# ELECTRON MOMENTUM SPECTROSCOPY OF CARBON MONOXIDE AND HYDROGEN SULFIDE

by

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#### ABSTRACT

The binding energies and momentum profiles for each of the valence orbitals of CO and  $H_2S$  have been measured by high momentum resolution electron momentum spectroscopy.

The experimental momentum profiles are compared on a quantitative basis within the Target Hartree-Fock Approximation to theoretical calculations using SCF wavefunctions ranging in quality from minimal basis to Hartree-Fock limit. Calculated momentum distributions for the  $5\sigma$  orbital of CO are shown to be very basis set dependant while calculated momentum distributions of the CO  $3\sigma$ ,  $4\sigma$  and  $1\pi$  orbitals change very little with improvements in the wavefunction beyond the double-zeta level. The CO  $1\pi$  orbital is not very well described in the low momentum region even at the Hartree-Fock limit with basis set saturation including diffuse functions. While the  $4a_1$  and  $2b_2$  momentum profiles of  $H_2S$  are well described using even minimal basis calculations, diffuse functions must be included in the basis set to describe the  $2b_1$  and  $5a_1$  momentum profiles.

The experimental momentum profiles of  $H_2S$  are also compared with full ion-neutral overlap calculations incorporating correlation in the ground state and correlation and relaxation in the final ion state. These calculations are very similar to the Hartree-Fock level momentum distributions, indicating that correlation is not very important in describing the momentum profiles of  $H_2S$ .

ii

The binding energy spectra and momentum profiles of the inner valence region of both CO and  $H_2S$  are studied in detail. Peaks in the CO binding energy spectrum at 24.1 and 28.3 eV are assigned as satellites  $4\sigma$  and  $1\pi$ main lines respectively while the structure above 30 eV is shown to be predominantly due to satellites of the  $3\sigma$  orbital. The intense structure in the inner valence region of  $H_2S$  is found to arise predominantly from the  $4a_1$ orbital. The assignments of the inner valence spectra of both molecules is confirmed within experimental uncertainties by the spectroscopic sum rule.

# TABLE OF CONTENTS

Abstract	ii					
Table of contents i	v					
List of tables	vi					
List of figures vii						
List of abbreviations ix						
Acknowledgements xi						
Chapter 1. Introduction 1.1. A brief history 1.2. Applications of EMS 1.2.1. Binding energy spectra 1.2.2. Momentum distributions 1.2.3. Assignment of peaks in the binding energy spectrum	1 2 2 3 m 4					
1.3. This work1.3.1. Rationale1.3.2. Previous studies1.3.3. Plan of the thesis	6 6 8 10					
Chapter 2. Theory 1   2.1. Kinematic conditions 1   2.1.1. The determination of binding energy 1   2.1.2. The determination of momentum 1   2.2. The EMS cross section 1   2.3. Calculation of the ion-neutral overlap 1   2.3.1. Explicit calculation of the ion-neutral overlap 1   2.3.2. Target Hartree-Fock Approximation 1   2.4. Quantitative comparison of theory to experiment 2   2.5.1. SCF calculations 2   2.5.2. Types of basis functions 2   2.5.2. Types of basis functions 2   2.5.2.1. Slater type orbitals 2   2.5.3.1. Minimal basis set 2   2.5.3.2. Double zeta and split valence 2   2.5.3.3. Polarization functions 2   2.5.3.4. Diffuse functions 2   2.5.4. Inclusion of correlation 3	11 13 15 15 15 15 15 15 15 15 15 15 15 15 15					
2.6. Chemistry in momentum space	32 32 33					

.

2.6.3. Molecular density reversal	33
2.6.4. Bond oscillations	30
Chapter 3. Experimental	36
3.1. An overview	36
3.2. Primary optics system	36
3.3. Collision region	38
3.4. Secondary optics system	38
3.5 Event counting	39
3.6. Operating conditions	41
Chapter 4. Carbon Monoxide	42
4.1. Binding energy spectra	42
4.2. Momentum distributions	44
4.2.1. Basis sets for SCF wavefunctions	44
4.2.2. Comparison of SCF and experimental moment	tum
profiles	47
4.2.3. Long range momentum density maps	55
4.3. Binding energy spectra of the inner valence region	58
4.4. Momentum profiles in the inner valence region	65
Chapter 5 Hydrogen Sulfide	72
5.1 Binding energy spectra	72
5.2 Momentum distributions	74
5.2. Momentain discriptions	74
5.2.1.1. Basis sets for SCF wavefunctions	74
5.2.1.2 Correlated wavefunctions from	the
122-GTO basis	76
5.2.2. Comparison of SCF and experimental moment	tum 78
5.2.2 STO 4.21G coloulations: Effects of polarization	and
diffuse functions. Effects of polarization	02
5.2.4 Effect of correlation on the calculated momen	tum
distributions	97
5.3. The inner valence region	98
5.3.1. Previous work	98
5.3.2. Inner valence binding energy spectra	99
5.3.3. Calculated inner valence binding energy spectra	103
5.3.4. Momentum profiles of the inner valence region	108
Summary and outlook	112
References	115

.

# List of tables

4.1	Properties of SCF wavefunctions for CO 46
4.2	Vertical ionization energies (eV) of the valence shell binding energy spectrum of CO
5.1	Properties of SCF and CI wavefunctions for $H_2S$
5.2	Inner valence pole strengths, ionization energies, and coefficients from the ${}^{2}A_{1}$ CI calculation for $H_{2}S$
5.3	Inner valence pole strengths, ionization energies, and coefficients from the $^2B_1$ CI calculation for $H_2S$ 80
5.4	Inner valence pole strengths, ionization energies, and coefficients from the ${}^2B_2$ CI calculation for $H_2S$
5.5	Inner valence pole strengths, ionization energies, and coefficients from the ${}^{2}A_{2}$ CI calculation for $H_{2}S$
5.6	Vertical ionization energies (eV) of the inner valence shell binding energy spectrum of $H_2S$ 102

# List of figures

•

2.1	EMS scattering kinematics in the non-coplanar symmetric geometry $\dots$ 12
3.1	Schematic of EMS spectrometer
3.2	Typical time spectrum
4.1	Binding energy spectra of the valence shell of CO at $\phi = 0^{\circ}$ and $\phi = 8^{\circ}$
4.2	The CO $5\sigma$ orbital
4.3	The CO $1\pi$ orbital
4.4	The CO $4\sigma$ orbital
4.5	The CO $3\sigma$ orbital
4.6	Long range momentum density maps of CO57
4.7	Binding energy spectra of the inner valence region of CO
4.8	Calculated and experimental inner valence binding energy spectra of CO
4.9	Experimental momentum profiles of the inner valence region of CO
5.1	Binding energy spectra of the valence shell of $H_2S$ at $\phi=0^\circ$ and $\phi=6.5^\circ$
5.2	Experimental and calculated momentum profiles of the H <sub>2</sub> S 2b <sub>1</sub> orbital83
5.3	Experimental and calculated momentum profiles of the H <sub>2</sub> S 5a <sub>1</sub> orbital
5.4	Experimental and calculated momentum profiles of the $H_2S_{2b_2}$ orbital
5.5	Experimental and calculated momentum profiles of the $H_2S_{4a_1}$ orbital
5.6	Effect of diffuse and polarization functions on the calculated momentum distributions of the valence orbitals of $H_2S$

.

5.7	Momentum and position density maps illustrating the effect of adding diffuse sp functions to the $4-31G(*)$
	basis for $H_2S$
5.8	Binding energy spectra of the inner valence region of $H_2S$ 100
5.9	Ion-neutral overlap distributions for poles 2-15 of ${}^{2}A_{1}$ symmetry 106
5.10	Calculated and experimental inner valence binding energy spectra of $H_2S$
5.11	Experimental momentum profiles of the inner valence region of $H_2S$

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# LIST OF ABBREVIATIONS

au	-	atomic units
BES	-	binding energy spectrum
CI	-	configuration interaction
СМА	-	cylindrical mirror analyser
D	-	Debye
DZ	-	double zeta
EMS	-	electron momentum spectroscopy
eV	-	electron volt
fwhm	-	full width at half maximum
GTO	-	Gaussian type orbital
INDO	-	intermediate neglect of differential overlap
IP	-	ionization potential
LCAO	-	linear combination of atomic orbitals
MBS	-	minimal basis set
MD	-	momentum distribution
МО	-	molecular orbital
OVD	-	ion-neutral overlap distribution
PES	-	photoelectron spectroscopy
POLCI	-	polarization configuration interaction
PWIA	-	plane wave impulse approximation
SECI	-	single excitation configuration interaction
STO	-	Slater type orbital
THFA	-	target Hartree-Fock approximation
XMP	_	experimental momentum profile

ix

XPS – x-ray photoelectron spectroscopy

2ph-TDA – 2 particle-hole Tamm Dancoff Approximation

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xi

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#### **CHAPTER 1. INTRODUCTION**

Electron momentum spectroscopy (EMS), or binary (e,2e) spectroscopy, is an electron scattering technique used to investigate the electronic structure of atoms and molecules. In the (e,2e) process,

$$e_0 + M \rightarrow M^+ + e_1 + e_2$$
 (1.1)

a target atom or molecule M is ionized by a high energy electron  $\mathbf{e}_0$ , and both outgoing electrons  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are detected in coincidence. The premise of EMS is quite simple: if the momentum and energy of the incoming electron and both outgoing electrons are determined experimentally, the momentum and binding energy of the struck electron prior to ionization can be calculated. A binding energy spectrum (BES) is obtained at a given momentum by measuring the coincidence rate as a function of binding energy. If the momentum is scanned at fixed binding energy, the result is an experimental momentum profile (XMP).

#### **1.1. A BRIEF HISTORY**

Papers discussing the feasibility of determining electron momentum profiles by binary (e,2e) spectroscopy first appeared in the literature around 1968 [1-3]. The first EMS determination of a momentum profile, that of the carbon 1s orbital in a carbon film, was made in 1972 [4] at the Comitato Nazinale Energia Nucleare in Italy by Camilloni *et al.*. In 1973 Weigold *et al.* of the Flinders University of South Australia [5] reported the first resolved valence orbital momentum distributions, those of the 3s and 3p orbitals of argon. Brion

1

#### Introduction / 2

et al. (this group) at the University of British Columbia and Coplan et al. at the University of Maryland began reporting the results of EMS experiments on molecules in 1976 [6] and 1978 [7] respectively. These four groups have performed EMS experiments on many atoms and small molecules; a bibliography of the studies done before 1984 has recently been published [8]. Much of the theory was developed in the 1970's [9-12] and has been extensively reviewed [13-17]. Many general review articles discussing the results of EMS and possibilities for future work have been published [18-23].

#### **1.2. APPLICATIONS OF EMS**

The three main applications of EMS are the determination of binding energy spectra, the measurement of binding energy selected momentum profiles, and the assignment of binding energy peak origin, which is especially useful in the inner valence region.

#### 1.2.1. Binding energy spectra

The EMS technique can be used to measure binding energy spectra of both the outer and inner valence regions of atoms and molecules. The ability to determine valence binding energy spectra is not unique to EMS. Binding energy spectra can be obtained at high resolution in photoelectron spectroscopy (PES) using noble gas resonant lamp sources. The most widely used light source of this type, the HeI line, is limited to the study of the outer valence region of the spectrum by the incident photon energy of 21.22 eV. The inner valence region is accessible using X-ray photoelectron spectroscopy (XPS) and dipole (e,2e) spectroscopy<sup>\*</sup> at resolution similar to that obtained in EMS, or with monochromatized synchrotron radiation sources at higher resolution. However, EMS is the only technique currently available in which the binding energy spectrum can be obtained as a direct function of target electron momentum.

#### 1.2.2. Momentum distributions

The major advantage of EMS lies in the ability to determine experimental momentum profiles (XMPs) at any selected binding energy. Momentum profiles are also available through Compton scattering [25] and positron annihilation [26], but as these are not resolved by binding energy, they represent a sum of the momenta of all electrons in the molecule.

In the independent particle (Hartree-Fock) model, the momentum distribution of each electron is given by the square of its orbital wavefunction in momentum space [13]. Momentum and position space wavefunctions are related to each other by the Fourier transform. Thus electron momentum profiles measured by EMS can be compared directly to squared orbital wavefunctions, which in the case of gaseous targets must be spherically averaged because of the random orientation of the target molecules. The EMS technique is sensitive enough to distinguish between the predicted momentum distributions of wavefunctions of different quality and thus provides a direct experimental test of quantum

<sup>\*</sup> The dipole (e,2e) technique [24] simulates photoelectron spectroscopy and provides different information than EMS, which is also known as binary (e,2e) spectroscopy

#### Introduction / 4

mechanical calculations [13]. The comparison of the predictions of wavefunctions of different size and type to experiment momentum profiles will be considered in detail in this work.

### 1.2.3. Assignment of peaks in the binding energy spectrum

EMS provides a simple and direct method of assigning controversial bands in the molecular binding energy spectrum by comparison of the shape of the experimental momentum profile to that predicted by molecular orbital calculations. This is especially important in the inner valence region (usually beyond 1S eV binding energy) where correlation and relaxation in the ion state can cause more than one peak ('satellite peaks') to appear in the binding energy spectrum corresponding to ionization from the same initial state orbital [27,28]. If initial state correlation is not important, all satellites corresponding to a given orbital will have XMPs of the same shape [13].

The assignment of peaks in the binding energy spectrum is traditionally made in PES by comparing the observed binding energies to those calculated by Koopmans' theorem and by examining the band vibrational structure. Information on peak symmetry can also be obtained in principle by examining the variation in photoelectron intensity with ejection angle  $\theta$ . For unpolarized light this intensity  $I_i(\theta)$  is given by [29]

$$I_{i}(\theta) = \frac{\sigma_{i}}{4\pi} \left[ 1 + \frac{\beta_{i}}{2} \left( \frac{3}{2} \sin^{2} \theta - 1 \right) \right], \qquad (1.2)$$

where  $\sigma_i$  is the total photoelectron intensity for the state i. Similar equations

#### Introduction / 5

can be derived for polarized and partly polarized light sources. The asymmetry parameter  $\beta_i$  equals 2 for atomic s orbitals and varies with photoelectron energy between 2 and -1 for orbitals with higher angular momentum *l* [29]. Although *l* is not a good quantum number for molecules the asymmetry parameter reflects the relative contribution of s and p atomic orbitals to the molecular orbital. It has been proposed [30] that different states arising from ionization of the same orbital could be identified by their similar asymmetry parameters. One of the very few experiments of this type to be reported is an analysis of the  $\beta$  parameters of the structure in inner valence region of H<sub>2</sub>S [31].

Satellite structure has also been studied theoretically by configuration interaction (CI) and Green's function methods. In the configuration interaction method [32], correlated wavefunctions are calculated for each final ion state, and ideally also for the ground state. The separation energy of each CI root is obtained by subtracting the energy of the initial state from the final state. The momentum distribution can also be calculated. The Creen's function method is a perturbation approach which avoids the calculation of the ion state wavefunctions [33]. Binding energies and intensities are obtained as 'poles' and 'pole strengths' respectively of the one particle Green's function. The results of both theoretical methods are used in this thesis to help assign satellite structure.

#### 1.3. THIS WORK

In the present work the small molecules carbon monoxide and hydrogen sulfide were studied by electron momentum spectroscopy.

#### 1.3.1. Rationale

Both CO and  $H_2S$  have received considerable theoretical interest because their symmetry and small size make them good model compounds for *ab initio* calculations. Therefore a large number of theoretical calculations, including newly developed wavefunctions with properties near the Hartree-Fock limit [34], are available for comparison with the XMPs of CO and  $H_2S$ .

The dipole moment of CO has received much theoretical attention because its magnitude and sign (-0.122 D [35]) are incorrectly predicted by self-consistent field (SCF) calculations at the Hartree-Fock limit even [34, 36, 37, 38].Experimentally, the carbon end of the dipole is negative, contrary to both simple chemical intuition and Hartree-Fock limit calculations [34,36,37,38] which assign the negative end to oxygen. The correct sign is predicted only when correlation is included in the calculation [39]. Since the dipole moment of CO is not accurately described by SCF calculations, it is of interest to see if this level of calculation adequately models the CO XMPs.

The study of  $H_2S$  reported in this thesis is part of an ongoing investigation in this laboratory of the XMPs of second [40-43] and third [40,44] row hydrides at high momentum resolution. These studies, as well as previous

#### Introduction / 7

EMS studies of the second row hydrides at lower momentum resolution have shown that the intensities of the XMPs in the low momentum region are seriously underestimated even using wavefunctions of Hartree-Fock quality [6,40,41,42,43,45,46] while the theoretical description of the shape of the third row hydrides is quite good even with less accurate wavefunctions [40,47,48]. In the case of water, it was necessary to include diffuse functions and correlation in the calculation to accurately describe the experimental momentum profile [42]. Thus in this work the momentum distributions calculated using both Hartree-Fock level and correlated wavefunctions have been compared to the experimental momentum profiles of  $H_2S$ .

