Electronic State Excitations in the Water Molecule by Collisions with Low Energy Electrons

A Thesis
Presented for the Degree of
Doctor of Philosophy

by

Penny Anne Thorn BSc. (Hons.)

at

Flinders University of South Australia
Faculty of Science and Engineering
School of Chemistry Physics and Earth Sciences

14th July 2008

Contents

Summary iii

Declaration iv

Acknowledgements v

1 Introduction **1**

2 Spectroscopy of Water **9**

3 Experimental Procedures **25**

3.1 Apparatus 26

3.2 Spectral Deconvolution 36

3.3 Differential Cross Sections 39

3.4 Molecular Phase Shift Analysis Technique 43

4 Results and Discussion **46**

4.1 Preamble 46

4.2 Differential Cross Sections 47

4.3 Integral Cross Sections 63

5 Modelling Calculations **79**

5.1 Calculation Methods 80

5.2 Results of the Present Calculations 84

6 Conclusions 93

A Additional Differential Cross Section Plots and Tables 97

B Additional Integral Cross Section Plots and Table 112

Bibliography 118

Summary

This thesis reports on a series of electron scattering experiments with H_2O, made with a high resolution crossed beam spectrometer. From the results of those experiments absolute cross sections for the electronic state excitations were ultimately determined. In many cases the present work represents the first time such cross sections have been measured.

What motivated us to measure these cross sections is outlined in Chapter 1. This chapter also contains a discussion of relevant theoretical works, as well as some previous experimental investigations which were important precursors to the present study.

Chapter 2 presents a detailed description of the many previous studies on the spectroscopy of H_2O. This was a crucial part of this thesis, as the spectroscopy of H_2O underpins the interpretation of the complicated electronic structure found in the measured energy loss spectra.

In Chapter 3 we discuss the experimental apparatus and our measurement techniques and calibration procedures, including some alterations that were made during the course of the present experiments. The spectral deconvolution procedure for determining the differential cross sections and the molecular phase shift analysis technique for deriving the integral cross sections, are also described in this chapter.

Our experimentally determined cross sections are presented and discussed in Chapter 4 for the first six excited electronic states, with this discussion largely being framed in terms of a comparison to the currently available theoretical data. The cross sections for the remaining states, which could not be compared to theory, are presented in the appendices A and B.

Chapter 5 discusses the use of the present cross sections in order to calculate some parameters useful in atmospheric modelling. Finally the major findings of the present study are highlighted in Chapter 6, where recommendations are also made for future work.

Declaration

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

....

Penny A. Thorn

Acknowledgements

Firstly I would like to thank my parents, because they were the first to offer me their support and have never ceased providing it. I would also like to thank my parents, sister and grandparents for being a source of encouragement and inspiration for longer than I can remember.

The guidance of my supervisor Associate Professor Michael Brunger, throughout this project, has been invaluable. I would like to thank him for his support and encouragement and for sharing his expertise. Dr Laurence Campbell's advice and expertise were also important to the success of this project, and along with the wise counsel of Emeritus Professor Peter Teubner were greatly appreciated.

I would like to acknowledge the research group of Professor Hiroshi Tanaka at Sophia University in Japan, for the measurements they made to cross check with ours. I would also like to acknowledge Dr. Tom Rescigno and Dr. Yong-Ki Kim (deceased) for their helpful comments in regard to the theoretical calculations.

The assistance of the talented staff of the Electronics and Engineering Workshops was much appreciated. I am grateful to them for all their help maintaining the apparatus and with a variety of technical problems that I encountered along the way.

Thank you to my fellow postgraduate students for helping to make the working environment at Flinders happy and productive. For helping me to remember the other important thing in life, like how to have fun, I also have to thank all my friends.

Finally I would like to thank the Ferry Trust and the ARC Centre of Excellence for Antimatter and Matter Studies, who provided me with a scholarship. Thanks also to Flinders University for the award of a Research Student Conference Travel Grant.

