

Rotational Absorption Spectral Studies and *Ab Initio* Quantum Chemical Calculations of Molecules in Gas Phase

By

Pradeep Risikrishna Varadwaj

Experimental Condensed Matter Physics Division,
Saha Institute of Nuclear Physics,
Block-AF, Sector - I, Bidhannagar, Kolkata - 700 064, India

Thesis submitted for the Degree of Doctor of
Philosophy in Science
in the
Jadavpur University, Jadavpur, India
· June, 2007 ·

Contents

Preface	ix
Acknowledgments	xi
List of Publications	xiii
1 An Introductory Survey of the Theory of Molecular Rotations	1
1.1 Introduction	1
1.2 The Moments of Inertia Tensor	3
1.3 Classification of Molecules based on Rotational Behavior	5
1.4 Hamiltonian of a Rotating Molecule	6
1.4.1 Hamiltonian of a rigid rotor	7
1.4.2 The linear rotor	8
1.4.3 The symmetric top rotor	14
1.4.4 The asymmetric top rotor	15
1.5 Hamiltonian for Nuclear Quadrupolar Interaction	24
1.5.1 Introduction	24
1.5.2 Electric field gradient	25
1.5.3 Hamiltonian for molecules with a single quadrupole nucleus	25
1.5.4 Hamiltonian for molecules having two quadrupole nuclei	29
1.6 Molecular Structure Determination	31
1.6.1 Equilibrium structure (r_e)	31
1.6.2 Substitution structure (r_s)	32
1.6.3 Effective structure (r_0)	35
1.7 Vibrational Effects on Rotation	36
1.8 The Theory of Molecular Vibrations: Normal Mode Analysis	37
Bibliography	43
2 An Introductory Review of the <i>Ab Initio</i> Quantum Chemical Methods	44
2.1 Introduction	44
2.2 Key Points and Basic Principles of Quantum Mechanics	45

2.2.1	The Schrödinger wave-equation	45
2.2.2	Expectation value	46
2.2.3	The variational principle	46
2.3	Schrödinger Equation for a Many-Body System	47
2.4	The Born-Oppenheimer Approximation	47
2.5	Molecular Orbital (MO) <i>Ab Initio</i> Calculation	50
2.6	The Hartree-Fock Self-Consistent-Field (HF-SCF) Method	50
2.7	Møllar-Plesset Perturbation Theory (MPPT) Method	54
2.8	Density Functional Theory (DFT) Formalism	57
2.8.1	Introduction	57
2.8.2	The Hohenberg-Kohn theorems	57
2.8.3	The self-consistent Kohn-Sham's DFT equations	61
2.8.4	The exchange-correlation energy functionals	62
2.9	Slater and Gaussian Type Basis Sets	72
2.10	Basis Set Superposition Error (BSSE)	75
	Bibliography	80
3	Experimental Details	81
3.1	Introduction	81
3.2	Microwave sources, detectors, and frequency doublers	82
3.3	The Microwave Spectrometer	83
3.3.1	The detection system	85
3.3.2	The frequency measurement system	86
3.4	The Millimeter-wave Spectrometer	87
3.5	Radio-Frequency Microwave Double Resonance (RFMWDR) Technique	88
3.5.1	Introduction	88
3.5.2	The RFWDR spectrometer	90
3.6	Sensitivity and Resolution of the Spectrometers	92
	Bibliography	94
4	Studies on Linear Polyatomic Molecules	95
4.1	Introduction	95
4.2	Cyanogen Chloride (ClCN)	97
4.2.1	Introduction	97
4.2.2	Experimental details	98
4.2.3	Analysis of the millimeter-wave spectrum	98
4.2.4	Computational details	100
4.2.5	Potential energy surface (PES)	101

4.2.6	Molecular structure	104
4.3	Cyanogen Bromide (BrCN)	105
4.3.1	Introduction	105
4.3.2	Experimental details	105
4.3.3	Analysis of the millimeter-wave spectrum	106
4.3.4	Molecular structure	110
4.4	Cyanogen Iodide (ICN)	111
4.4.1	Introduction	111
4.4.2	Experimental Details	111
4.4.3	Analysis of the millimeter-wave spectrum and discussion	112
4.5	Chloroacetylene (ClCCH)	118
4.5.1	Introduction	118
4.5.2	Experimental details	119
4.5.3	Analysis of the millimeter-wave spectrum	120
4.5.4	Molecular Structure	121
4.6	Chlorocyanoacetylene (ClCCCN)	123
4.6.1	Introduction	123
4.6.2	Experimental details	124
4.6.3	Analysis of the millimeter-wave spectrum	124
4.6.4	Computational Details	125
4.6.5	Results and discussion	126
4.7	Conclusion	130
	Bibliography	134
5	Studies on the Rotational Spectra of Asymmetric Top Molecules	135
5.1	Introduction	135
5.2	2-Fluorobenzonitrile (C ₇ H ₄ FN)	136
5.2.1	Introduction	136
5.2.2	Experimental details	137
5.2.3	Computational details	138
5.2.4	Analysis of the observed millimeter-wave spectrum	139
5.2.5	Discussion	141
5.3	2,3-difluorobenzonitrile (C ₇ H ₄ F ₂ N)	143
5.3.1	Introduction	143
5.3.2	Experimental Details	144
5.3.3	Computational details	145
5.3.4	Analysis of the millimeter-wave spectrum	145
5.3.5	Discussion	147
5.4	3-Chlorobenzonitrile (C ₇ H ₄ ClN)	149

5.4.1	Introduction	149
5.4.2	Experimental	150
5.4.3	Computational details	151
5.4.4	Results	152
5.4.5	Nuclear hyperfine splitting	156
5.4.6	Discussion	159
5.5	Conclusion	160
	Bibliography	163
6	DFT Studies on the Y-CN...HX/DX Linear Hydrogen-Bonded Complexes	164
6.1	Introduction	164
6.2	Wide-spread Features of the Red-shifted H-bonded Systems Containing -C≡N: and HX	166
6.3	The YCN...HX/DX Inter-molecular H-bonded Complexes	167
6.3.1	Introduction	167
6.3.2	Computational procedures	168
6.3.3	Results	170
6.3.4	Discussion	171
6.3.5	Conclusion	191
	Bibliography	196