Both the  $H_2S$  and CO molecules display interesting structure in their inner valence binding energy spectra. PES [30,31,49,50] and dipole (e,2e) [51] experiments show the inner valence region of  $H_2S$  contains many peaks spread over at least 20 eV binding energy with no single dominant parent peak. Although Green's function [49,52] calculations predict most of this structure to be due to splitting of the innermost valence orbital, the presence of an intense outer valence satellite has recently been postulated [31] based on measurements of the photoelectron asymmetry parameter  $\beta$ . If such a satellite exists, EMS should be able to identify it by its momentum profile. The satellite structure of CO is much less intense than for  $H_2S$ , but configuration interaction [53,54,55] and Green's function [55-58] calculations have predicted the presence of relatively intense outer valence satellites. It is therefore of interest to attempt to observe the momentum profiles of these satellites experimentally and confirm their origin.

#### 1.3.2. Previous studies

Both CO and  $H_2S$  have been studied previously by electron momentum spectroscopy, but in less detail than in the present work. EMS studies of the binding energy spectra and valence momentum distributions of CO have been reported by Dey *et al.* [59] and Tossell *et al.* [60]. More recently Chornay *et al.* have compared the binding energy spectra and momentum distributions of free CO [60] and  $Cr(CO)_6$ . [61]. A study of the binding energy spectra, momentum distributions and satellite structure of  $H_2S$  was published in 1980 by Cook *et al.* [47]. A preliminary report of the same work compared the EMS binding energy spectrum to a dipole (e,2e) binding energy spectrum [51].

The conclusions of the EMS studies by Dey *et al.* (CO) [59] and Cook *et al.* (H<sub>2</sub>S) [47] are limited by the resolutions of their respective spectrometers. The energy resolution affects the ability to separate the momentum profile of one orbital or ion state from the next which is particularly important in the complex inner valence region. Good momentum resolution is also required for the comparison of theoretical momentum distributions to experimental momentum profiles at low momentum. Dey *et al.* [59] had energy resolution of 2.3-3 eV fwhm and did not report their momentum resolution (estimated to be ~0.4 au). Cook *et al.* [47] reported a momentum resolution of 0.4 au and a quite good energy resolution of 1.6 eV. The spectrometer used in the present study has an energy resolution of 1.7-1.8 eV fwhm and momentum resolution of 2.0 eV fwhm and momentum resolution of 0.1 au, comparable to that of the present work, but

#### Introduction / 9

the points in the experimental momentum profiles [60] show a wide scatter particularly for the  $1\pi$  orbital.

In addition, the comparison between experimental and calculated momentum distributions was limited in the CO study reported by Tossell *et al.* [60] and the  $H_2S$  study of Cook *et al.* [47] by the fact that each measured orbital momentum distribution was separately height normalized to theory. Procedures have been developed which enable the correct relative intensities between the different orbital momentum distributions to be established by normalization on the relative peak areas in the binding energy spectra at a given momentum [42,59]. In the present work measurement of the momentum profiles of both molecules is therefore repeated with better resolution and quantitative comparison to theory.

Dey et al. [59] and Cook et al. [47] also report limited studies of the inner valence spectra of CO and  $H_2S$  respectively. Dey et al. [59] recorded XMPs at six binding energies in the inner valence region of CO. Each XMP exhibited symmetry corresponding to ionization from the innermost  $(3\sigma)$  valence orbital. Cook et al. [47] recorded XMPs at four different binding energies in the inner valence region of  $H_2S$  and also found them to be consistent with innermost valence orbital (4a<sub>1</sub>) ionization. In both cases the momentum profiles were recorded at representative energies in the binding energy spectrum and thus do not include all the structure present. Again, the conclusions were limited by the experimental resolutions. Therefore in the present work the structure of the inner valence region of both molecules is investigated in more detail and at

higher resolution than previously reported.

## 1.3.3. Plan of the thesis

Chapter two outlines the theory of the binary (e,2e) reaction as it applies to the determination of binding energy spectra, experimental momentum profiles, and satellite origin. Various approximations for the calculation of momentum distributions from *ab initio* wavefunctions are discussed, and the general features of the basis sets used to construct these wavefunctions are outlined. The chapter concludes with a discussion of the properties of wavefunctions in momentum space. The experimental method is given in chapter three, and the results are presented in chapter four (CO) and five (H<sub>2</sub>S). In each of these last two chapters the binding energy spectra, experimental and theoretical momentum profiles, and assignment of the inner valence region are discussed in turn.

#### **CHAPTER 2. THEORY**

## 2.1. KINEMATIC CONDITIONS

The information obtained from (e,2e) experiments depends on the scattering kinematics, that is, the impact energy, the energies of the detected outgoing electrons and the angles of the detectors relative to the incident electron beam. In EMS we want to determine as directly as possible the momentum and binding energy of the struck electron by measuring the momentum and energy of the ionizing electron beam and the two outgoing electrons. The collision between the two electrons must therefore be the strongest interaction in the scattering event so that the ionization process can be considered a two body reaction between the incident and struck electrons, with the rest of the molecule simply a spectator. This is called the binary encounter approximation and is best realized by ensuring that there is a large momentum transfer between the incident and struck electrons [1].

Maximum momentum transfer is achieved using either coplanar or non-coplanar symmetric geometry (figure 2.1). The term 'symmetric' refers to the fact that the two outgoing electrons have equal energy and exit at equal polar angles  $\theta$  to the incident electron beam. High energy *asymmetric* kinematics with low momentum transfer are used in dipole (e,2e) spectroscopy to simulate photoelectron spectroscopy and to obtain absolute oscillator strengths [24]. The dipole (e,2e) experiment is not suitable for measuring electron momentum distributions.

11

Theory / 12



Figure 2.1

EMS scattering kinematics in the non-coplanar symmetric geometry

#### Theory / 13

In the coplanar symmetric geometry, both electron detectors lie on the same plane as the incident electron beam at equal and opposite angles  $\theta$ . Momentum is scanned by varying  $\theta$ . Camilloni *et al.* used this arrangement in the first determination of a momentum distribution, that of the 1s electrons in a thin carbon film [4]. This geometry is quite sensitive to the details of the reaction mechanism and thus has been used to study the range of validity of approximations used to interpret binary (e,2e) data (section 2.2) [13,62-64].

In the non-coplanar symmetric geometry (figure 2.1), the polar angle  $\theta$  is fixed (typically at  $\theta_1 = \theta_2 = 45^\circ$ ) and the relative azimuthal angle  $\phi$  is varied. This geometry is much less sensitive to the collision mechanism and is therefore the method most widely used to obtain information on electronic structure. This non-coplanar symmetric geometry was used in the experiments reported in this thesis.

The theoretical aspects of the non-coplanar symmetric (e,2e) reaction at high energy will be briefly outlined below. Further details of the theory can be found in references [9-17].

#### 2.1.1. The determination of binding energy

The (e,2e) reaction involves electron impact ionization (eq. (1.1)) where the energy conservation condition is

$$E_0 = E_1 + E_2 + B.E.$$
 (2.1)

In this equation  $E_0$  is the energy of the incident electron beam,  $E_1$  and  $E_2$  are the energies of the outgoing electrons, and B.E. is the binding energy of the ionized electron. In the symmetric non-coplanar geometry  $E_1 = E_2$ . The binding energy spectrum is scanned by fixing  $E_1$  and  $E_2$  and varying  $E_0$ .

#### 2.1.2. The determination of momentum

The momentum of the system is also conserved and therefore

$$\vec{p}_{0} = \vec{p}_{1} + \vec{p}_{2} + \vec{p}_{ion}$$
, (2.2)

where  $\vec{p}_0$  is the incident electron momentum and the two outgoing electrons have momentum  $\vec{p}_1$  and  $\vec{p}_2$ . The recoil momentum of the ion,  $\vec{p}_{ion}$ , is in the binary encounter approximation equal in magnitude and opposite in sign to the momentum ( $\vec{p}$ ) of the ionized electron prior to knockout [13]. Therefore

$$\vec{p} = -\vec{p}_{ion} = \vec{p}_1 + \vec{p}_2 - \vec{p}_0$$
 (2.3)

In the symmetric non-coplanar geometry (figure 2.1),

$$|\vec{p}| = \{(2p_1\cos\theta - p_0)^2 + (2p_1\sin\theta\sin(\phi/2))^2\}^{1/2}, (2.4)$$

where  $\theta$  is the angle between the electron beam and each of the outgoing electrons and  $\phi$  is the relative azimuthal angle between the two outgoing electrons.

Two different methods are used in this thesis to obtain experimental momentum profiles. In both cases the measured distributions represent a spherical average due to to random orientation of the gaseous target molecules. In the first method the relative azimuthal angle  $\phi$  is scanned at a fixed binding energy  $E_0$ . Both positive and negative angles are scanned to check that the distribution is symmetrical about  $\phi = 0^{\circ}$ . This method works best on well separated outer valence peaks and has the advantage that the XMPs of the most intense parts of the binding energy spectrum are recorded directly, with no time spent scanning the regions between the binding energy peaks. The second method is used where there are many overlapping peaks of low intensity (usually the inner valence region). Here the binding energy spectrum is recorded at a series of azimuthal angles  $\phi$ . Each spectrum is deconvoluted with a Gaussian peak profile in which the peak positions and widths are fixed and only the heights allowed to vary. The area of each peak is then plotted against the momentum derived from  $\phi$  and the mean binding energy to obtain the XMP. This method has the advantage that XMPs can be recorded simultaneously over the entire binding energy range and the XMPs of overlapping peaks can be separated in the deconvolution procedure.

#### 2.2. THE EMS CROSS SECTION

In atomic units, the EMS experimental cross section  $\sigma_{\text{EMS}}$  is given by [15]:

$$\sigma_{\text{EMS}} = (2\pi)^4 \frac{p_1 p_2}{p_0} \int d\Omega |T_f(p_0, p_1, p_2)|^2 .$$
(2.5)

Spherical averaging over all directions  $\int d\Omega$  is included to account for the random orientation of the gaseous target molecule. The cross section should ideally be

averaged over degenerate initial states and summed over unresolved final states, including rotational and vibrational states. It has been shown that the vibrations can be neglected if the cross section is calculated at the equilibrium molecular geometry [13,65].

The square of the scattering amplitude  $T_f(p_0, p_1, p_2)$  is the probability of a transition from the initial to the final state. The scattering amplitude must incorporate an expression for the initial state, consisting of a target molecule with wavefunction  $\Psi_0^N$  and an incident electron with wavefunction  $\chi_0$ , an expression for the final state made up of an ion state with wavefunction  $\Psi_f^{N-1}$  and two outgoing electrons ( $\chi_1$  and  $\chi_2$ ), and a transition operator  $t_f$  between the initial and final states. In Dirac bra-ket notation the transition amplitude is written:

$$T_{f}(p_{0}, p_{1}, p_{2}) = \langle \chi_{1}(p_{1}) \chi_{2}(p_{2}) \Psi_{f}^{N-1} | t_{f} | \Psi_{0}^{N} \chi_{0}(p_{0}) \rangle.$$
(2.6)

In general the electron waves  $\chi$  behave as plane waves far from the target but are distorted by the potential of the target at short range. Distorted wave expressions have been used to calculate transition amplitudes for atoms, but this is computationally difficult for molecules [13]. Instead, the electrons are treated as plane waves  $\chi = e^{ip \cdot r}$  throughout the ionization process, that is, the electron waves are considered not to be distorted by the target except at the moment of impact. This approximation has been shown experimentally to be valid for the non-coplanar symmetric geometry at high impact energy ( $E_0 \approx 1000 \text{ eV}$ ) and low momentum (below  $\approx 2$  au) [13,41]. Use of plane waves and the binary encounter approximation described in the previous section together make up the Plane Wave Impulse Approximation (PWIA) [13].

Within the PWIA, the transition operator  $t_f$  depends only on the the relative initial momentum  $\bar{k} = 1/2(\bar{p}_0 - \bar{p})$  and the relative final momentum  $\bar{k}' = 1/2(\bar{p}_1 - \bar{p}_2)$  of the interacting electrons, with the rest of the target merely a spectator to the reaction [13]. Thus transition amplitude  $T_f$  can be factored into two parts, the first an electron-electron collision amplitude and the second an ion-neutral overlap:

$$T_{f} = \langle k' | t_{f} | k \rangle \langle \vec{p} \Psi_{f}^{N-1} | \Psi_{0}^{N} \rangle .$$
 (2.7)

The square of the electron-electron collision amplitude  $\langle k' | t | k \rangle$  is given by the half-off-shell Mott scattering cross section,  $\sigma_{Mott}$  [15,66], which has a simple form in the non-coplanar symmetric geometry [15]:

$$||^{2} = \sigma_{MOTT} = \frac{1}{4\pi^{4}} + \frac{2\pi A}{(e^{2\pi A} - 1)} + \frac{1}{K^{4}},$$
 (2.8)

where

$$K^{2} = p_{0}^{2} + p_{1}^{2} - 2p_{0}p_{1}\cos\theta , \qquad (2.9)$$

and

$$A = \frac{1}{2p_1 \sin\theta \sin(\pi - \phi)}$$
(2.10)

The Mott cross section is effectively constant over the experimental range of  $\phi = -32^{\circ}$  to  $32^{\circ}$  with  $E_0 = 1200 \text{ eV} + \text{B.E.}$  and  $E_1 = E_2 = 600 \text{ eV}$  [67]. Thus in the Plane Wave Impulse Approximation the scattering amplitude  $T_f$  reduces to a

constant times the overlap between the initial and final state wavefunctions expressed in momentum space and the EMS cross section is given by

$$\sigma_{\text{EMS}} = (2\pi)^{4} \frac{p_{1}p_{2}}{p_{0}} \sigma_{\text{Mott}} \int d\Omega |\langle \bar{p}\Psi_{f}^{N-1} |\Psi_{0}^{N} \rangle|^{2}$$
(2.11)

= constant 
$$\cdot \int d\Omega |\langle \vec{p} \Psi_f^{N-1} | \Psi_0^N \rangle|^2$$
. (2.12)

Therefore the experimentally determined cross section,  $\sigma_{\rm EMS}$ , may be compared directly with calculated spherically averaged ion-neutral overlaps  $|\langle \bar{p}\Psi_{\rm f}^{\rm N-1} | \Psi_{\rm O}^{\rm N} \rangle|^2$ . In practice relative rather than absolute cross sections are measured, so theory and experiment must be normalized at one point if they are to be compared quantitatively.

## 2.3. CALCULATION OF THE ION-NEUTRAL OVERLAP

The form the ion-neutral overlap takes depends on the model used to calculate the ion and neutral wavefunctions  $\Psi_{f}^{N-1}$  and  $\Psi_{0}^{N}$ .

### 2.3.1. Explicit calculation of the ion-neutral overlap

A precise calculation of the ion-neutral overlap must allow for correlation in the ground state and both correlation and relaxation in the final ion state. In the method of configuration interaction (CI) the target ground state  $|\Psi_0^N\rangle$  is expressed as a linear combination of N-electron Slater determinants  $|\Theta_A\rangle$  where the determinants are made up of molecular orbitals  $\psi$ ,

Theory / 19

$$|\Psi_0^{\mathbf{N}}\rangle = \sum_{\mathbf{A}} \mathbf{a}_{\mathbf{A}} |\Theta_{\mathbf{A}}\rangle .$$
(2.13)

The ion wavefunction for the final state 'f' consists of a hole in orbital  $\psi_j$  coupled to the target configurations  $|\Theta_A\rangle$  with coefficient  $t_{jA}^f$ ,

$$|\Psi_{f}^{N-1}\rangle = \sum_{j A} \sum_{j A} t_{jA}^{f} \psi_{j}^{\dagger} |\Theta_{A}\rangle . \qquad (2.14)$$

If the ground and ion state wavefunctions are constructed from the same set of determinants  $|\Theta_{\lambda}\rangle$ , then the overlap is given by

$$\langle \vec{p} | \Psi_{f}^{N-1} | \Psi_{o}^{N} \rangle = \sum_{A j} \sum_{a} a_{A} t_{jA}^{F} \langle \vec{p} | \Psi_{j} \rangle$$
 (2.15)

Momentum profiles calculated incorporating ground and ion state correlation by this method are referred to in this thesis as ion-neutral overlap distributions (OVDs). Use of this term avoids confusion with the less accurate momentum distributions (MDs) calculated using the Target Hartree-Fock Approximation (section 2.3.2).

#### 2.3.2. Target Hartree-Fock Approximation

Calculation of correlated neutral and ion state wavefunctions in order to generate OVDs is difficult and expensive. Instead, in most cases the Target Hartree Fock Approximation (THFA) is invoked in the comparison of theory to experimental results. In the THFA, ground state correlation is assumed to be less important than final ion state correlation, and of course relaxation is only relevant for the ion state. The ground state is therefore expressed as a single Slater determinant, and the ion state as a linear combination of such determinants. Equation (2.15) then reduces to [13]

Theory / 20

$$\langle \vec{p}\Psi_{f}^{N-1} | \Psi_{0}^{N} \rangle = \sum_{j} t_{j0}^{F} \langle \vec{p} | \Psi_{j} \rangle = \sum_{j} t_{j0}^{F} \phi_{j}(p)$$
 (2.18)

The term  $\langle \vec{p} | \psi_j \rangle$  is simply the Fourier transform of the position space orbital wavefunction  $\psi_j(\mathbf{r})$ . It is equivalent to the momentum space orbital wavefunction  $\phi_j(\mathbf{p})$ . Therefore, the EMS cross section is

$$\sigma_{\text{EMS}} \propto \int d\Omega \sum_{j} S_{j0}^{F} |\phi_{j}(p)|^{2}$$
(2.19)

where the spectroscopic factor  $S_{j0}^{F} = (t_{j0}^{F})^{2}$  is the probability that the f<sup>th</sup> ion eigenstate contains the configuration with the hole orbital  $\phi_{j}(p)^{\dagger}$  [13].