Chapter 1

Introduction

The Infrared Space Observatory (ISO) of the European Space Agency (ESA) has confirmed the existence of water vapour in several galaxies including our own, and water-ice in several more. The ISO has also confirmed water-ice and vapour exists in comets [1]. Due to measurements from the ISO, the precipitable water on Mars has been determined to be 15μm, while water was also discovered in the atmospheres of the giant planets; Jupiter, Saturn, Uranus and Neptune, as well as on Titan (Saturn's largest moon) [1]. Indeed water is the 3rd most plentiful molecule in the universe [2,3], and is even present in the atmosphere of our Sun [2]. The discovery of water in so many different places is of great scientific and human interest, at least in part because water is fundamental to life on Earth.

Without water, life on Earth as we know it would not be possible. Water is an important component of the biological cell, and hence an essential part of plant and animal tissue, making up about 70% of the total mass of mammals [3]. In the Earth's atmosphere water is a very important greenhouse gas owing to it's strong absorption in the infrared (IR) spectral region, so that it absorbs significant radiation emanating from the planet's surface thereby reducing heat loss to space. As such H_2O contributes $\approx$65% to the total 33K of natural warming [4], without which Earth would be uninhabitable. The surface of the Earth is made up of more than 70% water, with its oceans being responsible for a large amount of the latitudinal distribution of heat around the Earth. This effect thus helps to create a larger inhabitable area on our planet.

Accurate cross sections for the different possible outcomes of an electron - water molecule collision, are important in improving our understanding of processes that occur wherever free electrons and water coexist. Since water is so common these scenarios of coexistence are numerous, occurring in the fields of space science, plasma physics, biophysics and in atmospheric science. For example, cross sections for electron scattering from both liquid and vaporous water are fundamental to an understanding and hence further development of plasma electrosurgical devices [3]. In addition calculations in the field of industrial plasma physics, by Tas *et al* [5], for the removal of NO_x species from a flue gas by plasma processes, required cross sections for all components of the flue gas including water vapour. The importance of accurate cross sections for electron-water collisions in modelling the effects of radiation on biological tissue (by the calculation of electron tracks) is also well known, having been summarized by Uehara *et al* [6] and Muñoz *et al* [7].

The current state of scattering theory is such that the level of agreement between calculated and measured cross sections, is quite good for many electron-atom scattering processes. As discussed by Bray *et al* [8] the convergent close-coupling (CCC) method gives very good results, when compared with available experiments, for electron scattering from both atomic hydrogen and helium atoms, as well as the alkali atoms and alkaline-earth atoms. In a more recent review Buckman and Sullivan [9] considered the general accord between theory and experiment in cross sections for electron (and also positron) scattering from atoms and molecules. They also noted that results for calculations of electron-atom scattering for many processes are quite good. Furthermore they concluded this was also the case for some light molecular species e.g. N_2. However they also highlighted the significant discrepancies that exist between theory and experiment for many polyatomic systems.

The water molecule is one target for which reliable cross sections have yet to be determined for many scattering processes. In fact as we shall see later, for some processes there is a total lack of experimental data with which to compare to the calculated values. This lack of data and an inconsistency between theory and experiment where the data does exist, is not entirely surprising since water does present some significant challenges to both theorists and experimentalists. Water's strong dipole moment of 1.8546±0.0004 D, as measured by Dyke and Muenter [10], can create major difficulties for theorists. Water can also be a problematic substance in a vacuum system and can be potentially harmful to components of an apparatus inside a vacuum chamber, due to its tendency to stick to and condense on surfaces.

The state of our knowledge on cross sections for electron collisions with H_2O was reviewed by Karwasz *et al* [11] in 2001, and more recently by Itikawa and Mason [12] in 2005. One of the objectives of Itikawa and Mason was to try and determine a set of recommended values for the cross sections, for every major electron collision process in H_2O. In attempting this, the shortcomings in the present state of knowledge for electron impact cross sections in the water molecule were clearly highlighted. Nonetheless Itikawa and Mason did produce a recommended set of cross sections for total scattering, elastic scattering, momentum transfer, rotational excitation, vibrational excitation, attachment, ionisation, some neutral dissociation channels and some radiative emission cross sections. There was, however, no data set recommended for electronic state excitations in H_2O, essentially because there were no experimentally determined absolute cross sections available for those excitations. In addition, there was little consistency in the electronic-state results from the few theoretical studies so that no data could be assembled from that work.

