

NEUTRAL AND IONIC FLUORESCENCE OF MOLECULAR GASES  
BY PHOTON IMPACT

SYED MAQBOOL AHMED

PH.D. THESIS  
JULY 1990

043



B14250

PHYSICAL RESEARCH LABORATORY

NEUTRAL AND IONIC FLUORESCENCE OF MOLECULAR GASES  
BY PHOTON IMPACT

by

*SYED MAQBOOL AHMED*

A THESIS  
SUBMITTED FOR THE DEGREE OF

*DOCTOR OF PHILOSOPHY*

OF THE GUJARAT UNIVERSITY

JULY 1990

PHYSICAL RESEARCH LABORATORY  
AHMEDABAD - 380 009  
INDIA

## CONTENTS

*Certificate*

*Statement*

*Acknowledgement*

### CHAPTER - 1 : INTRODUCTION

1.1 Photochemical Processes	1
1.2 Quantum States of Molecules	3
1.2.1 Diatomic molecules	3
1.2.1.1 Rotational energy levels of diatomic molecules	3
1.2.1.2 Vibrational energy levels of diatomic molecules	4
1.2.1.3 Electronic energy levels of diatomic molecules	8
1.2.2 Polyatomic molecules	10
1.2.2.1 Rotational energy levels of polyatomic molecules	10
1.2.2.2 Vibrational energy levels of polyatomic molecules	11
1.2.2.3 Electronic energy levels of polyatomic molecules	12
1.3 Primary Processes in Diatomic Molecules	14
1.3.1 Predissociation in diatomic molecules	16
1.4 Primary Processes in Triatomic Molecules	17
1.4.1 Photodissociation in triatomic molecules	18
1.4.2 Predissociation in triatomic molecules	20

1.5	Photoabsorption	20
1.5.1	Validity of Beer-Lambert Law	23
1.6	Photoionization	24
1.7	Fluorescence	25
1.7.1	Fluorescence from neutral molecules	26
1.7.1.1	Fluorescence and other competing processes	27
1.7.2	Ionic fluorescence	28
1.8	Fluorescence Quantum Yield	29
1.9	Selection Rules	31
1.10	Survey of Experimental Methods	32
1.11	Need for a New Experimental System	34
1.12	Choice of the Target Molecules	37

## CHAPTER - 2 : EXPERIMENTAL SET - UP

2.1	Introduction	39
2.2	Argon Min-arc Light Source	40
2.2.1	Operation of the source	41
2.2.2	Power supply	42
2.2.3	Performance and spectrum of the light source	42
2.2.4	Light attenuator	44
2.3	1-Meter Monochromator	45
2.3.1	Resolution of the monochromator	45
2.4	Beam Splitter	46

<b>2.5 Absorption/Fluorescence Chamber</b>	47
2.5.1 0.2-meter monochromator	48
<b>2.6 Vacuum System and Related Instruments</b>	49
2.6.1 Vacuum systems	49
2.6.2 Pressure measurements	50
2.6.3 Gas handling	51
<b>2.7 Light Intensity Measurements</b>	53
2.7.1 Detectors	54
2.7.2 Data acquisition system	56
<b>2.8 Operation of the Instrument</b>	58
2.8.1 Absorption cross section measurement	59
2.8.2 Fluorescence cross section measurement	60
<b>2.9 Performance of the Instrument</b>	61
2.9.1 Resolution	61
2.9.2 Wavelength calibration of the system	62
2.9.3 Effect of using 0.2-meter monochromator	63

## CHAPTER - 3 : METHOD

<b>3.1 Photoabsorption Cross Section Measurement</b>	65
<b>3.2 Total Fluorescence Cross Section Measurement</b>	67
3.2.1 Fluorescence signals measured perpendicular to the optic axis	67
3.2.2 Fluorescence signals measured along the optic axis	69



## CHAPTER - 4 : ERROR ANALYSIS

4.1	Pressure Measurement	73
4.2	Thermal Transpiration Effect	75
4.3	Uncertainty in Optical Path Length	76
4.4	Counting Statistics	76
4.5	Gas Impurity	77
4.6	Conclusion	77

## CHAPTER - 5 : RESULTS AND DISCUSSION

5.1	Sulphur Dioxide	79
5.1.1	SO <sub>2</sub> : Spectral region 188 - 231 nm	79
5.1.2	SO <sub>2</sub> : Spectral region 278.7 - 320 nm	83
5.2	Carbon Disulphide	86
5.2.1	CS <sub>2</sub> : Spectral region 188.2 - 213 nm	86
5.2.2	CS <sub>2</sub> : Spectral region 287.5 - 339.5 nm	91

## CHAPTER - 6 : IONIC FLUORESCENCE

6.1	Experimental Set-Up	94
6.2	Results and Discussion	98
6.2.1	Carbon disulphide	98

6.2.1.1	$CS(A\ ^1\Pi \rightarrow X\ ^1\Sigma^+)$ system	99
6.2.1.2	$CS_2^+(B\ ^2\Sigma_u^+ \rightarrow X\ ^2\Pi_g)$ system	100
6.2.1.3	$CS_2^+(A\ ^2\Pi_u \rightarrow X\ ^2\Pi_g)$ system	101
6.2.2	Sulphur dioxide	103

## CHAPTER - 7 : CONCLUSION AND SCOPE FOR FUTURE WORK

7.1	Conclusion	107
7.2	Scope for Future Work	109

## LIST OF PUBLICATIONS

## REFERENCES