If a single Hartree-Fock determinant of ground state molecular orbitals (with a hole in one molecular orbital) is used to represent the ion state wavefunction,  $S_{j0}^{F}$  must be unity if the hole is in molecular orbital  $\phi_{j}(p)$  and zero otherwise. In this case, called the Frozen Orbital Approximation because the ion state orbitals are unchanged from those of the ground state, the cross section reduces to

$$\sigma_{\rm EMS} \propto \int d\Omega |\phi_{\rm j}(p)|^2 \qquad (2.20)$$

where  $|\phi_j(\mathbf{p})|^2$  is the Hartree-Fock orbital momentum distribution. The effect of including correlation in the ion state wavefunction is to split the Hartree-Fock orbital into fragments, each corresponding to a different ion state  $\Psi_f^{N-1}$ , with momentum distributions given by equation 2.19 [13].

Only orbitals of the same symmetry can contribute to the sum in equation (2.19) for any final ion state  $\Psi_{f}^{N-1}$ , and in order for appreciable mixing to occur the orbitals  $\phi_{j}$  must be close in energy [13]. Thus for atomic orbitals,

or valence molecular orbitals where there are no other valence orbitals of the same symmetry, equation (2.19) reduces to

$$\sigma_{\text{EMS}} \propto \int d\Omega \ S_{j0}^{\text{F}} |\phi_{j}(p)|^{2} , \qquad (2.21)$$

and  $|\phi_j(\mathbf{p})|^2$  is referred to as the characteristic orbital. The origin of satellite peaks in the binding energy spectrum can therefore be determined by examining their XMPs, which in the THFA will have the same shape as the Hartree-Fock momentum distributions of the characteristic orbital from which the electron was ionized. In addition, the assignment can be checked by the spectroscopic sum rule [15] which requires that if all the peaks corresponding to a characteristic orbital are found experimentally, the sum of their spectroscopic factors  $\mathbf{S}_{j0}^{\mathbf{F}}$  will equal unity.

Some molecules have more than one valence orbital of the same symmetry. For example, CO has three valence orbitals of  $\sigma$  symmetry, and H<sub>2</sub>S has two valence a<sub>1</sub> orbitals. Such valence molecular orbitals may be close enough in energy to allow more than one term to appear in the summation of equation (2.19). In this situation the XMPs of these molecules would correspond not to one of these characteristic orbitals, but rather to a linear combination of characteristic orbitals. In the case where one term predominates it is possible to determine experimentally which orbital makes the dominant contribution to the observed XMP [13].

# 2.4. QUANTITATIVE COMPARISON OF THEORY TO EXPERIMENT

The Target Hartree-Fock Approximation is the interpretation used most often in comparing theory to experimental results. In using the THFA, the ion-neutral overlap is not calculated explicitly; rather, the squared spherical average of the Hartree-Fock momentum space hole orbital (characteristic orbital) is found. The spectroscopic sum rule [15] tell us that all the XMPs belonging to the same characteristic orbital should be summed if theory and experiment are to be compared on a quantitave basis. In the case of outer valence orbitals there is usually only a single hole state ( $S_{j0}^F = 1$ ), but this is often not true for inner valence orbitals where the ionization strength may be split into many poles. Instead of summing over the XMPs of all these poles for a quantitative comparison to theory, the following procedure is employed.

- 1. Binding energy spectra are recorded over the entire valence region, typically at two different azimuthal angles  $\phi$ .
- 2. The peaks in the binding energy spectrum are fitted with a Gaussian profile. In the outer valence region the peak positions are fixed at the vertical ionization energies measured by high resolution PES and the widths are given by the PES Franck-Condon envelope convoluted by the EMS experimental energy resolution. The more complex inner valence region is fitted with a multipeak profile based on both the present EMS data and any available PES and XPS measurements recorded in that region.
- 3. XMPs of each peak are recorded by one of the two methods described in section 2.1.2. Since outer valence peaks have usually been studied in detail by PES their assignment is generally straightforward. The inner valence

peaks are assigned based on the shape of their XMPs and consideration of ionization pole strengths and symmetries calculated by CI overlap or Green's function methods.

- 4. The measured XMP of each orbital is scaled at some momentum to its relative cross section determined from the binding energy spectrum recorded at the angle  $\phi$  corresponding to that momentum. The orbital relative cross section is equal to the sum of the fitted areas of all binding energy peaks assigned to that orbital. The XMPs are then on the correct relative intensity scale.
- 5. Equation (2.21) relates the calculations (which are absolute) to the experimental cross section within one undetermined constant. The calculations are therefore normalized relative to a single point on one of the calculations on one orbital. All calculations for all orbitals can then be compared quantitatively to experiment.

In addition to enabling quantitative comparisons to be made between calculations, this normalization procedure is a useful consistency check of the peak assignments. Provided the calculated momentum distributions accurately describe the experiment, the experimental relative orbital cross sections will correspond to those predicted by the calculations if the peaks are assigned correctly.

#### 2.5. WAVEFUNCTIONS

While much of chemistry deals with the properties of position space wavefunctions  $\psi(\mathbf{r})$  and their associated spatial charge distributions, in EMS the experimental results are more directly related to momentum space wavefunctions
$\phi(p)$ . The two representations contain the same information since they are related by the Fourier transform:

$$\phi(\vec{p}) = (2\pi)^{-3/2} \int e^{-i\vec{p}\cdot\vec{r}} \psi(\vec{r})d\vec{r} \qquad (2.22)$$

The Schroedinger equation can in principle be solved directly in momentum space, but the integrals involved are difficult to evaluate. Therefore the usual approach is to solve the Schroedinger equation in position space and Fourier transform the resulting wavefunctions to momentum space.

## 2.5.1. SCF calculations

The simplest *ab initio* calculations on molecules are done using the Hartree-Fock self-consistent field (SCF) method [68]. In the linear combination of atomic orbitals (LCAO) SCF method the solution to the Schrodinger equation is approximated as a single antisymmetrized Slater determinant of molecular orbitals constructed from a set of atomic orbital basis functions [68]. The results obtained in SCF calculations depend on the size and type of basis set chosen. The ideal wavefunction would contain a very large number of basis functions to adequately model the core, bonding and long range parts of the molecular charge distribution. Unfortunately, the computing time (and therefore cost) of SCF calculations increases approximately as  $n^4$  where n is the number of primitive functions [69]. The challenge is therefore to select the smallest basis which adequately models the properties of interest.

Usually basis set quality is evaluated primarily on the calculated total

## Theory / 25

energy, since energy minimization according to the Variational Theorem is the criterion normally used for convergence. However, energy minimization emphasizes the atomic cores and may not give an optimum description of the bonding and especially the long range portions of the charge distribution which are less important in determining the total energy. Therefore, in assessing the performance of a particular basis set, the predictions of experimental observables such the dipole moment and quadrupole moments and the equilibrium geometry must also be examined [70].

The Target Hartree-Fock Approximation (section 2.3.2) predicts that in the absence of ground state correlation, the experimental momentum profile observed in EMS is proportional to the spherically averaged square of the momentum space molecular orbital wavefunction. Thus EMS provides a direct method of examining the predictions of SCF wavefunctions. Momentum profiles determined by EMS are most sensitive to the low (<2 au) momentum portion of the wavefunction, which corresponds roughly to the long range charge distribution [25]. The performance of various wavefunctions for CO and  $H_2S$  will be assessed by EMS in chapters four and five. To provide a background for this assessment, the features of the main classes of wavefunctions are outlined below.

## 2.5.2. Types of basis functions

The two main types of basis functions used for atomic and molecular calculations are Slaters and Gaussians.

## 2.5.2.1. Slater type orbitals

In spherical polar coordinates, Slater type orbitals (STOs) are defined

$$x_{nlm} = N r^{n-1} e^{-\zeta r} Y_{lm}(\theta, \phi) , \qquad (2.23)$$

where  $\Psi_{lm}(\theta, \phi)$  are the spherical harmonics and the normalization constant N is defined so that

$$< x_{nlm} | x_{nlm} > = 1$$
 (2.24)

The exponents  $\zeta$  depend on n and l and are variationally determined for each atom. The main advantage of using Slater type orbitals is that they have the proper short range (cusp at the nucleus) and long range (tail) behavior for calculations on atoms. Unfortunately, integrals of STOs are difficult to evaluate. requiring much computing time.

## 2.5.2.2. Gaussian type orbitals

Integrals of Gaussian type orbitals (GTOs) are easier to calculate than those of Slater type orbitals, so GTOs are widely used in molecular orbital calculations. GTOs have the form

$$x_{nlm} = N r^{2n} e^{-\zeta r^2} Y_{lm}(\theta, \phi)$$
 (2.25)

Gaussian type orbitals do not model wavefunction tails and cusps as well as STOs. To make up for this deficiency, more Gaussian primitive functions are needed than STOs to model a wavefunction to the same level of accuracy.

Like the STOs, the exponents  $\zeta$  are chosen to minimize the SCF energy of the atom. Linear combinations of these basis functions are used to describe the molecular orbital wavefunctions with the coefficients optimized variationally. Because of the relatively large number of basis functions in a Gaussian type calculation, it is usual to constrain groups of functions to have a fixed ratio of coefficients. The individual functions are called primitives, and the resultant linear combination is called a contracted Gaussian.

# 2.5.3. Characteristics of basis sets

Basis sets of differents sizes can be built using either Slater or Gaussian type orbitals. The major classes and features of basis sets will be considered below.

## 2.5.3.1. Minimal basis set

The smallest calculations use a minimal basis set (MBS). One basis function is included for each atomic orbital. Hydrogen and helium have a single 1s orbital while second row (Li-Ne) atoms have 1s, 2s,  $2p_x$ ,  $2p_y$  and  $2p_z$ functions. In the MBS third row atoms also have 3s and  $3p_x$ ,  $3p_y$  and  $3p_z$ , functions but no 3d functions. In Slater-type calculations, each basis function consists of one Slater-type orbital. If Gaussians are used, the basis function may be a single primitive Gaussian or a linear combination (contraction) of such primitives.

The minimal basis set is quite limited in its flexibility. All atoms in the same row are represented by the same number of basis functions. As well, generally all the p-orbitals in a given atom are constrained to have the same exponents, which is unrealistic in a linear molecule such as CO where the  $p\sigma$  orbitals would be expected to be quite different from the  $p\pi$  orbitals.

## 2.5.3.2. Double zeta and split valence

One way to increase the flexibility of the basis set is to include more than one basis function per atomic orbital. If each basis function of a Slater minimal basis set is replaced by two basis functions with different exponents, the result is referred to as a double zeta basis. An equivalent size Gaussian basis would contain two contracted Gaussians per atomic orbital. A split valence basis, for example the 4-31G basis [71,72] used in this work for calculations on  $H_2S$ , has one basis function or contracted Gaussian representing each core atomic orbital and two for each valence orbital. Since core orbitals contribute to the total energy of the molecule but not very much to the description of bonding, split valence basis sets give nearly as good results as double zeta sets but require much less computing time.

## 2.5.3.3. Polarization functions

The minimal basis and double zeta basis sets do not provide a good description of polar charge distributions. For example, the hydrogen atom, which is described by s-orbitals only in these basis sets, must have a spherical charge distribution, which is not realistic when hydrogen is bonded to a more electronegative atom (such as in  $H_2O$  or  $H_2S$ ). One way to polarize the charge distribution to one side of the hydrogen atom is to add a p-orbital to the hydrogen basis set. Similarly, d and f orbitals can be added to the atomic basis sets to allow for polarization of charge. Basis sets of third row atoms (Na-Ar) commonly include d functions because the empty 3d orbitals are close in energy to the filled orbitals.

## 2.5.3.4. Diffuse functions

One area where many basis sets are lacking is in diffuse basis functions. Inclusion of these functions allows charge to be placed very far from the nucleus and helps to model the long range charge distribution, which is not well described by GTOs. These orbitals make very little contribution to the total energy and because of the energy minimization criterion normally used for convergence, they are often not included in the basis set. However, diffuse functions have been shown to be important in descriptions of electron affinities [73], proton affinities [74,75], inversion barriers [76,77,78], exterior electron densities [79,80] and momentum distributions [42,81], all of which depend on the long range charge distribution.

## 2.5.3.5. Larger basis sets

More and more basis functions can be added to a wavefunction in an effort to reach the Hartree-Fock limit. For small molecules, the Hartree-Fock limit properties can be calculated exactly by numerical methods [82], providing a standard for judging the quality of large basis sets. It is very time-consuming to choose the exponents of the s and p functions in a large basis set by optimizing each exponent individually in an atomic SCF calculation, as is done for small basis set. One way of choosing the exponents is to use an even-tempered basis set [83], where the s and p exponents,  $\zeta$ , form a geometric sequence

$$\xi_i = a\beta^i \quad (i=1,2,...,N)$$
 (2.26)

Only the parameters a and  $\beta$  need to be optimized for each atomic number and type of function (s or p). Polarization and diffuse functions are then added to complete the basis set.

The momentum distributions predicted by various wavefunctions in the above classes will be compared to the XMPs of CO and  $H_2S$  in chapters four and five. The effect of increasing the basis size, adding polarizing or diffuse functions, or using Gaussian rather than Slater basis functions will be assessed in the comparison of theory and experiment.

The SCF wavefunctions used in this thesis were obtained as position space wavefunctions (basis sets and molecular orbital coefficients) from various sources. Some were taken from the literature (the appropriate references will be given in chapters four and five). P. Bagus at IBM provided one of the CO wavefunctions (DZ+P) [84] and E.R. Davidson of Indiana University calculated the even-tempered near Hartree-Fock wavefunctions for CO and H<sub>2</sub>S [34]. Four additional H<sub>2</sub>S wavefunctions were generated as part of this work using the GAUSSIAN 76 program [85]. All wavefunctions from all sources were Fourier transformed to momentum space using the HEMS computer program developed by this group, spherically averaged and convoluted with the experimental momentum resolution for comparison to the measured XMPs.

## 2.5.4. Inclusion of correlation

As described in section 2.3, momentum distributions calculated in the Target-Hartree Fock Approximation do not include correlation effects. If correlation is included in the ground state wavefunction by the method of configuration interaction (CI), the full ion-neutral overlap (OVD, see equation 2.15) must be evaluated to predict the EMS cross section. Therefore CI wavefunctions must also be generated for the final ion state. The accuracy of the resulting OVD depends on the basis set used as well as the size of the CI expansion for both the ion and neutral wavefunctions [42,86]. An OVD calculation has been performed using a large even-tempered basis set by E.R. Davidson of Indiana University for comparison to the XMPs of  $H_2S$  [86] and will be presented in chapter 5. Similar OVD calculations have recently been reported for  $H_2O$  [42] and  $NH_3$  [43]. Such calculations allow the effect of ground and ion state correlation on the predicted momentum distribution to be assessed.

# 2.6. CHEMISTRY IN MOMENTUM SPACE

In this thesis the properties of wavefunctions in position and momentum space are explored using calculated position and momentum density maps for oriented molecules [87,88]. These maps are generated from SCF wavefunctions by computing the density of an orbital wavefunction

$$\rho(\mathbf{p}) = \phi^*(\mathbf{p})\phi(\mathbf{p}) \tag{2.27}$$

or

$$\rho(\mathbf{r}) = \psi^{\star}(\mathbf{r})\psi(\mathbf{r}) \qquad (2.28)$$

in a 100 X 100 point planar grid and interpolating contours between the points.

The properties of wavefunctions in momentum space and their relationship with Compton profiles were explored by Coulson and Duncanson in a series of articles published in the early 1940s [89]. These ideas were later extended by Epstein and Tanner [90]. Density maps in position and momentum space have also been discussed in relation to EMS momentum profiles [87]. The relationship between positon and momentum space wavefunctions can be summarized by a few simple rules [87-90]:

## 2.6.1. Preservation of symmetry

Spherical harmonics are invarient under Fourier transformation, so symmetry is preserved on going from r-space to p-space. Therefore, an orbital which has a nodal plane of symmetry in position space (such as the  $1\pi$  orbital of CO and the  $2b_1$  and  $2b_2$  orbitals of  $H_2S$ ) must retain this plane in momentum space. Inversion symmetry is automatically added (otherwise the electron would have a net motion in one direction).

## 2.6.2. Spatial reversal

A wavefunction which is spatially extended in a given direction in one space will be contracted in the same direction in the other space. This follows from the Fourier transform relationship between the two spaces, since the Fourier transform of a narrow function is a broad function. Therefore core orbitals, which are more compact in position space than valence orbitals, have broader momentum distributions than valence orbitals.

## 2.6.3. Molecular density reversal

This concept is similar to spatial reversal but applies to molecular bonding. In position space, bonding is maninfested by an increase in charge density between the bonded atoms. In momentum space, however, bonding leads to an increase of density *perpendicular* to the bond direction.