The present study was therefore largely concerned with measuring accurate absolute values for the electronic state excitation cross sections in H_2O, in the incident electron energy range 15eV to 50eV. It is hoped that these data will eventually help to improve the current state of electron - molecule scattering theory, as well as being useful in the fields of modelling discussed earlier where these cross sections are important input parameters. Further, as an illustration of this latter point, the cross sections determined here were used to calculate some quantities of importance in atmospheric modelling, with the eventual aim being to include these parameters in a statistical equilibrium model of Earth's ionosphere. Note that the statistical equilibrium approach was initially developed by Cartwright *et al* [13], and was implemented previously to predict the absolute population density of vibrationally excited N_2 (Campbell *et al* [14]), O_2 (Jones *et al* [15]) and NO (Cartwright *et al* [13]) over a range of altitudes. H_2O will also ultimately be included in our ionospheric model in order to calculate population densities for its dissociative excited states. The aim of that work is to improve our understanding for the role of electron-driven processes in the production of vibrationally excited OH in our atmosphere. It is known that vibrationally excited OH molecules produce the Meinel bands upon de-excitation, (Meinel [16], [17]), but the source of this vibrationally excited OH could be chemical, or electron driven, or a mixture of both. As an initial step in achieving this aim, the present thesis reports electron energy transfer rates and electron impact excitation rates calculated with the integral cross sections determined in this study. This is detailed in Chapter 5.

There have been several previous studies into electron collision induced electronic excitations in H_2O. No previous experimental study, however, has published absolute cross sections for these processes, although many experimental and theoretical studies have managed to elucidate the excited state spectroscopy of H_2O. Some of the foremost spectroscopic studies include Trajmar *et al* [18], Goddard and Hunt [19], Chutjian *et al* [20], Jureta [21] and Mota *et al* [22]. These spectroscopic studies, along with the multitude of other electron impact, photoabsorption and theoretical works, were a necessary precursor to the present study; enabling the accurate and reliable interpretation of the measured energy loss spectra. Full details and evaluations of all that work are provided in Chapter 2.

Another essential precursor to the present work was the availability of accurate elastic differential cross sections (DCSs), as they are used to put the DCSs measured in the present study on an absolute scale. This procedure is detailed in Chapter 3. Fortunately there have been quite a few studies into elastic scattering cross sections at the energies of interest to us, with the most recent experimental study being that by Cho *et al* [23] in 2004. Cho *et al* used a crossed beam spectrometer with a magnetic angle changing (MAC) device, to measure elastic DCSs for scattering angles from 10° to 180° and incident electron energies from 4eV to 50eV, with an uncertainty of typically ≈10%. One of the most recent calculations was that from Faure *et al* [24], also in 2004, who used the R-matrix method to calculate corresponding DCSs for incident electron energies up to 7eV. While this was not the energy range of interest to us, the comparison of the DCSs from Faure *et al* with those from Cho *et al* at 4eV is very good. This is particularly encouraging as previous theory at 4eV incident electron energy, being that from Varella *et al* [25], did not have a good shape agreement with any of the experimental data (including Cho *et al*). In fact the elastic DCSs calculated by Varella *et al* seemed to give some spurious structure in the angular distribution for incident electron energies of 10eV and below, while those from Okamoto *et al* [26] deviated somewhat from the experimental results at incident electron energies below about 6eV. In the energy and angular range of interest to this study the elastic cross sections of Cho *et al* [23], Shyn and Cho [27], Johnstone and Newell [28], Danjo and Nishimura [29], Okamoto *et al* [26] and Varella *et al* [25] are generally in good agreement. The results from Cho *et al*, Johnstone and Newell and Okamoto *et al* are in particularly good accord, although it still can not be said that all their results are within each others experimental uncertainty. The cross sections of Cho *et al* were chosen to normalise our data, largely because of their low uncertainty and because in many cases they represent an approximate mean of the other elastic DCS data sets. We note that this choice is largely in accord with some recent reviews of cross section data bases [30].

Several theoretical calculations for differential and integral cross sections exist in the literature for some of the lower lying electronic excitations. In particular the $\tilde{b}^3\mathrm{A}_1$ state, with an excitation energy ≈9.46eV, has received the most attention.

