

**TEMPERATURE DEPENDENCE OF
THE COTTON-MOUTON EFFECT IN GASES**

BY

MICHAEL HANK COONAN

BSc (Hons) (Sydney)

A thesis submitted to the
University of New England,
in fulfilment of the requirements
for admission to the degree of
Doctor of Philosophy

FEBRUARY, 1995

PREFACE

This thesis describes research undertaken at the University of New England, Armidale, under the supervision of Professor G.L.D. Ritchie.

I certify that the substance of this thesis has not already been submitted for any degree and is not currently being submitted for any other degree or qualification.

I certify that any help received in preparing this thesis, and all sources used, have been acknowledged in this thesis.

..... 

ACKNOWLEDGEMENTS

It is a great pleasure to express my gratitude and sincere appreciation to the many people who have given so generously of their time and resources during the course of this research. I am particularly indebted to my supervisor, Professor G.L.D. Ritchie, for his constant support, encouragement and patience; Professor A.D. Buckingham FRS for the continued loan of the magnet and the magnet power supply, and for the gift of another set of Pockels glass windows, without which this project would not have been possible; Dr. D.R. Laver for much valuable assistance with the modifications and data collection in the early stages of measurements; Dr. M.P. Bogaard, Dr. I.R. Gentle, Dr. M.R. Hesling and Dr. M.A. Spackman for many helpful discussions and productive collaborations; Mr. E.W. Blanch, Mr. A.J. Russell and Mr. J.N. Watson for kindly providing unpublished data which assisted the analysis of the measurements; Mr. B.D. Jones, Mr. L. Hodges and Mr. J. Zylmans for their craftsmanship; and Mr. I.E. Craven for his generous help with the electronic aspects of the project.

The award of a Commonwealth Postgraduate Research Award is gratefully acknowledged.

Particular thanks must go to many friends, colleagues, staff and students, for their unfailing encouragement throughout the course of the project. Finally, I wish to thank Gabrielle Whittle and my family for their support and kindness.

SUMMARY

The Cotton-Mouton effect in gases can provide valuable information about certain fundamental molecular properties which determine the interaction of matter with electric and magnetic fields, and an analysis of such properties provides insight into the charge distributions and structures of molecules. In this thesis, improvements to apparatus designed and constructed for the purpose of measuring the temperature dependence of the Cotton-Mouton effect in gases and vapours of liquids are described. This apparatus is capable of determining the magnetic field-induced retardance at pressures up to ≈ 1000 kPa and over a temperature range of 260-500 K, and it incorporates an automated detection system offering a limit of resolution of 2×10^{-7} rad.

Measurements were performed on fifteen species: methyl fluoride, methyl bromide, and methyl iodide; acetylene; dimethyl ether, dimethyl sulfide, oxirane (ethylene oxide), furan, and thiophene; carbon dioxide, carbonyl sulfide, and carbon disulfide; ethane; pyridine; and ethylene. Reliable values for the magnetic hyperpolarizability anisotropy and, in conjunction with data from other methods, the elements of the polarizability or magnetizability tensors, and other related molecular properties, were derived and discussed for all of these species.

TABLE OF CONTENTS

	Page
CHAPTER 1 INTRODUCTION AND THEORY OF THE COTTON-MOUTON EFFECT	1
1.1 INTRODUCTION	1
1.2 THEORIES OF THE COTTON-MOUTON EFFECT	2
1.2.1 Classical statistical mechanical theories	2
1.2.2 Quantum mechanical theories	4
1.3 SOME RELEVANT ELECTRIC AND MAGNETIC PROPERTIES	6
1.3.1 The electric polarizability	6
1.3.2 The magnetizability	10
1.3.3 The second magnetic hyperpolarizability	12
1.4 DISCUSSION	14
1.5 REFERENCES	17
CHAPTER 2 PRINCIPLES AND OPERATION OF THE COTTON-MOUTON EFFECT APPARATUS	23
2.1 INTRODUCTION	23
2.2 PRINCIPLES OF THE COTTON-MOUTON EFFECT APPARATUS ..	25
2.3 INSTRUMENTATION	31
2.3.1 Apparatus	31
2.3.2 Procedures	39
2.4 REFERENCES	42
CHAPTER 3 THE MAGNETIC ANISOTROPIES OF THE METHYL HALIDES	43
3.1 INTRODUCTION	43
3.2 EXPERIMENTAL RESULTS	44

3.3	ANALYSIS AND DISCUSSION	45
3.4	REFERENCES	59
CHAPTER 4 THE MAGNETIC ANISOTROPY AND THE QUADRUPOLE MOMENT OF ACETYLENE		62
4.1	INTRODUCTION	62
4.2	EXPERIMENTAL RESULTS	62
4.3	ANALYSIS AND DISCUSSION	63
4.4	REFERENCES	75
CHAPTER 5 THE MOLECULAR POLARIZABILITIES OF DIMETHYL ETHER, DIMETHYL SULFIDE, OXIRANE, FURAN AND THIOPHENE		78
5.1	INTRODUCTION	78
5.2	EXPERIMENTAL RESULTS	79
5.3	ANALYSIS AND DISCUSSION	85
5.4	REFERENCES	103
CHAPTER 6 THE MAGNETIC ANISOTROPIES OF CARBON DIOXIDE, CARBONYL SULFIDE AND CARBON DISULFIDE		105
6.1	INTRODUCTION	105
6.2	EXPERIMENTAL RESULTS	105
6.3	ANALYSIS AND DISCUSSION	106
6.4	REFERENCES	125
CHAPTER 7 THE TEMPERATURE DEPENDENCE OF THE COTTON-MOUTON EFFECT OF ETHANE		129
7.1	INTRODUCTION	129
7.2	EXPERIMENTAL RESULTS	131
7.3	ANALYSIS AND DISCUSSION	131

7.4	REFERENCES	148
CHAPTER 8 CONCLUSIONS		151
	REFERENCES	158
APPENDIX I THE PRINCIPAL POLARIZABILITIES OF PYRIDINE		159
AI.1	INTRODUCTION	159
AI.2	EXPERIMENTAL RESULTS	159
AI.3	ANALYSIS AND DISCUSSION	160
AI.4	REFERENCES	167
APPENDIX II THE PRINCIPAL POLARIZABILITIES OF ETHYLENE		168
AII.1	INTRODUCTION	168
AII.2	EXPERIMENTAL RESULTS	168
AII.3	ANALYSIS AND DISCUSSION	169
AII.4	REFERENCES	178