## 2.6.4. Bond oscillations

The location of the nuclei cannot be plotted directly on the momentum density maps as they can on the position density maps. However, geometry information can be inferred in the momentum density maps from bond oscillations, which arise from interferences between basis functions centered on different atoms. If the two basis functions have the same sign in position space, the momentum space wavefunction will have constructive interference at  $\vec{p} = \frac{2\pi n}{\vec{r}}$  and destructive interference at  $\vec{p} = \frac{(2n+1)\pi}{\vec{r}}$  where  $\vec{r}$  is the internuclear spacing. Interference between two functions of opposite sign shows the same pattern in reverse. Bond oscillations in momentum density maps can be complex, even for diatomic molecules, because the map reflects the contributions of all the basis functions making up the orbital, some of which have 'same sign' interference and others which have 'opposite sign' interference.

EMS experiments are typically performed on gases and the resulting XMPs represent a spherical average of the momentum density. Thus, calculated momentum densities must also be spherically averaged, obscuring some of their features. However, some symmetry information remains in the spherically averaged momentum distributions. Orbitals such as the  $1\pi$  of CO and the  $2b_1$  and  $2b_2$  of  $H_2S$ , which have a nodal plane of symmetry in position and momentum space, still have zero intensity (within experimental momentum resolution) at p=0 after spherical averaging. These orbitals are classified as 'p-type' since their momentum distributions are similar to those of p atomic orbitals. A second class of momentum distribution is 's-type', which has maximum intensity at p=0. Orbitals in this class must be totally symmetric (ie the  $3\sigma$  and  $5\sigma$  orbitals of CO and the  $4a_1$  orbital of  $H_2S$ ). It is also possible for the momentum distribution of a totally symmetric orbital to maximize at a momentum greater than zero; such distributions are classed as p-type. The  $4\sigma$  orbital of CO and the  $5a_1$  orbital of  $H_2S$  are examples of this class of

momentum distribution.

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# **CHAPTER 3. EXPERIMENTAL**

All EMS studies reported in this thesis were done on an existing symmetric non-coplanar spectrometer which has previously been described in detail [41,67,91]. The main features of the spectrometer are described briefly in this chapter.

# 3.1. AN OVERVIEW

A diagram of the EMS spectrometer in shown in figure 3.1. The electron beam is produced and focussed in the primary optics system. The electrons emerging from the collision region are sorted by energy and direction and counted in the two secondary optics systems. The spectrometer is housed in an aluminum vacuum chamber evacuated by two alkylated diphenyl ether oil diffusion pumps roughed by rotary pumps. The spectrometer is isolated from the earth's magnetic field by an external  $\mu$ -metal shield. No magnetic materials are used inside the shielded area. A system of control electronics processes the pulses from the two electron detectors, powers the spectrometer components and scans the experimental variables  $E_0$  and  $\phi$ . The spectrometer operation and data storage is controlled by a PDP11/03 computer.

# **3.2. PRIMARY OPTICS SYSTEM**

The electron beam is produced using a Cliftronics CE5AH electron gun by electrically heating a thoriated tungsten hairpin filament (F) with a DC

36



Figure 3.1 Schematic of EMS spectrometer EG - Electron Gun, F - Filament, G - Grid, A - Anode, EL - Eiznel Lens, D1,D2 - Quadrupole Deflectors, P1,P2,P3 - Spray Plates, FC - Faraday Cup, GC - Gas Cell, AIL - Asymmetric Immersion Lens, CMA - Cylindrical Mirror Analyser, CEM - Channel Electron Multiplier, RT - Rotatable Turntable (from reference [67]).

## Experimental / 38

current of 2.2 A. An accelerating potential (1200 eV plus the binding energy) is applied between the anode (A) and the filament (F), and some focussing is done by the grid (G). Further focussing inside the gun is achieved by a three element einzel lens (EL). The beam is then aligned using a beam collimator consisting of two sets of quadrupole deflectors (D1,D2). The intensity and alignment of the beam is monitored by three spray plates (P1,P2,P3) and a faraday cup (FC). The operator adjusts the voltages on the grid, einzel lens and quadrupole deflectors to maximize the current reaching the faraday cup and minimize that collected by the spray plates. The electron gun chamber is differentially pumped to protect the hot electron gun filament from reactive target gases.

# 3.3. COLLISION REGION

The sample gas is admitted by a leak valve directly to the collision region, which is enclosed in a brass cylinder (gas cell, GC). This arrangement permits the pressure in the gas cell to be about two orders of magnitude higher than that in the rest of the spectrometer. Slots in the gas cell allow passage of the incoming and outgoing electrons.

## 3.4. SECONDARY OPTICS SYSTEM

In this experiment we wish to detect two electrons, each with energy 600 eV, exiting at  $\theta = 45^{\circ}$  to the incident electron beam. A three element asymmetric immersion lens (AIL) located in each secondary optics system at this angle retards the outgoing electrons by 500 eV and directs them to the 135°

sector cylindrical mirror analysers (CMA) which are set to pass electrons with energy 100 eV. Electrons emerging from the CMA enter a single channel electron multiplier (CEM) which produces a pulse for each electron detected. One secondary optics system is kept stationery while the other sits on a turntable (RT) which can be rotated though a range of azimuthal angles from  $\phi = -35^{\circ}$  to  $35^{\circ}$ .

## 3.5. EVENT COUNTING

The two outgoing electrons must be detected in coincidence to ensure they come from the same scattering event. A single delay timing method is used for this purpose [13]. The current pulses from the two channel electron multipiers are each amplified and converted to a voltage pulse by an ORTEC 9301 fast preamplifier followed by an ORTEC 454 timing filter amplifier and an ORTEC 463 constant fraction discriminator. One pulse is then fed directly to a time to amplitude converter (ORTEC 476) as a "start" pulse while the other is delayed by passage through a length of coaxial cable and acts as a "stop" pulse. The time to amplitude converter produces a voltage pulse with height proportional to the time elapsed between the "start" and "stop" pulses. A typical pulse height distribution (also known as a time spectrum) is shown in figure 3.2. The time spectrum is sampled by two ORTEC 406A single channel analyzers which pass pulses falling within the 'COINC' and 'RAND' windows (figure 3.2) to the computer. The total number of coincidences is equal to the number of counts falling within the SCA window labelled 'COINC'. A background of accidental coincidences must be subtracted to obtain the true count rate. The size

Experimental / 40



of this background is determined by counting the number of pulses within the SCA window labelled 'RAND'. The true count rate is given by

$$N_{true} = N_{coinc} - N_{rand}/x$$
 (3.1)

where  $\mathbf{x}$  is the ratio of the widths of the random to coincidence SCA windows. The standard deviation is

$$\Delta N_{\text{true}} = \left(N_{\text{coinc}} + N_{\text{rand}}/x^2\right)^{1/2} . \qquad (3.2)$$

The standard deviation decreases as x increases, so the random window is usually made larger than the coincidence window. In this work x=8.

## **3.6. OPERATING CONDITIONS**

Both CO and  $H_2S$  were obtained from Matheson lecture bottles (99.5% purity) and used without further purification. The ambient pressure was  $<10^{-6}$  torr with no sample gas in the spectrometer and  $5\times10^{-5}$  torr with sample gas. The spectrometer was calibrated with Ar before and after the experiments with each gas. Experimental resolution was 0.15 au for momentum and 1.7 and 1.8 eV fwhm for energy for the  $H_2S$  and CO experiments respectively.

# **CHAPTER 4. CARBON MONOXIDE**

# 4.1. BINDING ENERGY SPECTRA

In the independent particle picture CO has the configuration

 $(1\sigma)^{2}(2\sigma)^{2} \qquad (3\sigma)^{2} \qquad (4\sigma)^{2}(1\pi)^{4}(5\sigma)^{2}$ core inner valence outer valence

Binding energy spectra and momentum distributions in both the outer and inner

valence regions will be discussed with reference to this picture.

Binding energy spectra recorded at the relative azimuthal angles  $\phi = 0^{\circ}$ and  $8^{\circ}$  in the binding energy range 11 to 53 eV are shown in figure 4.1. These conditions correspond to momenta of approximately 0.1 and 0.6 au respectively. The binding energy scale was calibrated using the position of the  $5\sigma$ (vertical IP = 14.01 eV) in the high resolution photoelectron spectrum peak reported by Turner et al. [92]. The Gaussian peaks shown fitted to the the three outer valence peaks in figure 4.1 have widths corresponding to the respective Franck-Condon vibrational widths reported by Turner et al. [92] convoluted with the EMS experimental energy resolution (1.8 eV). The outer valence structure is much better resolved in figure 4.1 than in the EMS binding energy spectrum reported by Dey et al. [59] where the energy resolution was 2.3 eV. Beyond 21 eV, in the inner valence region, the wide distribution of intensity indicates a breakdown of the independent particle picture of ionization. Nine Gaussian peaks are shown fitted to the inner valence region with positions and widths suggested by the intensity distribution observed in the present work



Figure 4.1 Binding energy spectra of the valence shell of CO at  $\phi=0^{\circ}$  and  $\phi=8^{\circ}$ The inset shows the inner valence region X2.

and the profile of the XPS spectrum reported by Gelius et al. [93].

The two binding energy spectra were recorded sequentially with repetitive scans alternating the values of  $\phi$ , and are presented on a common intensity scale, enabling quantitative comparisons to be made between peak intensities at the two angles. The  $5\sigma$  peak at 14.0 eV which dominates the  $\phi=0^{\circ}$  spectrum and the  $3\sigma$  peak at 38.7 eV each have lower intensity in the  $\phi=8^{\circ}$  than in the  $\phi=0^{\circ}$  spectrum, indicating they have s-type symmetry. The  $1\pi$  and  $4\sigma$  peaks at 17.0 and 19.6 eV have relatively larger cross sections at  $\phi=8^{\circ}$  than  $\phi=0^{\circ}$  and thus are of p-type symmetry. Experimental momentum profiles of these four peaks will be discussed in the next section (4.2).

Overall, the inner valence region (22-53 eV) has less intensity at  $\phi = 8^{\circ}$  than  $\phi = 0^{\circ}$ , indicating that the structure in this region is dominantly s-type. Binding energy spectra and experimental momentum profiles of the inner valence region will be discussed in sections 4.3 and 4.4 respectively.

# 4.2. MOMENTUM DISTRIBUTIONS

## 4.2.1. Basis sets for SCF wavefunctions

In this section experimental momentum profiles (XMPs) for the valence orbitals of CO are compared to spherically averaged momentum distributions (MDs) calculated using a range of *ab initio* SCF LCAO-MO wavefunctions in the Target Hartree-Fock Approximation (THFA) according to equation (2.21). These wavefunctions range in quality from minimal basis to essentially Hartree-Fock limit and include both Slater and Gaussian type basis sets. The total energies and dipole moments given by these wavefunctions are shown in table 4.1.

The wavefunctions and basis sets are:

1. MBS

This Slater-type minimal basis calculation reported by Lefebvre-Brion *et al.* [94,95] uses exponents proposed by Roothan [96].

2. DZ GTO

This Gaussian-type reported by Snyder and Basch [97] is equivalent to double zeta in quality.

3. DZ+P GTO

This basis Bagus [84] consists constructed by of two contracted Gaussian-type functions for each atomic s-orbital. three contracted Gaussian-type p-orbitals, and one d orbital ( $\xi = 1.0$ ) composed of a single primitive Gaussian function.

4. HUO STO

This Slater-type basis developed by Huo [36,37] is near Hartree-Fock limit in quality. 3s and 3d functions are included on each atom and a 4f function is added on carbon to describe the  $\pi$  orbital.

5. 136-GTO

This extended Gaussian-type wavefunction by Feller *et al.* [34] is considered to be essentially at the Hartree-Fock limit since the calculated properties are almost identical to those obtained using the Numerical Hartree-Fock method [38] (see table 4.1). The s- and p-functions are an even tempered

# Table 4.1Properties of SCF wavefunctions for CO

Wavefunction		Туре	Basis Set	Energy (au)	Dipole Moment (D)	Reference
1.	MBS	Slater	(25.10)	-112.3276	not given	[94,95]
2.	DZ GTO	Gaussian	(95,5p)/ [45,2p]	-112.6763	0.394	[97]
3.	DZ+P GTO	Gaussian	(9s,4p,td)/ [4s,3p,td]	- 122 7666	0.386	[84]
4.	Huo STO	Slater	(4s,3p,1d,1f)	-112.7860	0.274	[36,37]
5.	136-GTO	Gaussian	(19s.10p.4d.2f)/ [10s.6p.4d.2f]	- 112 . 7903	O . 266	[34]
Hartree-Fock limit			- 1 12 . 7909 <sup>a</sup>	0.265 <sup>a</sup>		
Experiment			- 113.326 <sup>b</sup>	-0.122 <sup>C</sup>		

a Numerical Hartree-Fock, reference [38]. Experimentally derived, non-relativistic energy as quoted in reference [34]. C Reference [35] Carbon Monoxide / 46

set with one additional diffuse function included of each type. Four d- and two f-functions, each consisting of a single primitive Gaussian function, are also included on each atom.

All calculations were carried out at the experimental equilibrium bond length, 2.132 au, except for DZ+P GTO (3) which was done at 2.15 au. The results of the various calculations are indicated on figures 4.2-4.5 with the numbers 1-5 and/or the acronyms as shown above, All calculated momentum distributions have been convoluted with the experimental momentum resolutions ( $\Delta p = 0.15$  au).

## 4.2.2. Comparison of SCF and experimental momentum profiles

Experimental momentum profiles (XMPs) characteristic of the  $5\sigma$ ,  $1\pi$ ,  $4\sigma$ and  $3\sigma$  orbitals are compared with spherically averaged theoretical momentum distributions (MDs) calculated using the basis sets described in section 4.2.1 in the upper panels of figures 4.2-4.5. The experimental momentum profiles were obtained by varying the azimuthal angle  $\phi$  at the fixed (sitting) binding energy indicated on each figure. The four XMPs were placed on a common intensity scale using the areas of the corresponding peaks in the  $\phi = 0^{\circ}$  and  $\phi = 8^{\circ}$ binding energy spectra shown in figure 4.1 and taking into account the assignments of the various regions of the inner valence spectrum (figure 4.7) to characteristic oribitals. This procedure will be discussed further in section 4.4. The 136-GTO calculation was normalized to experiment at the momentum (0.66 au) corresponding to  $\phi=8^{\circ}$  on the  $4\sigma$  XMP (figure 4.4).

Shown in figures 4.2-4.5 (b) and (c) are momentum and position density



(a) Comparison of experimental momentum profiles and calculated spherically averaged momentum distributions

(b) Momentum density map generated from the DZ+P wavefunction

(c) Position density map generated from the DZ+P wavefunction





- (b) Momentum density map generated from the DZ+P wavefunction
- (c) Position density map generated from the DZ+P wavefunction



(a) Comparison of experimental momentum profiles and calculated spherically averaged momentum distributions

(b) Momentum density map generated from the DZ+P wavefunction

(c) Position density map generated from the DZ+P wavefunction





(b) Momentum density map generated from the DZ+P wavefunction

(c) Position density map generated from the DZ+P wavefunction

### Carbon Monoxide / 52

maps calculated for an oriented CO molecule using the DZ+P GTO (3) basis [84]. In these maps carbon is at the origin and oxygen is at +2.15 au on the z-axis. The contours shown are 80%, 50%, 20%, 8%, 5%, 2%, 0.8%, 0.5%, and 0.2% of the maximum density of each orbital. Along the side of each map are projections of the density along the axes indicated by the dotted lines. All dimensions are in atomic units in both momentum and position space.

The momentum distributions calculated with different basis sets are quite similar to each other for each of the  $1\pi$ ,  $4\sigma$  and  $3\sigma$  orbitals with the exception of the MBS (1) calculation. The poor performance of the MBS model is not surprising in view of its very limited flexibility; this inadequacy is also reflected in the poor prediction of the total energy (table 4.1). It is interesting to note that despite the large differences in predicted energies and dipole moments very similar MDs are obtained for each of these orbitals with the other four basis sets which range in quality from double zeta (2) to near Hartree-Fock (4,5) and which use either Slater (4) or Gaussian (2,3,5) type functions.

In contrast, calculated momentum distributions for the  $5\sigma$  orbital are quite sensitive to basis set as can be seen in figure 4.2(a). The calculations give progressively narrower MDs with higher intensity at p = 0 au as the basis size increases and as the total energy decreases (table 4.1). The momentum density map orbital shown in figure 4.2(b) clearly shows the dominant s-character of the  $5\sigma$  orbital. The shoulders on the line projection on the right hand side of the map (momenta parallel to the CO bond direction) indicate the smaller contribution of p orbitals. These shoulders, which are not present in the perpendicular component of momentum are largely 'washed out' by spherical averaging and are thus not apparent in the experimental measurements. The local maxima at  $p \sim 4$  au on the momentum density map are bond oscillations (section 2.6.4).

Figure 4.3(a) shows that although  $1\pi$  theoretical MDs are in close agreement with one another (except for the MBS), the agreement of theory with experiment is not good for shape and magnitude at low momentum. Serious disagreement between theory and experiment below 0.8 au was also shown in the EMS study on CO by Dey et al. [59] which also shows correct relative normalizations. In the EMS study by Tossell et al. [60] the theory was height normalized to fit the data between p=0 and p=0.7 au, resulting in the calculation having greater intensity than experiment at momenta higher than 0.7 au. Because the  $2\pi$  orbital is the lowest unoccupied molecular orbital of CO. correlation between the  $1\pi$  and  $2\pi$  orbitals is expected to be quite important [39,98], and thus the  $1\pi$  orbital in CO is not expected to be well described by SCF level calculations. In fact singly substituted  $1\pi \rightarrow n\pi$  configurations make a large contribution to the change in magnitude and sign of the dipole moment from the SCF value in CI calculations on CO [39]. Thus the disagreement between theory and experiment for the  $1\pi$  orbital is probably not due to inadequacies of the basis sets but rather to the failure of the Hartree-Fock (SCF) description of this orbital.

