperature dependence of γ and δ coefficients	96	4.1.2.2.	SO ₂ line broadening by foreign gases	174
3.2.4.	Vibrational dependence of γ and δ coefficients	99	4.1.3.	O ₃ molecule	174
3.2.5.	Influence of the rotational dependence of dipole moment and polarizability.....	101	4.1.4.	NO ₂ molecule	182
3.2.6.	Influence of accidental resonances	102	4.2.	Vibrotational lines of ethylene	183
3.2.7.	Influence of the trajectory model.....	103	4.3.	Vibrotational lines of symmetric tops	189
3.3.	Analytical representation for self-broadening parameters of water vapour.....	104	4.3.1.	NH ₃ molecule	191
3.3.1.	Two-dimensional surface for $\gamma^{(J_i, J_f)}(K_i, K_f)$	108	4.3.2.	PH ₃ molecule	201
3.3.2.	Temperature dependence of $\gamma(sur)$	111	4.3.3.	CH ₃ A-molecules (A = Cl, F, D)	204
3.4.	Semi-empirical approach to calculation of water vapour line widths and shifts	112	4.3.3.1.	Methyl chloride CH ₃ Cl	204
			4.3.3.2.	Methyl fluoride CH ₃ F	205
			4.3.3.3.	Monodeuterated methane CH ₃ D	209
			4.4.	Broadening coefficients of vibrotational lines of methane	211
			4.5.	Linear molecules	219
			4.5.1.	CO ₂ molecule	220

4.5.2. N ₂ O molecule	222
4.5.3. HCN molecule	224
4.5.4. C ₂ H ₂ molecule	226
4.6. Diatomic molecules.....	230
4.6.1. Vibrotational energy levels and wave functions	230
4.6.2. Influence of vibration-rotation coupling on the line shifts	232
4.6.3. CO molecule	234
4.6.4. NO molecule	239
4.6.5. OH molecule	242
4.6.6. HF and HCl molecules	244
Bibliography.....	250
Appendix A. Matrix elements of operators of physical quantities	264
Appendix B. Parameters of intermolecular interaction potentials	269
Appendix C. Relations used in calculation of resonance functions	275
Appendix D. Second-order contributions from atom–atom potential in the parabolic trajectory model	278
Appendix E. Resonance functions in the parabolic trajectory model	282
Appendix F. Resonance functions in the exact trajectory model	285
Index	289