Here we note the integral cross section (ICS) calculations by Pritchard *et al* [31], Gil *et al* [32], Lee *et al* [33], Morgan [34] and Gorfinkiel *et al* [35]. A comparison of the results from these studies shows considerable disparity, in both magnitude and shape, between the various theories. This observation can also be generalised to the other common electronic states they considered. The extent of this disparity is somewhat surprising, as there are some significant similarities between some of these different theoretical approaches. For example four of these calculations, namely Pritchard *et al*, Gil *et al*, Lee *et al* and Morgan, were carried out in the fixed nuclei (FN) approximation at the equilibrium geometry, while Gorfinkiel *et al* used the adiabatic nuclei (AN) approximation. Pritchard *et al* and Lee *et al* also both carried out two state calculations, with Pritchard *et al* using the Schwinger multichannel method and Lee *et al* the distorted-wave approximation. Gil *et al* employed five target states within the complex Kohn variational method and like Pritchard *et al* and Lee *et al* calculated both ICS and DCS values. Finally, we note that both Morgan and Gorfinkiel *et al* made seven state R-matrix calculations of the ICSs for the $\tilde{b}^3\mathrm{A}_1$ state. All these computations are discussed in detail in Chapter 4.

Gil *et al* [32], Morgan [34] and Gorfinkiel *et al* [35] also calculated cross sections for the $\tilde{a}^3\mathrm{B}_1$, $\tilde{A}^1\mathrm{B}_1$ and $\tilde{B}^1\mathrm{A}_1$ states. In addition, Lee *et al* [33] computed cross sections for a second state with $^3\mathrm{A}_1$ symmetry, but with a higher excitation energy. Gil *et al* found their DCSs for the singlet transitions ($\tilde{A}^1\mathrm{B}_1$ and $\tilde{B}^1\mathrm{A}_1$) to be strongly forward peaked, but the triplet states were not so. Both Morgan and Gil *et al* found resonances in all their integral cross sections, while Gorfinkiel *et al* [35] calculated structureless cross sections with their AN method. These apparently conflicting results suggest that either the FN resonances are simply an artefact of the calculation and therefore not physical, or that the AN approach does not effectively treat for resonances.

The most recent calculation was performed by Kim [36], who computed ICSs for the $\tilde{A}^1\mathrm{B}_1$ state, with a scaled Born method, at incident electron energies from its threshold to 1000eV. This method involves applying a scaling factor (an accurate value for the optical oscillator strength) to the plane wave Born cross section in order to improve the accuracy of the Born cross section. This is particularly important at lower incident electron energies and this approach has been successful in other systems, but it is unfortunately only applicable to the calculation of cross sections for dipole - allowed transitions. We note that the calculation for H_2O represents the first time this technique has been used for a triatomic molecule. The $\tilde{A}^1B_1$ state ICSs from this theory were considerably smaller than most of the previously discussed theories. Indeed it is approximately 50% smaller than the unscaled Born cross section, which is of a similar magnitude to that from Gorfinkiel *et al* [35]. The scaled Born cross section from Kim is relatively featureless, with a maximum at approximately 30eV incident electron energy. Full details can again be found in Chapter 4.

Despite the paucity of data pertaining to cross sections for electronic state excitation in H_2O by electron collisions, cross sections for many other electron collision processes in H_2O have been somewhat more thoroughly studied. Some of the cross sections for these other processes can be indirectly compared to our measured cross sections, and thus provide a useful self - consistency test for our work. For example grand total cross sections (GTSs) for electron-water scattering should be equal to the sum of the integral cross sections for all the possible electron collision processes. These grand total scattering cross sections have been measured by several experimentalists, including Szmytkowski [37] and a recommended data set was compiled for them by Itikawa and Mason [12]. We were hence able to compare to these GTSs, a summation of the ICSs for all the electron collision processes for which we have values including the present measured electronic excitation integral cross sections. We can also compare the cross sections from Harb *et al* [38], who measured absolute cross sections for the production of ground state OH by electron impact on H_2O for incident electron energies from threshold to 300eV, to a subset of the present cross sections for water's dissociatively excited states. A further self-consistency check for the present ICSs is provided by the cross sections calculated by Muñoz *et al* [7]. These cross sections [7] are for in-elastic processes (ionisation plus electronic state excitation) for incident electron energies from 7.5eV to 10keV. The results from all these self - consistency checks are also presented in Chapter 4.