The XMPs of the  $1\pi$  (figure 4.3(a)) and the  $4\sigma$  (figure 4.3(b)) orbitals have almost identical shape, but due to the degeneracy of the  $1\pi$  orbital its cross section is on average twice that of the  $4\sigma$ . The  $4\sigma$  (p-type) maximum cross section is of necessity very low compared to the 5 $\sigma$  (s-type) because the orbitals wavefunctions of both must obey the normalization condition  $4\pi \int |\psi(p)|^2 p^2 dp = 1$ . Thus p-type orbitals with their maximum intensity at p>0 have a lower maximum EMS cross section than s-type orbitals which maximize at p=0. The p-type symmetry of the  $4\sigma$  orbital can be understood by examining the position density map of figure 4.4. The charge density on carbon and oxygen corresponds to parts of the wavefunction of opposite sign separated by a nodal surface; the  $4\sigma$  orbital thus resembles an atomic p-orbital. The momentum density map shows a p-type momentum distribution with some filling in at p=0 as expected [87] from the heteronuclear nature of CO. The corresponding  $2\sigma_{11}$  orbital of nitrogen is symmetrical and thus, neglecting resolution effects, has zero cross section at p=0.

The  $3\sigma$  (figure 4.5) like the  $5\sigma$  (figure 4.2) XMP also shows s-type character but the half-width of the  $3\sigma$  XMP is much greater. The  $3\sigma$  orbital is predominantly an oxygen 2s orbital; the position density map of figure 4.5(c) shows most of the charge density in a sharp spike near the oxygen nucleus (this is clearly seen in the line projection on the right of the position density map). Since the charge density increases so steeply near the oxygen nucleus, one would expect density to occur at relatively high momentum in the momentum density map because of the Fourier transform relationship between the two representations (the spatial reversal property, section 2.6.2). This is indeed the case and results in the relatively broad s-type momentum profile for the  $3\sigma$ orbital. Looking back at the position density map for the  $5\sigma$  orbital (figure 4.2(c)) it can be seen that much of the  $5\sigma$  charge density occurs where the density contours are widely spaced, implying a small charge density gradient. This results in much more of the  $5\sigma$  momentum density being at momentum less than 0.5 au than is the case for the  $3\sigma$  orbital.

It is interesting to note that the three Gaussian-type calculations (DZ, DZ+P, 136-GTO) all have similar predicted momentum distributions for the  $3\sigma$  orbital while the Slater-type calculations (MBS, HUO STO) have higher predicted maximum cross sections.

In summary, the  $5\sigma$  orbital seems to be the most sensitive to the basis set used to calculate the momentum distribution. Slater-type and Gaussian-type basis sets give different predicted momentum distributions for the  $3\sigma$  orbital. Otherwise, the basis sets give quite similar momentum distributions at the double-zeta level or above for the  $1\pi$ ,  $4\sigma$  and  $3\sigma$  orbitals, and inclusion of polarization or diffuse functions does not seem to affect the calculated MDs. It would be interesting to examine the effect of correlation on the predicted momentum distributions, especially for the  $\pi$  orbital which is poorly described at low momentum by the SCF wavefunctions.

# 4.2.3. Long range momentum density maps

The properties of the momentum space wavefunctions of CO were discussed briefly in the last section in conjunction with the spherically averaged momentum distributions and momentum density maps of figures 4.2-4.5. Although not presently observable experimentally by EMS, the long range behaviour of momentum space wavefunctions is quite interesting. This behaviour is explored in this section using long range momentum density maps (figure 4.6).

The momentum density maps shown in figure 4.6 were calculated using the DZ+P (3) wavefunction, which was also used for the maps in figures 4.2-4.5. Eighteen contours are shown in six decades from 0.0002, 0.0005, and 0.0008 to 20, 50 and 80% of the maximum momentum density of each orbital. The CO bond direction is the (vertical) z-axis, as in figures 4.2-4.5. The lines on the top and right side of each map are projection of the density along the zand y- axes respectively and are plotted on a logarithmic scale in order to show the large variation in momentum density. All dimensions are in atomic units.

The shorter range (0-5 au) momentum density maps presented in figures 4.2-4.5 emphasize the differences between the orbital momentum densities. In contrast, the three valence sigma orbitals look quite similar to each other in the longer range (0-10 au) maps of figure 4.6, and the  $1\pi$  orbital is easily identified by its nodal plane of symmetry along the z-axis.

All four orbitals exhibit bond oscillations, although they are much weaker in the  $\pi$  than the  $\sigma$  orbitals. The adjacent maxima are, as expected, (section 2.6.4) approximately 3 au apart ( $\frac{2\pi n}{\overline{r}}$ ) in the z- (bond axis) direction. The  $5\sigma$ and  $3\sigma$  orbitals show predominantly 'same sign' interference while the antibonding  $4\sigma$  orbital exhibits predominantly 'opposite sign' interference. Since CO is heteronuclear, the  $4\sigma$  orbital is not truly antisymmetric and the oscillation minima are filled in somewhat.





Bond oscillations in a diatomic molecule can only occur in the direction of the bond axis. The nodes observed along the y axis on the sigma orbital momentum maps must arise from nodes in the position space wavefunction.

# 4.3. BINDING ENERGY SPECTRA OF THE INNER VALENCE REGION

As can be seen from figure 4.1, there is considerable low intensity structure in the inner valence binding energy spectrum beyond 22 eV in addition to the main  $3\sigma$  peak at 38.7 eV. In order to examine this region in more detail, ten binding energy spectra were recorded at azimuthal angles  $\phi = 0^{\circ}$ ,  $2^{\circ}$ , 4°, 6°, 8°, 10°, 13°, 16°, 20°, and 24° in the binding energy range 22-53 eV. These spectra are presented in figure 4.7. The spectra were recorded sequentially and repetitively so that the relative cross sections shown in the figure are correct. Total collection time was seventy minutes per point. A flat background which represents  $\sim 5\%$  of the highest points in the  $\phi = 0^{\circ}$  spectrum was subtracted off each spectrum to compensate for a small error which is believed to occur in the subtraction of the background random coincidences (section 3.5). Such a small subtraction error would not normally be noticeable, but it is detectable in this case because the experimental intensity is so weak in this part of the spectrum. Each of the ten binding energy spectra was fitted with the same nine Gaussian peak profile used in the equivalent region of the spectra shown in figure 4.1 with only the peak heights being allowed to vary. Experimental momentum profiles (XMPs) based on the variation of each of the nine peak areas with azimuthal angle  $\phi$  will be presented and discussed in section 4.4.



Figure 4.7 Binding energy spectra of the inner valence region of CO
## Carbon Monoxide / 60

Other binding energy spectra of CO previously reported in this energy region include the HeII spectra of Potts and Williams [99] and Asbrink *et al.* [100], the synchrotron radiation PES measurements of Krummacher *et al.* [101] and the XPS spectra of Gelius *et al.* [93] and Siegbahn *et al.* [102]. Vertical IPs reported in these studies are compared to the results of the present work in table 4.2. The peak assignments made in these studies, as well as the results of several theoretical calculations of the CO binding energy spectrum, are briefly reviewed here to assist in the assignment of the EMS inner valence binding energy spectrum.

The earliest study of the inner valence region of CO was the XPS spectrum reported by Siegbahn *et al.* [102]. Several broad partially resolved and unidentified bands were indicated on the spectrum below ~40 eV. However a reexamination of the experimental points suggests the presence of further structures on the high binding energy side of the main  $3\sigma$  transition at 38.3 eV even though a flat background was drawn through the points in the original work. The satellite structure of CO was not discussed by Siegbahn *et al.* [102] but three fairly intense lines in the same region of the isoelectronic molecule N<sub>2</sub> were attributed to shake-up from ionization from the  $\sigma_u$  2s orbital, which corresponds to the  $4\sigma$  orbital of CO. The XPS spectrum reported by Gelius *et al.* [93] in 1973 shows the satellite structure between 21 and 44 eV in more detail than the earlier XPS spectrum [102] but again no discussion was given.

The two HeII spectra of the inner valence region of CO quoted in table 4.2 [99,100] were both reported in 1974. In the same year Okuda and Jonathan

# Table 4.2 Vertical ionization energies (eV) of the valence shell binding energy spectrum of CO

EMS			Photoelectron Spectroscopy					
a Designation	Assignment		Hel	He(11)		Synchrotron XPS Radiation		
							мака	мдка
		This work	[92]	[99]	[ 100 ]	[101]	[ 102 ]	[93]
	50	14.01	14.01				14.5	14.0
	1π	17.03	16.91	16.91			17.2	17.0
	40	19.60	19.72	19.69			20.1	19.7
				22.7	22.73	22.9		22.0
A	40	24.1		23.4	23.38		23.7	23.6
	· ·			25.3	25.48		25.5	25.7
						27.0		
В	1#	28.3		28.1	28.09	27.9	28.0	28.0
С	30	31.6		31.8		31.4	32.0	31.9
						32.6		
D ·	30	34.1				33.7		
E	30	36.6		1		37.1	L.	36.t
F	30	38.7		37.3		38.2	38.3	38.19
G	30	41.4						
н	30	45.5		1				
J	30	49.0						

a see figure 4.7 b used for calibration of outer valence region

#### Carbon Monoxide / 62

[103] published configuration interaction INDO calculations on the  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states of CO<sup>+</sup>. Based on this study Potts and Williams [99] assigned bands of their HeII spectrum at 22.7 and 28.1 eV to final ion states of  ${}^{2}\Pi$  symmetry and those at 23.4, 25.3 and 31.8 eV to  ${}^{2}\Sigma$  symmetry. Asbrink *et al.* [100] gave a similar interpretation of their HeII spectrum but assigned the peak at 28.09 eV to  ${}^{2}\Sigma$  symmetry.

In 1977 Bagus and Viinikka [53] published a detailed theoretical study of the satellite structure of CO using configuration interaction methods. These authors constructed correlated wavefunctions for the  ${}^{2}\Sigma$  and  ${}^{2}\Pi$  states of CO<sup>+</sup> and modelled the ground state by an SCF wavefunction. It was predicted that most of the  $1\pi^{-1}$  intensity occurred in the main line at 17.0 eV, and the satellite structure observed beyond 22 eV was predominantly attributed to final state CI between the  $3\sigma$ ,  $4\sigma$  and  $5\sigma$  orbitals. A state near 24 eV was predicted to be mostly  $4\sigma^{-1}$ , and the peaks above 30 eV were considered to derive most of their intensity from  $3\sigma^{-1}$  ionization. This calculation [53] was also used in the interpretation of the EMS study of CO reported by Dey *et al.* [59] where *it*, was concluded that virtually all strength beyond 26 eV could be assigned to the  $3\sigma$  orbital based on experimental momentum profiles recorded at six binding energies between 28 and 60 eV. This EMS study [59] also reported weak unresolved states in the CO binding energy spectrum up to the limit of the data at 63 eV.

Since the CI calculation by Bagus and Viinikka [53] was published, several additional calculations of the binding energy spectrum of CO have been

## Carbon Monoxide / 63

reported using configuration interaction methods [54,55] as well many-body Green's functions methods [55-58]. Binding energy spectra generated from a selection of these calculations are shown in figure 4.8. The vertical lines in the figure represent pole strengths, except for the  $\pi$  poles which were multiplied by two to reflect the  $\pi$  orbital degeneracy. Each pole is labelled to indicate its origin and is shown convoluted with a Gaussian of fwhm 2.5 eV (the width of the main peak at 38.7 eV) to produce the spectral envelope shown. Poles of mixed origin are labelled with the orbital which makes the dominant contribution to the pole. If two orbitals make roughly equal contributions to the pole, both are indicated. No attempt was made to correct these calculated spectra for the differences in the momentum dependence of the EMS cross section for states of different symmetry. The experimental spectrum shown for comparison in figure 4.8(a) is the sum of all the binding energy spectra taken at ten different angles as shown in figure 4.7. This angle integrated spectrum shows contributions from both s- and p-type peaks and thus provides a reasonable basis for comparison with the pole strength calculations.

The general shape and structures of the calculated binding energy spectra shown in figure 4.8 are quite similar although the calculations differ in the predicted origin of some of the peaks. Notice also that spectra (b), (c), (f) and (i) predict the largest pole to be above 40 eV while experimentally it is at 38.7 eV. When comparing these spectra to experiment the predicted peak positions could be shifted 2-4 eV towards lower binding energy.

The most recent experimental study referred to in table 4.2 is the 1983



Figure 4.8 Calculated and experimental inner valence binding energy spectra of CO

(a) sum of the experimental binding energy spectra recorded at ten azimuthal angles  $\phi$  shown in figure 4.7

(b)-(e) theoretical binding energy profiles calculated using CI wavefunctions (b) ref. [53] (c) ref. [54] (d) SECI of ref. [55] (e) POLCI of ref. [55]

(f)-(i) theoretical binding energy profiles from pole strengths calculated by Green's function methods (f) extended 2ph-TDA, ref. [56] (g) extended 2ph-TDA, ref. [57], (h) 2ph-TDA, ref. [58], (i) 2ph-TDA, ref. [55]. Pole strengths shown as solid vertical lines are convoluted with Gaussians of fwhm 2.5 eV, summed and scaled (X2.5) to yield the theoretical binding energy profile (solid curve).

photoelectron spectrum of CO obtained by Krummacher *et al.* [101] using monochromatized synchrotron radiation with photon energies between 34 and 100 eV. Based on comparison with Green's function calculations [55,57] ((g) and (i) in figure 4.8) and measurement of relative cross sections Krummacher *et al.* concluded that the structure between 22 and 25 eV was due mostly to  $4\sigma$  and  $5\sigma$  ionization, and that between 25 and 30 eV to the  $(1\pi)^{-1}$  process. The structure above 30 eV was attributed mainly to the  $(3\sigma)^{-1}$  ionization process.

# 4.4. MOMENTUM PROFILES IN THE INNER VALENCE REGION

The origin of the the satellite states of CO beyond 22 eV binding energy was investigated by comparing the respective XMPs to those of the main peaks (section 4.2) and using the calculations depicted in figure 4.8 as a guide. Experimental momentum profiles were generated from the binding energy spectra shown in figure 4.7 by plotting peak area versus momentum for each of the nine deconvoluted peaks shown. The momentum was calculated for each peak on each binding energy spectrum from the angle  $\phi$  and the mean binding energy. The resulting XMPs are shown in figure 4.9. The XMPs corresponding to peaks H and J (45.5 and 49.0 binding energy) are shown summed together. The mean binding energy used in calculating the momentum (equation 2.4) and possible assignments of each XMP are shown on the figure. The square points correspond to the areas of the same peak on the  $\phi=0^{\circ}$  and 8° wide range binding energy spectra shown in figure 4.1. The error bars are the uncertainties in area given by the Gaussian fitting program. The solid lines shown are proportional to the shapes of the DZ+P GTO (3) MDs calculated for the orbitals indicated and





Solid circles correspond to the areas of the peaks indicated in the binding energy spectra of figure 4.7. Squares represent areas of the same peaks in the binding energy spectra of figure 4.1. Solid lines are fractions of the predicted momentum distribution (DZ+P) of the orbital indicated.

represent an estimated best fit to the data.

The experimental points in the XMPs shown in figure 4.9 are widely scattered and their error bars large, which is to be expected given the very low intensity of the structure in this region. The theoretical binding energy spectra shown in figure 4.8 predict states of more than one symmetry in the energy range covered by some of these XMPs. Nevertheless, the XMPs should indicate the dominant ion state contribution(s) to each peak in the binding energy spectrum. The XMPs of peaks A (24.1 eV) and B (28.3 eV) show p-type character while peaks D (34.1 ev), E (36.6 eV), F (38.7 eV) and G (41.4 eV) are s-type. The symmetry of the XMPs of peaks C and (H+J) is more open to question but they appear to have significant s-type character.

All calculated binding energy spectra (figure 4.8) predict the first satellite pole between 22 and 26 eV to be either  $4\sigma$  or a mixture of  $4\sigma$  and  $5\sigma$ . The assignment of the experimental peak at 24.1 eV (peak A) to  $4\sigma$  is consistent with the p-type distribution of its XMP (figure 4.9).

The XMP of peak B (28.3 eV) is more difficult to assign. The experimental points derived from the inner valence binding energy spectra of figure 4.7 (solid circles) indicate this XMP is p-type. A p-type symmetry implies that the experimental intensity must come from either  $1\pi$  or  $4\sigma$  ionization or both. Unfortunately, the shapes of the  $1\pi$  and  $4\sigma$  XMPs are very similar (figures 4.3 and 4.4) and therefore the origin of peak B cannot be assigned on the basis of its XMP alone. None of the calculated binding energy spectra (figure

4.8) show much intensity around 28 eV although spectra (d), (e), (g) and (i) do predict small contributions from  $1\pi$  states in this region. On this basis peak B has been tentatively assigned to the  $1\pi$  orbital. This assignment agrees with the synchrotron PES study of CO by Krummacher *et al.* [101], where the structure between 25 and 30 eV binding energy is attributed to  $1\pi$  ionization based on the variation of the partial photoionization cross section with photoelectron energy. However, the assignment of peak B to the  $1\pi$  orbital differs from the earlier EMS study by Dey *et al.* [59] of momentum distributions in the inner valence region of CO where it was concluded that all of the structure above 26 eV could be assigned to the  $3\sigma$  orbital. However, the XMP they show at 28 eV binding energy consists of only five points with large error bars, and the shape is not inconsistent with p-type symmetry. In addition, the lower energy resolution (2.3 eV fwhm) of the previous EMS study [59] might have prevented the separation a of p-type state at 28 eV from the s-type structure above 30 eV.

All the calculated binding energy spectra (figure 4.8) predict that the structure between about 32 and 45 eV is overwhelmingly due to ionization from the  $3\sigma$  orbital. Accordingly, peaks C (31.6 eV), D (34.1 eV), E (36.6 eV), F (38.7 eV) and G (41.4 eV) binding energy eV are assigned to the  $(3\sigma)^{-1}$  process. The fit of the calculated  $3\sigma$  orbital DZ+P MD to these XMPs (figure 4.0) is quite good. The  $5\sigma$  MD is also s-type but as it is much narrower than the  $3\sigma$  MD it would not adequately describe the XMPs of peaks C-J.

The XMPs of peaks H (45.5 eV) and J (49.0 eV) were summed to give the XMP shown in the lower right hand corner of figure 4.9 because the error

### Carbon Monoxide / 69

bars in each were very large. These two broad peaks were included in the fit to the binding energy spectra (figure 4.1 and 4.7) because EMS [59] and synchrotron radiation PES [101] experiments indicate states are present above 42 eV in the binding energy spectrum. However neither of the spectra [59,101] show any definitely resolved structure presumably because many low intensity states are present in this region. The calculated  $3\sigma$  MD shown with the XMP of peaks (H+J) shows that the symmetry of this region is not inconsistent with  $3\sigma$ origin although the presence of other states cannot be ruled out.

As described in chapter two, the assignment of ion states in the binding energy spectrum of CO can be checked by the spectroscopic sum rule: the spectroscopic factors of ion states arising from the same ground state orbital sum to unity and the XMPs of all the fragments of that orbital state should therefore sum to the Hartree-Fock momentum distribution (in the Target Hartree-Fock Approximation). The procedure for comparing theory and experiment on a quantitative basis has been described in section 2.4. As discussed in that section, the measured XMP of each orbital is scaled according to the relative cross section of all the structure assigned to it in the binding energy spectrum (in this case, figure 4.1). Each XMP was scaled at its maximum intensity, the  $5\sigma$  and  $3\sigma$  XMPs at  $\phi=0^{\circ}$  and the  $1\pi$  and  $4\sigma$  XMPs at  $\phi=8^{\circ}$ . The relative cross section of the outer valence peaks at 14.0, 17.0 and 19.7 eV is simply the area of the fitted Gaussian peak in the appropriate binding energy spectrum in figure 4.1. In the inner valence region peak areas were not used to determine the relative cross sections because the points in this region of the binding energy spectrum (figure 4.1) widely scattered, are giving large

uncertainties in the fitted peak areas. Instead, the relative intensities at  $\phi=0^{\circ}$ or 8° of the calculated MDs shown with each XMP (figure 4.9) was converted to a relative area. This procedure takes into account the trend of all the data points in each XMP. Thus the  $5\sigma$  XMP shown in figure 4.2(a) is scaled to the relative area of the peak at 14.0 eV in the  $\phi=0^{\circ}$  spectrum of figure 1. The  $1\pi$  XMP in figure 4.3(a) is scaled at  $\phi=8^{\circ}$  to the relative areas of the peak at 17.0 eV plus peak B at 28.3 eV. Similarly the  $4\sigma$  (figure 4.4(a)) XMP is scaled at the momentum corresponding to  $\phi=8^{\circ}$  to the sum of the areas of the peak at 19.6 eV and peak A. The  $3\sigma$  XMP of figure 4.5(a) was scaled to match the sum of the relative intensities of peaks C, D, E, F, G, H and J at  $\phi=0^{\circ}$ . Since theory and experiment are compared on a correct relative intensity scale with one undetermined constant, the 136-GTO MD was normalized to experiment on the  $4\sigma$  XMP (figure 4.4(a)) at the momentum corresponding to  $\phi=8^{\circ}$ .

The calculated MDs give a fairly good quantitative fit to the  $1\pi$  (figure 4.3(a)),  $4\sigma$  (figure 4.4(a)) and  $3\sigma$  (figure 4.5(a)) orbitals. As discussed in section 4.2.2 the  $5\sigma$  (figure 4.2(a)) MDs are quite basis set dependent so the lack of quantitative fit to this XMP is not surprising. The Green's function and CI calculations of the CO binding energy spectrum (figure 4.8) predict very little splitting of the  $5\sigma$  orbital so it is unlikely that much of the mismatch between theory and experiment is due to unassigned inner valence poles of  $5\sigma$  origin.

The fairly good quantitative fit of the MDs of the other three orbitals to the scaled XMPs (figure 4.3(a)-4.5(a)) strengthens the assignment of the inner

## Carbon Monoxide / 71

valence states. In particular, it was mentioned earlier that inner valence peak C at 31.6 eV had an XMP (figure 4.9) of rather indeterminate symmetry. Although some of the calculated binding energy spectra shown in figure 4.8 predict predominantly peaks of  $3\sigma$  origin in this region, four spectra (b,d,h,i) show  $4\sigma$  or mixed  $3\sigma$  and  $4\sigma$  poles. Therefore it is possible to assign all or part of peak C (31.6 eV) to  $4\sigma$  symmetry. However, assigning all the intensity of peak C to  $4\sigma$  would increase the relative magnitude of the  $4\sigma$  XMP shown in figure 4.4(a) by almost 30% and lower the  $3\sigma$  XMP (figure 4.5(a)) by about 10%. Clearly this is not consistent with the relative cross sections of the  $3\sigma$  and  $4\sigma$  orbitals predicted by the Hartree-Fock wavefunctions shown in figures 4.4 and 4.5. Peak C at 31.6 eV must be predominantly  $3\sigma$ .

In summary, a consideration of all the available evidence suggests that the structure at 24.1 eV in the inner valence binding energy spectrum of CO is dominantly  $4\sigma$ , that at 28.3 eV mostly  $1\pi$ , and the states beyond 30 eV have most of their intensity from  $3\sigma$  ionization.

## **CHAPTER 5. HYDROGEN SULFIDE**

# 5.1. BINDING ENERGY SPECTRA

The ground state, Hartree-Fock molecular orbital configuration of H2S is

K<sup>2</sup> L<sup>8</sup>  $(4a_1)^2$   $(2b_2)^2(5a_1)^2(2b_1)^2$ . core inner valence outer valence

Binding energy spectra for  $H_2S$  measured at azimuthal angles  $\phi$  of 0.5° and 6.5° over the binding energy range 6 to 39 eV are shown in figure 5.1. The angles correspond to momenta of approximately 0.07 and 0.54 atomic units respectively. The energy scale was calibrated with reference to the vertical ionization energy of the  $(2b_1)$  orbital as measured by PES [92]. The outer valence region (below 18 eV) was fitted with three Gaussian peaks, one for ionization from each of the  $2b_1$ ,  $5a_1$  and  $2b_2$  orbitals. The relative positions were taken from photoelectron spectroscopy [92] and the widths were obtained by convoluting the width of the PES Frank-Condon vibrational envelope [92] with the EMS experimental energy resolution (1.7 eV fwhm). All three outer valence peaks exhibit lower intensity at  $\phi = 0.5^\circ$  than at  $\phi = 6.5^\circ$ , indicating that they have 'p-type' momentum distributions. Momentum distributions of the three outer valence orbitals will be discussed in more detail in section 5.2 below.

Overall, the intensity above 18 eV is lower in the  $\phi = 6.5^{\circ}$  spectrum than at  $\phi = 0.5^{\circ}$  but of similar shape, indicating that the structure in this region can predominantly be attributed to ionization of the 4a<sub>1</sub> orbital, which has 's-type' symmetry. However, it is possible that satellites of the three outer



Figure 5.1 Binding energy spectrum of the valence shell of  $H_2S$  at  $\phi=0^\circ$ and  $\phi=6.5^\circ$ 

valence orbitals, with 'p-type' symmetry, are also present. To further investigate this possibility, additional binding energy spectra have been measured at a series of angles  $\phi$  between 0.5° and 25.5° over the entire inner valence region. These spectra and the momentum distributions derived from them at a series of inner valence binding energies are presented and discussed in section 5.3 below.

## 5.2. MOMENTUM DISTRIBUTIONS

## 5.2.1. Calculations

## 5.2.1.1. Basis sets for SCF wavefunctions

Experimental momentum profiles (XMPs) were compared to momentum distributions (MDs) calculated with a range of SCF wavefunctions using the Target Hartree-Fock Approximation. Six types of wavefunctions were examined ranging from minimal basis set to Hartree-Fock limit as follows:

1. MBS

This minimal basis Slater-type calculation of Boer and Lipscomb [104] uses one Slater-type function for each atomic orbital. A 3d function is included on sulfur.

2. 4-31G

The 4-31G basis [71,72] is split valence with each core atomic orbital represented by one contracted basis of four Gaussians while two basis functions, one a contraction of three primitive Gaussians and the other a single Gaussian, describe the valence atomic orbitals. The 4-31G basis was also used as a starting point in the construction of three additional basis sets (wavefunctions 3,4,5 below) used in the present work to explore the effects of polarization and diffuse functions in a wave function of medium complexity. All 4-31G type wavefunctions were generated as part of this work using the GAUSSIAN 76 package [85].

3. 4-31G(\*)

The 4-31G basis was augmented with a 3d function ( $\zeta = 0.65$ ) on sulfur for polarization [105].

4. 4-31G+

The 4-31G basis was augmented with diffuse sp functions on sulfur  $(\zeta_1 = 0.0405, \zeta_2 = 0.0135)$  and hydrogen  $(\zeta = 0.036)$ . The diffuse function on hydrogen and  $\zeta_1$  on sulfur are from the + basis set developed by Clark *et al.* for calculations on anions [78].

5. 4-31G(\*)+

Both 3d [105] and diffuse sp [78] functions were added to the 4-31G basis as above.

6. 122-GTO

The 122-GTO basis set [34] of Davidson was constructed from а (21s, 14p, 4d, 2f/10s, 3p, 2d)primitive Gaussian basis contracted to [12s,10p,4d,2f/6s,3p,1d]. The s and p symmetry GTO's were generated using an even-tempered basis which was energy optimized for the ground states of sulfur and hydrogen. An additional diffuse s and p function was included on each atom. Exponents for the d and f-type polarization functions of sulfur were partially optimized at the SCF level.

All calculations were carried out at the  $H_2S$  experimental geometry ( $r_{SH} = 1.328$  A,  $<_{HSH} = 92.2^{\circ}$ ) [106]. The total energies and and dipole moments calculated with these six wavefunctions are shown in table 5.1.

## 5.2.1.2. Correlated wavefunctions from the 122-GTO basis

In this study of the XMPs of  $H_2S$  extensive use has been made of CI wavefunctions calculated by Davidson of Indiana University using a 122-GTO basis [86]. This basis set and the SCF wavefunction calculated from it is described in the previous section. To explore the effect of including correlation in the ground and ion states wavefunctions on the predicted momentum distribution, Davidson constructed ion-neutral overlap distributions (OVDs) using frozen-core configuration interaction (correlated) wavefunctions for both the neutral molecule ( ${}^{1}A_{1}$ ) and the  ${}^{2}B_{1}$ ,  ${}^{2}A_{1}$  and  ${}^{2}B_{2}$  ion states. The total energy and dipole moment obtained using the CI wavefunction for the neutral molecule are shown in table 5.1. The first roots of  ${}^{2}B_{1}$ ,  ${}^{2}A_{1}$  and  ${}^{2}B_{2}$  symmetries states had energies -398.5537, -398.4456 and -398.3613 au and pole strengths 0.8432, 0.8550 and 0.8339 respectively.

The CI calculation on neutral  $H_2S$  is estimated to recover about 85% of the valence-valence correlation energy [86]. The rest of the difference between the calculated energy and the experimental energy of -400.81 eV [108] is due to the relativistic correction for the sulfur core electrons and core-core and core-valence correlation. Although it makes an important contribution to the total energy, core orbital correlation would be expected to contribute very little to the valence

Designation <sup>8</sup>	Wavefunction	Sulfur Basis Set	Hydrogen Basis Set	Energy (a.u.)	Dipole Moment (D)	Reference
1	MBS	(3s,2p,1d)	(15)	-397.8415	not given	[ 104 ]
2	4-31G	(12s,8p)/ [4s,3p]	(45)/ [26]	- 398 . 2029	1.7800	[71,72]
3	4-31G( • )	(12s,8p,td)/ [4s,3p,td]	(45)/ [26]	-398.2424	1.3115	[71,72,105]
4	4-31G+	(148,10p)/ [63,5p]	(5s,1p)/ [3s,1p]	- 398 . 2 133	1.8592	[71,72,78]
5	4-31G(*)+	{14s,10p,1d}/ [6s,5p,1d]	(5s, 1p)/ [3s, 1p]	- 398 . 2527	1.4054	[71,72,78,105]
6	122-GTO	(218,14p,4d,2f)/ [128,10p,4d,2f]	{10s,3p,2d}/ [6s,3p,1d]	-398.7191	1.0922	[34]
Hartree-Fock limit				- 398 . 7 193 <sup>6</sup>		
6c	122-G(CI)	(215,14p,4d,2f)/ [128,10p,4d,2f]	(10s,3p,2d)/ [6s,3p,1d]	- 398 . 9337 <sup>C</sup>	1.0214	(86)
Experimental				-400.81 <sup>d</sup>	1.0192	

Properties of SCF and CI wavefunctions for  $H_2S$ Table 5.1

a See figure 5.2-5.6 and text Ref. [107] Core orbitals frozen, 65% of valence-valence correlation energy is estimated to be recovered. The non-relativistic, non-vibrating total energy of HiS is estimated to be -399.42 au.[86] d Ref. [108] Ref. [109]

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Hydrogen Sulfide / 77 momentum distributions. The calculations on the ion states include a similar number of configurations and are expected to have comparable accuracy. As such these calculations are state-of-the art representations of the neutral and ion states of  $H_2S$  and thus should provide the most accurate model possible, within the plane wave impulse approximation, of the  $H_2S$  experimental momentum profiles.

To model the binding energy spectrum and momentum distributions of the inner valence region, a second CI calculation was made for the ion states of each symmetry [86], including  ${}^{2}A_{2}$  which does not have any occupied orbitals in the Hartree-Fock ground state. Within each symmetry, energies, pole strengths and OVDs were calculated for the first fifteen roots of lowest energy. The energies and pole strengths are given in tables 5.2–5.5. Also shown are the squared coefficients of the valence 122-GTO MO contributions, where the CI overlap is expressed in the SCF MO basis (ie as a linear combination of primary hole orbitals). The energies of the first roots are -398.4352, -398.5409, -398.3441 and -398.1641 au for ion states of  ${}^{2}A_{1}$ ,  ${}^{2}B_{1}$ ,  ${}^{2}B_{2}$  and  ${}^{2}A_{2}$ symmetry respectively. The 4a<sub>1</sub> OVD was generated from this second CI calculation of the  ${}^{2}A_{1}$  ion state.

## 5.2.2. Comparison of SCF and experimental momentum profiles

Measured XMP's and calculated spherically averaged MDs (solid curves) and OVDs (dotted curves) for the  $2b_1$ ,  $5a_1$ ,  $2b_2$ , and  $4a_1$  orbitals are shown in figures 5.2, 5.3, 5.4, and 5.5 respectively together with calculated density maps in both momentum and position space for oriented  $H_2S$  molecules. Table 5.2Inner valence pole strengths, ionization energies, and<br/>coefficients from the  ${}^{2}A_{1}$  CI calculation for  $H_{2}S$ 

Pole	<u>Energy (eV)</u>	<u>Pole</u> Strength	<u>C<sup>2</sup>(4a<sub>1</sub>)</u>	<u>C²(5a</u> )
2	20.69	0.0886	0.958	0.024
3	23.00	0.2884	0.991	0.008
4	23.86	0.0999	0.993	0.002
5	24.38	0.0463	0.982	0.000
6	26.04	0.0013	0.767	0.178
7	26.28	0.0103	0.981	0.013
8	26.54	0.0124	0.926	0.048
9	27.27	0.0008	0.378	0.175
10	27.57	0.0034	0.101	0.834
11	28.09	0.0247	0.992	0.001
12	28.74	0.0353	0.993	0.000
13	28.77	0.0084	0.204	0.774
14.	29.48	0.0100	0.987	0.003
15	30.53	0.0533	0.965	0.000

Table 5.3Inner valence pole strengths, ionization energies, and<br/>coefficients from the  ${}^{2}B_{1}$  CI calculation for  $H_{2}S$ 

Pole	<u>Energy (eV)</u>	<u>Pole Strength</u>	$C^{2}(2b_{1})$
2	22.56	0.0005	0.768
3	23.24	0.0001	0.526
4	24.00	0.0004	0.203
5	24.45	0.0004	0.618
6	25.10	0.0013	0.476
7	25.92	0.0003	0.687
8	26.13	0.0074	0.906
9	26.35	0.0009	0.139
10	27.31	0.0010	0.727
11	27.80	0.0028	0.981
12	28.85	0.0003	0.202
13	29.03	0.0034	0.911
14	30.06	0.0003	0.936
15	31.06	0.0011	0.526

Table 5.4Inner valence pole strengths, ionization energies, and<br/>coefficients from the  ${}^{2}B_{2}$  CI calculation for  $H_{2}S$ 

Pole	Energy (eV)	Pole Strength	$C^2(2b_2)$
2	19.69	0.0052	0.987
3	24.86	0.0009	0.003
4	26.52	0.0003	0.975
5	27.08	0.0003	0.361
6	28.15	0.0003	0.759
7	28.60	0.0016	0.980
8	28.92	0.0012	0.568
9	29.26	0.0011	0.337
10	30.11	0.0021	0.525
11	30.15	0.0001	0.073
12	30.33	0.0010	0.045
13	30.98	0.0042	0.745
14	31.06	0.0056	0.989
15	31.32	0.0001	0.001

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Table 5.5Inner valence pole strengths, ionization energies, and<br/>coefficients from the  ${}^{2}A_{2}$  CI calculation for  $H_{2}S$ 

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Pole 1	Energy (eV) 20.94	Pole Strength 0.00004
2	22.80	0.00040
3	24.86	0.00120
4	25.26	0.00058
5	26.21	0.00004
6	27.56	0.000002
7	27.80	0.00009
8	28.61	0.00025
9	28.99	0.00001
10	29.64	0.00002
11	29.86	0.00005
12	31.24	0.0001
13	31.63	0.00004
14	31.92	0.00001
15	32.64	0.00001



Experimental and calculated momentum profiles of the  $H_2S$  2b, orbital

Hydrogen Sulfide / 83



Figure 5.3

Experimental and calculated momentum profiles of the  $H_2S$  5a  $_1$  orbital



Figure 5.4 Experimental and calculated momentum profiles of the H<sub>2</sub>S 2b<sub>2</sub> orbital



Figure 5.5 Experimental and calculated momentum profiles of the  $H_2S$  4a 1 orbital

The three outer valence XMPs were measured at the respective peak binding energies with the azimuthal angle being varied from  $-32^{\circ}$  to  $32^{\circ}$ . The data points for the  $4a_1$  inner valence momentum distribution shown on figure 5.5 were obtained by summing the area of the fitted peaks at 22.4 eV and 24.1 eV (see figure 5.1) at each  $\phi$  value for a series of 11 inner valence binding energy spectra\* (see figure 8 and section 4.4 below). All four momentum distributions were placed on a common intensity scale by normalizing (at the appropriate momenta) to the respective relative peak areas for the ion states in the 6.5° binding energy spectrum (figure 5.1). For this purpose the area due to ionization from the  $4a_1$  orbital was taken to be the sum of the areas of the nine Gaussian peaks fitted between 18 and 39 eV in the  $\phi=6.5^{\circ}$  spectrum (figure 5.1b). At  $\phi=6.5^{\circ}$  the variation in momentum over the 18-39 eV energy range is negligible. This procedure assumes that all structure in this region is due to the  $4a_1^{-1}$  process and will be discussed further in section 5.3.

Also shown on figures 5.2-5.5 are the results of calculations of the spherically averaged momentum distributions using the minimal basis set wave function reported by Boer and Lipscomb [104], the GAUSSIAN 76 [85] calculation using the 4-31G( $^{\circ}$ ) basis [71,72,105], the Hartree-Fock limit (122-GTO) [34] and the CI overlap (122-G(CI)) [86] calculations. The instrumental resolution (0.15 au) was folded into all calculations. The calculations were scaled to experiment by normalizing the 122-GTO Hartree-Fock limit calculation, which is indistinguishable from the 122-G(CI), on the highest point of the 2b<sub>1</sub> orbital. All

<sup>\*</sup> This procedure was limited to the 22-24 eV region because of the variation of momentum with binding energy over the wide range of the inner valence binding energy spectrum at values of  $\phi$  less than 3°.

other experimental and calculated points for all four orbitals can then be compared on an absolute basis, relative to this single point normalization.

Beside each momentum distribution are two sets of momentum density and position (charge) density maps for the indicated planes of an oriented  $H_2S$ molecule. These maps were generated from the 122-GTO Hartree-Fock limit and the Boer and Lipscomb minimal basis set wave functions respectively. The contours shown are at 80%, 50%, 20%, 8%, 5%, 2%, 0.8%, 0.5%, and 0.2% of the maximum density of the 122-GTO Hartree-Fock limit calculations for each orbital. The same absolute contours are retained in the Boer and Lipscomb MBS maps to facilitate a direct comparison of the two wavefunctions. Projections of the density along the axes indicated by the dotted lines are plotted at the side of the maps. All dimensions are in atomic units in both momentum and position space.

Considering first the comparison of the SCF calculations (the 122-G(CI) calculation will be discussed in section 5.2.4) with the measured momentum profiles it can be seen that the 125-GTO Hartree-Fock limit calculation fits the data quite well for all four orbitals and much better than the minimal basis set calculation of Boer and Lipscomb or the split valence 4-31G(\*) calculation. For the outer three orbitals, the latter two wavefunctions place the maximum at too large a momentum and underestimate the experimental intensity at low momentum. This discrepancy is largest for the  $2b_1$  orbital.

Although the 122-GTO Hartree-Fock limit calculation fits the data quite

well, the calculation is still slightly lower than the experimental points below 0.5 au, particularly for the  $5a_1$  and  $2b_2$  orbitals. This discrepancy is not nearly as large as that found for the corresponding orbitals of  $H_2O$  [41,42] at the Hartree-Fock limit. These observations confirm the conclusions arising from the earlier EMS study by Cook *et al.* in that better agreement with experiment is obtained for the shape of the momentum distributions of  $H_2S$  than for  $H_2O$  using theory at or near the Hartree-Fock limit [47]. Better description at the Hartree-Fock level of the XMPs of third row hydrides than their second row analogs has also been demonstrated in EMS studies of NH<sub>3</sub> [6,43]. PH<sub>3</sub> [48], HF [40], and HCl [40].

The differences between the MBS and 122-GTO calculations may be better understood by examining the position and momentum density maps also shown on figures 5.2-5.5. Starting with the 2b<sub>1</sub> orbital, where the differences between the predictions of the two wavefunctions is the greatest, it can be seen that the 122-GTO Hartree-Fock limit calculation is much more *spatially* diffuse than the MBS. Diffuse functions were included in the 122-GTO calculation (see section 5.2.1.2) to accurately model the long-range behaviour of the wavefunction in position space. Such diffuse functions have been found to be especially important in describing the outer valence orbital momentum distributions of  $H_2O$ [42] and  $NH_3$  [43] as well as the exterior electron densities [79,80] of the outer valence orbitals of  $H_2S$  (2b<sub>1</sub>),  $H_2O$  (1b<sub>1</sub>), and  $NH_3$  (2a<sub>1</sub>). In momentum space the 122-GTO calculation is correspondingly more compact than the MBS as would be expected from the 'spatial reversal' property of the Fourier transform (section 2.6.2). The plane of symmetry is retained on going from position to momentum space as described in section 2.6.1. For this reason the non-bonding  $2b_1$  orbital, which is essentially an atomic-like 3p-orbital on sulfur, is of the same qualitative shape in momentum space, and when spherically averaged, gives a momentum distribution with a minimum at the origin.

Since spherical harmonics are invariant under the Fourier transform (section 2.6.1), two lobes separated by a node are present on each side of the origin in both the position and momentum space representations of the  $2b_1$ orbital. The position of the secondary momentum lobe maximum, at about 4 au, is analagous to that calculated for argon using a Hartree-Fock wavefunction [67]. While the secondary lobes are quite prominant in the position density map (figure 5.2), they are of low intensity in the momentum density map, indicating that most of the momentum density is concentrated in the first lobe. Notice also the charge density is more concentrated in the first lobe in the MBS position map than the 122-GTO, possibly because the MBS wavefunction density overemphasizes the core in position space. On going to momentum space, the second lobe has more density in the MBS representation than the 122-GTO, as if the position space features have been turned 'inside out' in momentum space. Unfortunately the secondary lobes would be too weak to be seen in the spherically averaged wavefunction on a linear intensity scale, but their relative importance can be estimated using the normalization condition. Since  $4\pi \int |\psi(p)|^2 p^2 dp = 1$ , the lobes at large momentum make a considerable contribution to the normalization. Thus the MBS MD has a lower maximum cross section than the 122-GTO at least in part because its secondary lobes are relatively larger in momentum space. Experimentally the observation of nodes and

lobes at large p would be complicated not only because of low intensity but also because of the effects of plane wave distortion expected at large momentum under the presently used symmetric non-coplanar kinematics [13].

The  $5a_1$  orbital (figure 5.3), which can be thought of as the 'angle-forming' bond between the p-orbital on sulfur and the two hydrogen s-orbitals, also shows the Hartree-Fock limit orbital as being more diffuse in position space than the minimal basis set orbital. Although this orbital has  $a_1$  symmetry, its charge distribution is that of a sulfur 3p orbital, distorted slightly due to contributions from the hydrogen 1s orbitals. The momentum distribution is therefore p-type, with some filling in of the minimum at p=0. Beyond  $p\approx 2$  the momentum maps become more complex. In addition to the secondary lobes mentioned before, the momentum density exhibits bond oscillations (section 2.6.4).

The  $2b_2$  orbital (figure 5.4) is also a sulfur-hydrogen bonding orbital. The four theoretical momentum distributions are more in agreement with each other than for the outer two orbitals, and this agreement is reflected in the general similarity of the 122-GTO and MBS density maps. The momentum distribution is 'p-type' because the nodal plane of symmetry is preserved in momentum space. Again, the H-S bonding is manifested in the momentum maps as bond oscillations similar to the situation in the  $5a_1$  bonding orbital (figure 5.3). In contrast the essentially non-bonding  $2b_1$  orbital (figure 5.2) does not show bond oscillations.

The  $4a_1$  orbital (figure 5.5) is largely non-bonding sulfur 3s in character.

The momentum distribution is thus s-type, with some bonding implied by the position density contours and also by the oscillations in the momentum density map beyond p=2.0 au. The maps and also the momentum distributions predicted using the two wave functions are quite similar indicating that these features of this largely atomic-like orbital are already quite well described by the minimal basis set.

In summary, the XMPs of the  $2b_2$  and  $4a_1$  orbitals are quite well described by all three levels of calculation, while the the  $2b_1$  and  $5a_1$  MDs are more basis set dependant. The major difference between the minimal basis and Hartree-Fock limit calculations is the larger spatial extent of the 122-GTO  $2b_1$ and  $5a_1$  orbitals in position space. This leads to more contracted orbitals in momentum space for the 122-GTO Hartree-Fock limit calculations. Bonding in the inner three valence orbitals is manifested in the momentum space maps as bond oscillations.

# 5.2.3. STO 4-31G calculations: Effects of polarization and diffuse functions

To further explore the charactersitics of basis sets in momentum space at the SCF level, some additional calculations were done using the Gaussian 76 program developed by Pople and coworkers [85]. STO 4-31G was chosen as a test basis since it is widely used and incorporates some flexibility but is not so large as to be prohibitively expensive to use on larger molecules. As described in section 5.2.1, calculations were done at the experimental geometry using STO 4-31G alone, and with added bonding d (polarization) and/or diffuse sp functions.

Momentum distributions from the four calculations (STO 4-31G, STO 4-31G( $^{\circ}$ ), STO 4-31G+, and STO 4-31G( $^{\circ}$ )+) are shown compared to experiment in figure 5.6. The normalization is identical to that of figures 5.2 to 5.5 so the calculations can be compared directly. Although the 4-31G( $^{\circ}$ )+ and 4-31G+ wavefunctions give an overall agreement with the XMPs of comparable quality to that given by the 122-GTO and 122-G(CI) calculations (figures 5.2-5.5), it should be noted that the total energies and dipole moments obtained with the STO 4-31G type wavefunctions are quite poor as shown in table 5.1.

All four 4-31G type calculations give similar MDs for the  $2b_2$  and  $4a_1$  orbitals. For the outer two orbitals, inclusion of diffuse sp functions (4-31G+ and 4-31G(\*)+) gives MDs in good agreement with the XMPs. Calculations without diffuse functions, on the other hand, (4-31G and 4-31G(\*)), have  $p_{max}$  at too high a momentum and too low a maximum momentum cross section for the  $2b_1$  and  $5a_1$  orbitals. Although inclusion of polarizing d functions (4-31G(\*) and 4-31G(\*)+) somewhat improves the calculated total energy and dipole moment (table 5.1), polarization makes very little difference to the momentum distributions (compare 2 with 3 and 4 with 5 on figure 5.6) as has been noted earlier by Cook *et al.* using different basis sets [47].

Momentum and position density difference maps ([4-31G(\*)+] - [4-31G(\*)])were generated for the 2b<sub>1</sub> and 5a<sub>1</sub> orbitals to illustrate the effect of adding diffuse sp functions to the 4-31G(\*) wavefunction. These are shown in figure 5.7. Regions where the 4-31G(\*)+ calculation has more density than the 4-31G(\*) have solid contours, and dashed lines indicate regions of negative density



Figure 5.6 Effect of diffuse and polarization functions on the calculated momentum distributions of the valence orbitals of H<sub>2</sub>S

difference. The lines along the top and right side of the maps indicate the density difference along the indicated axis.

The momentum density difference maps of the  $2b_1$  and  $5a_1$  orbitals (figure 5.7, left hand side) show in two dimensions what the spherically averaged MDs indicate in one dimension: momentum density increases at low momentum at the expense of density at higher momentum when diffuse sp function are added to the basis set. The effect of adding diffuse functions on the position density is quite simple for the  $2b_1$  orbital: the charge density increases beyond r=2 au and decreases closer to the nucleus. Thus the diffuse functions improve the description of the tail of the atomic-like  $2b_1$  orbital. The  $5a_1$  position density difference map is more complex. The charge density increases far from the molecule, but it also increases between the atoms. Thus the addition of diffuse functions changes the description of not only the long range but also the bonding portion of this orbital.

Although the fit of the calculated momentum distributions to the data is quite good when the calculation includes diffuse functions, it must be remembered that these calculations give total energies and dipole moments which are far inferior to those given by the Hartree-Fock limit wavefunction. The quality of a wavefunction cannot be assessed solely on the basis of its predicted momentum distribution. A good universal wavefunction should calculate sufficiently accurate values of properties in all chemically important regions of phase space. However, inclusion of diffuse functions in a calculation at this level does dramatically improve the description of the momentum distribution and also gives a slight


Figure 5.7 Momentum and position density maps illustrating the effect of adding diffuse sp functions to the  $4-31G(^*)$  basis for  $H_2S$ Contours are at  $\pm 80$ ,  $\pm 40$ ,  $\pm 8$ ,  $\pm 4$ ,  $\pm .8$ ,  $\pm .4$ ,  $\pm .08$  and  $\pm .04\%$  of the maximum density difference. All dimensions are in atomic units.

improvement to the calculated values of the total energy and dipole moment. These simple model calculations also suggest that it is the outer spatial region (ie the long range tail) of valence orbitals which primarily determines the momentum distribution observed in EMS.

# 5.2.4. Effect of correlation on the calculated momentum distributions

Now that the momentum distributions of SCF wavefunctions have been examined, the effect of inclusion of correlation on the momentum distribution will be explored. The calculated spherically averaged OVDs obtained from the overlap of correlated 122-G(CI) wavefunctions of the neutral molecule (section 5.2.1.2) and ion are shown as dashed curves on the left hand panels of figures 5.2-5.5. For purpose of comparison with the MDs calculated with SCF wavefunctions (solid curves, section 5.2.1.1) the three outer valence OVDs have been renormalized to unity although their predicted pole strengths are 0.843, 0.855 and 0.834 respectively. The 4a<sub>1</sub> OVD was generated by summing the OVDs calculated for roots 2-15 of the fifteen root  ${}^{2}A_{1}$  calculation (root 1 corresponds to the 5a<sub>1</sub> orbital) weighted by their respective poles strengths. This 4a<sub>1</sub> OVD was also renormalized to unity consistent with the three outer valence orbitals.

Contrary to the case of water, where the OVDs improve the fit to the data quite dramatically [42], the inclusion of correlation in  $H_2S$  shifts the OVD only very slightly compared to the 122-GTO MD even though the energy and dipole moment improve (see table 5.1). It appears that electron correlation is very much less important in determining the momentum distributions of the

valence orbitals of  $H_2S$  than it is for the second row analogue,  $H_2O$ .

It is clear that the 122-GTO wave function gives the best description of total energy, dipole moment, and momentum distributions at the SCF level. While inclusion of correlation improves the total energy and dipole moment the effect on the predicted momentum distribution is minimal.

#### 5.3. THE INNER VALENCE REGION

#### 5.3.1. Previous work

The inner valence binding energy spectrum of  $H_2S$  was first recorded by Siegbahn *et al.* [102] using X-ray photoelectron spectroscopy (XPS) with a Mg Ka photon source but no recognition or discussion of inner valence structure was given at the time. The first detailed experimental observations of the inner valence region of the binding energy spectrum of  $H_2S$  were reported by Cook *et al.* [47,48] using low momentum resolution EMS and indicated the presence of numerous prominent peaks. Additional evidence for such many-body structures has also come from ultraviolet PES studies using using HeII [49,50] and synchrotron [30,31] light sources. In contrast to water, in which the 2a<sub>1</sub> band consists of a large main peak at 32.2 eV and a tail of less intense satellites extending up to about 40 eV [41,42], these studies of  $H_2S$  show that the inner valence region consists of at least seven peaks located at energies above 19 eV and with no clear parent. The earlier, low resolution EMS study of  $H_2S$  [47] reported momentum distributions at four different binding energies in the inner valence region. Each momentum distribution was found to exhibit s-type symmetry corresponding to ionization from the 4a<sub>1</sub> orbital [47]. However, from PES measurements of the binding energy spectrum and asymmetry parameters  $\beta$  using synchrotron radiation at low photon energies (40-70 eV), Adam *et al.* [31] have concluded that there is a significant contribution from an outer valence satellite ('p-type') between 22 and 23 eV binding energy.

# 5.3.2. Inner valence binding energy spectra

To examine this region in detail, eleven inner valence binding energy spectra were recorded from 18 to 39 eV at  $\phi = 0.5^{\circ}$ , 2.0°, 3.5°, 5.0°, 6.5°, 8.0°, 9.5°, 12.5°, 15.5°, 20.5°, and 25.5° respectively. The eleven spectra were recorded sequentially with a dwell time of thirty seconds per point. This procedure was repeated and signal averaging carried out until the total collection time was eighty minutes per point. As a result, the the angle resolved binding energy spectra shown in figure 5.8 have the correct relative intensity relationship to each other and can be used to generate momentum distributions at selected binding energies throughout the range.

In order to provide an initial analysis of the states present at an optimum signal to noise ratio, all eleven spectra were summed (figure 5.10(a)). Nine Gaussian peaks, each of 1.9 eV fwhm, were found to give a good fit to this angular integrated spectrum. This nine peak profile was then fitted to the



Figure 5.8 Binding energy spectra of the inner valence region of  $H_2S$ 

individual spectra at each azimuthal angle  $\phi$  (figure 5.8) with the peak positions and widths fixed and only the individual heights allowed to vary. A comparison between the present results for the inner valence binding energy spectrum and other EMS and PES studies is shown in table 5.6. In comparing the various different experiments it should be noted that the different peak widths quoted are essentially due to the large differences in experimental energy resolution.

The peak at 19.6 eV was originally ascribed to a nitrogen impurity when it was first seen by Siegbahn *et al.* using low resolution XPS [102], but its existence as part of the  $H_2S$  spectrum was predicted by Chipman [110] and confirmed by both the previous low resolution EMS study [48] and also by the more recent PES study using synchrotron radiation at medium resolution [31].

The structure in the inner valence region observed in the present EMS work generally corresponds quite well to that reported in the EMS study of Cook *et al.* [47,48] and also to that reported by Adam *et al.* [31] when the large differences in energy resolution are considered (see table 5.2). However, Adam *et al.* [31] do not report structure beyond 31 eV whereas the EMS studies [47,48] show structures continuing up to at least 38 eV. It should however be noted that the PES spectra shown by Adam *et al.* [31] were obtained at a photon energy of only 40 eV. Since this is quite near to threshold, particularly for the higher many-body states between 31 and 38 eV, the form of the partial photoionization cross section for the  $4a_1^{-1}$  process in  $H_2S$  [52,111] will result in these states showing very low cross sections. An added complication in the hv = 40 eV spectrum reported by Adam *et al.* [31] is the steeply rising

# Table 5.6

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Vertical ionization energies (eV) of the inner valence shell binding energy spectrum of  $H_2S$ 

	PES		EMS	
Hell	Hell	Synchrotron radiation		
Ref. [49]	Ref. [50]	Ref. [31]	ref. [47]	This work
		19.6	19.4	19.6
22.0	22.1	22.0	22.0	
	22.7	22.54		22.4
	23.0	23.05		
23.3	23.3	× 23.31	23.4	
		23.57		
		23.72		
		23.98		24.1
		24.5		
		26.7	27.0	26.9
		28.4	29.0	28.8
		29.6		
		31.0	31.0	30.5
			33.0	32.7
				34.9
				37.4

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background as the binding energy increases (ie the electron kinetic energy decreases towards zero). As such the base line cannot definitively be assigned and the choice shown precludes observation of any structures at higher binding energy. Similarily, the background in the XPS spectrum [102] is ill-defined and arbitrarily assigned in the original work. In EMS on the other hand there can be no sloping backgrounds. An alternative re-interpretation of both the PES [31] and the XPS [102] spectra with different estimates of the background contributions could well indicate more higher energy structures than were originally identified.

## 5.3.3. Calculated inner valence binding energy spectra

The origin of this inner valence ionization structrure has been studied theoretically by configuration interaction [86] and many-body Green's function [49] The results of these calculations will be considered in assigning the EMS inner valence structure.

As described in section 5.2.1, fifteen poles were generated in a 122-G(CI) overlap calculation by Davidson [86] for ion states of each symmetry for comparison to the present work. Of these, the first poles of  ${}^{2}A_{1}$ ,  ${}^{2}B_{1}$  and  ${}^{2}B_{2}$  symmetry correspond to the outer valence  $5a_{1}$ ,  $2b_{1}$  and  $2b_{2}$  peaks respectively and will not be considered further. It can be seen from tables 5.3-5.5 that all the poles of  ${}^{2}B_{1}$ ,  ${}^{2}B_{2}$  and  ${}^{2}A_{2}$  origin have poles strengths (S<sup>2</sup>) less than 0.01. Thus no single satellite of these symmetries is predicted to be prominent in the inner valence region. The squared CI overlap coefficients (C<sup>2</sup>) of the  $2b_{1}$ 

and  $2b_2$  Hartree-Fock orbitals (tables 5.3 and 5.4) are much less than unity for many roots, indicating that initial state correlation contributes to the appearance of these outer valence satellites. The  ${}^2A_2$  roots (table 5.5) are very small since no orbitals of this symmetry are occupied in the Hartree-Fock ground state. Any roots in the CI overlap of this symmetry must therefore arise from initial state correlation.

The momentum distributions of the poles of  ${}^{2}B_{1}$ ,  ${}^{2}B_{2}$  and  ${}^{2}A_{2}$  origin must be p-type by symmetry. As shown in section 5.2, the 5a<sub>1</sub> orbital has a p-type XMP and the 4a<sub>1</sub> orbital an s-type XMP. Even in the absence of ground state correlation it is possible for these two characteristic  ${}^{2}A_{1}$  orbitals to mix (see equation (2.19)). When initial state correlation is included, as in this work, higher Hartree-Fock orbitals can also contribute. Thus the  ${}^{2}A_{1}$  poles which dominate the calculated inner valence binding energy spectrum (see S<sup>2</sup> table 5.2) are not necessarily s-type.

To investigate the symmetry of the  ${}^{2}A_{1}$  poles, spherically averaged overlap distributions (OVDs) were generated for poles 2-15 of  ${}^{2}A_{1}$  symmetry. These are shown in figure 5.9. Poles 2 to 8, 11, 12, 14, and 15 all have very similar OVDs of highly dominant  $4a_{1}$  ('s-type') character. In particular, the calculation predicts that there are no 'p-type' poles of  ${}^{2}A_{1}$  symmetry between 19 and 26 eV. However, the present 122-G(CI) calculation does indicate that  ${}^{2}A_{1}$  satellites of 'p-type' character are expected in the region 27-29 eV. Poles 10 and 13 evidently have significant 'p-type' components in their OVDs as can be seen from their large  $5a_{1}$  character (see C<sup>2</sup>( $5a_{1}$ ) values in table 5.2). Pole 9

shows a complex shape and an examination of the 122-G(CI) overlap coefficients shows large  $6a_1$  and  $7a_1$  contributions. These three poles, like all the poles of  ${}^2B_1$ ,  ${}^2B_2$  and  ${}^2A_2$  symmetries, have pole strengths less than 0.02 and thus make small contributions to the binding energy spectra.

The binding energy spectrum predicted by the 122-G(CI) calculation is shown in figure 5.10(b). All the calculated poles listed in tables 5.2-5.5 were convoluted with the estimated  $4a_1$  single pole experimental width, 1.9 eV, to generate the upper curve of figure 5.10(b). A second binding energy spectrum was calculated using only s-type  ${}^2A_1$  poles (omitting poles 9, 10 and 13 of  ${}^2A_1$  symmetry). Those poles are indicated by the legend '1' in figure 5.10(b) and their convoluted spectrum is the lower line. The shaded area in figure 5.10(b) is therefore the calculated contribution of p-type states to the H<sub>2</sub>S inner valence binding energy spectrum.

Also shown in figure 5.10(c) for comparison is the 2ph-TDA Green's function calculation of Domcke *et al.* [49] using a (12s9p2d1f/4s1p) basis convoluted with the same experimental width of 1.9 eV. Only poles with strength greater than .01 are included. The peak positions and intensities given by the Green's function calculation vary somewhat with the basis chosen (see figure 3 of reference [49]); the particular basis shown in figure 5.10(c) has been selected because it is closest in size to the basis used in the present 122-G(CI) overlap calculation. The experimental binding energy spectrum shown in figure 5.10(a) is the sum of the the inner valence region binding energy spectra recorded at eleven azimuthal angles  $\phi$  (figure 5.8).



Figure 5.9 Ion-neutral overlap distributions for poles 2-15 of <sup>2</sup>A<sub>1</sub> symmetry





(a) sum of the experimental binding energy spectra recorded at eleven azimuthal angles  $\phi$  shown in figure 8; from figure 1; (b) and (c) theoretical binding energy profiles determined from pole strengths calculated using the 122-G(CI) wavefunction [86] and Green's function (12s,9p,2d,1f/4s,1p) basis [49] respectively. Pole strengths are shown as solid vertical lines and are convoluted with an experimental width of 1.9 eV fwhm.

Although the 122-G(CI) (figure 5.10(b)) calculation does not extend beyond a binding energy of 32 eV, it reproduces the experimental spectral shape quite well including the minimum near 26 eV, lower intensity peak at about 20 eV, the asymmetric peak between 21 and 26 eV and the lower broad peak between 26 and 32 eV. The Green's function calculation (figure 5.10(c)), although it does not reproduce the shape of the experimental section as well as the CI overlap, confirms that there is considerable structure at higher energies up to at least 36 eV. Both calculations underestimate the relative intensity of the poles at higher binding energy.

Figure 5.10(b) shows that below 26 eV the 122-G(CI) calculation predicts the  $H_2S$  inner valence binding energy spectrum to be dominated by four poles of  ${}^2A_1$  origin with s-type symmetry. Above 26 eV binding energy the situation is not as simple. Although the three largest poles (at 28.09, 28.74 and 30.53 eV) are s-type  ${}^2A_1$ , the three p-type  ${}^2A_1$  poles and the many  ${}^2B_1$ ,  ${}^2B_2$  and  ${}^2A_2$ poles sum to make up about 25% of the predicted intensity in this region. (shaded part of figure 5.10b). Thus based on this calculation the momentum distributions of  $H_2S$  above 26 eV binding energy would be expected to be dominantly s-type, with some p-type contributions.

#### 5.3.4. Momentum profiles of the inner valence region

Experimental momentum profiles were generated from the binding energy spectra shown in figure 5.8 by plotting peak area versus momentum for each of the nine deconvoluted peaks shown. The momentum was calculated for each peak on each binding energy spectrum from the angle  $\phi$  and the mean binding energy. The resulting XMPs are shown in figure 5.11 The error bars are the uncertainties in area given by the Gaussian fitting program.

Clearly all nine peaks exhibit a predominantly 's-type' momentum distribution. The solid line shown on each momentum distribution in figure 5.11 is the 122-GTO Hartree-Fock limit 4a, orbital momentum distribution, normalized according the the relative areas in the  $\phi = 0.5^{\circ}$  binding energy spectrum of figure 5.1 (square points). Only s-type states will effectively contribute at the momenta corresponding to this angle. The overall fit is remarkably good in each case. In particular peak 2 at 22.4 eV is clearly s-type, contrary to the assignment of Adam et al. of two peaks in the photoelectron spectrum between 22 and 23 eV outer valence satellites, based on measurements of the photoelectron as asymmetry parameter  $\beta$  [31]. The prediction of the 122-G(CI) calculation (section 5.3.2) that the structure below 26 eV is essentially all from  $4a_1$  ionization is supported by the shape of the momentum distributions at 19.6, 22.4 and 24.1 eV binding energy shown in figure 5.11. The XMPs recorded above 26 eV (figure 5.11) are consistent with s-type symmetry, although small p-type contributions as predicted by the 122-G(CI) calculation cannot be ruled out, especially for peaks 4 (26.9 eV) and 7 (32.7 eV). Overall, however, within the statistical precision of the data (figure 5.11) all other measured momentum profiles in the inner valence region exhibit overwhelming s-type character, suggesting they are predominantly from 4a<sub>1</sub> ionization.

In the quantitative comparison of the XMPs to theory (section 5.2.2), the





Solid circles correspond to the areas the peaks indicated in the binding energy spectra shown in figure 5.8. Open squares represent areas of the same peaks in the binding energy spectra of figure 5.1. Solid lines are fractions of the predicted momentum distribution (122-GTO) of the  $4a_1$  orbital.

 $4a_1$  XMP was normalized assuming that all structure above 18 eV could be assigned to  $4a_1$  ionization. The  $2b_1$ ,  $5a_1$  and  $2b_2$  XMPs were normalized assuming that the entire strengths of these three orbitals were contained in their outer valence lines. The quantitative fit of the SCF calculations to theory is quite good, confirming this assignment of the H<sub>2</sub>S binding energy spectrum.

## SUMMARY AND OUTLOOK

In this thesis the valence binding energy spectra and momentum profiles of CO and  $H_2S$  have been examined in detail. In this section the main results will be summarized and future improvements to the experiment will be considered briefly.

Consideration of the XMPs of CO and  $H_2S$  has led to the assessment of momentum distributions calculated using different levels of theory. At the SCF level, it was found that the predicted momentum distributions for the two outermost orbitals of  $H_2S$  were very sensitive to basis set quality. The calculated momentum distributions of these orbitals as well as the calculated position and momentum density maps demonstrated clearly that diffuse functions, which describe the long range charge distribution, are very important in accurately modelling the  $H_2S_{2b_1}$  and  $5a_1$  experimental momentum profiles. The XMPs of the 2b\_2 and 4a\_1 orbitals of  $H_2S$  were well modelled by all basis sets tested of double zeta quality or better, indicating that diffuse functions are much less important in the description of these two orbitals. Calculations using a split valence basis set demonstrated that inclusion of polarizing d functions in the basis set does not improve the  $H_2S$  momentum distributions. Unlike the case for  $\rm H_2O,$  inclusion of correlation in the calculation of ion-neutral overlaps of  $\rm H_2S$ does not significantly change the calculated momentum distribution from that predicted using a Hartree-Fock limit wavefunction.

The predicted momentum distributions of the CO valence orbitals, with

112

the exception of the  $5\sigma$  orbital, were found to be rather insensitive to basis set quality beyond the double zeta level. The predicted momentum distributions for the CO  $1\pi$  orbital underestimated the experimental intensity in the low momentum region of the  $1\pi$  XMP. Since all calculations at and beyond the double zeta level predicted similar momentum distributions for the  $1\pi$  orbital, this discrepancy is probably not due to a deficiencies in the basis set but rather to a failure of the SCF description of this orbital. In the future it is hoped that full ion-neutral overlap distributions will be calculated at least for the  $1\pi$  orbital in order to explore the effect of correlation on the  $1\pi$  momentum distribution.

The experimental momentum profiles of the inner valence region of both molecules were investigated in great detail. Both molecules were shown to have many binding energy peaks in this region corresponding mostly to ionization from the innermost valence orbital. No experimental evidence was found for any significant outer valence satellites in the inner valence region of  $H_2S$ . The predicted existence of satellites of two of the outer valence orbitals in the inner valence orbitals.

It was shown in this work that EMS is well suited the observation and assignment of the inner valence structure of molecules. However, many improvements can be made in this direction. Since inner valence features are quite weak, the data acquisition rate was very low in these studies. Even after four weeks of scanning the inner valence region of each molecule, the scatter of the data was still large, and the generated momentum distributions had large error bars. Much better assignment of inner valence structure could be made if

/ 113

the experimental count rate could be improved. In addition, the calculated inner valence binding energy spectra show that many states are expected in this region which cannot be resolved by the present instrument.

Work is underway in this laboratory to improve both the EMS experimental count rate and energy resolution. A new spectrometer is currently under construction which features position sensitive electron detection. This will allow all angular correlations to be detected simulataneously without the need to scan  $\phi$ . Currently the experimental energy resolution is limited by the energy spread of the electron beam produced by the hot tungsten filament and the resolution of the cylindrical mirror analysers (~1% of the pass energy). Decreasing the analyser pass energy decreases the analyser transmission efficiency, but with the increased intensity obtained by position sensitive detection this tradeoff should still lead to better data. In addition, the feasibility of using GaAs electron sources which emit electrons at room temperature is being studied.

Finally, position and momentum density maps of oriented CO and  $H_2S$  molecules were discussed extensively in this work. These maps are useful in demonstrating the features of the momentum space wavefunctions and showing how they relate to the position space charge distribution and the experimental momentum profiles. These investigations suggest that even more detailed information could be obtained in the future if EMS measurements were to be made on oriented molecules.

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