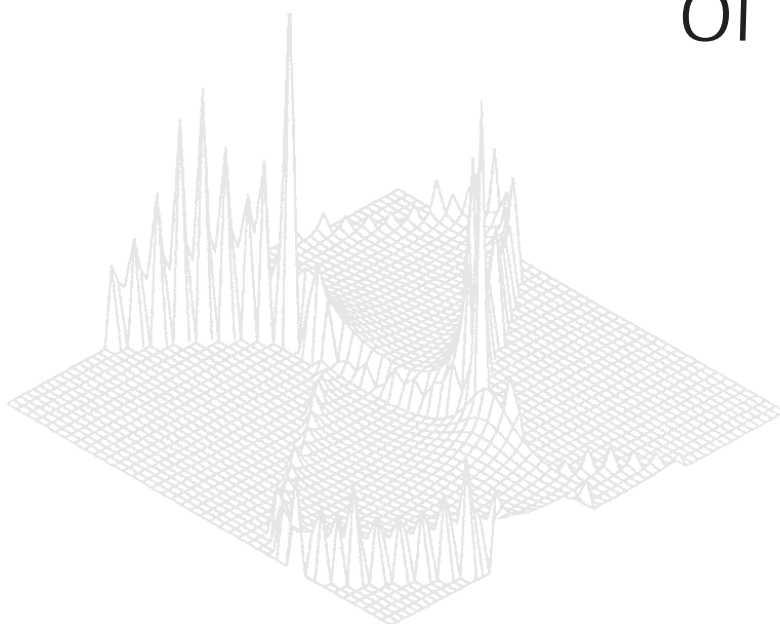

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Progress of Electron Momentum Spectroscopy in China*

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Abstract

Developments in the application of electron momentum spectroscopy (EMS) in China are described. Particular attention will focus on our progress in applying various generation EMS spectrometers to atomic and molecular targets of interest. Results from these experiments are presented.

1. Introduction

The technique of electron momentum spectroscopy (EMS) has made great progress during the past two decades (McCarthy and Weigold 1976, 1988, 1991; Byron and Jochain 1989; Lahmam-Bennani 1991; Chen and Zheng 1994*a*, 1994*b*; Brion 1992; Coplan *et al.* 1994). Many achievements have shown that EMS is a powerful tool for studying the microscopic structure of atoms, molecules, solid surfaces and films.

For well known historical reasons, the technique of EMS came rather late to China. In addition the pool of scientists who knew of its potential was limited. Nonetheless when the opportunity arose, in 1990, to work in this field we grasped it. Today there are two active EMS groups in China. One is based in Hefei at the University of Science and Technology of China (Xu's group), while my own is based in Beijing at Tsinghua University.

By 1995, Xu's group had developed an electron momentum spectrometer with an energy resolution of 1.8 eV (FWHM) and a momentum resolution of 0.15 a.u. This group has performed experiments on helium (He), argon (Ar), methane (CH₄), and so on (Chen *et al.* 1996*a*, 1996*b*; Pang *et al.* 1996), using their spectrometer. The development of my group can be divided into three stages. In the first stage (1990–93), an electron momentum spectrometer belonging to the first generation-type (single channel) was developed and some initial experiments were performed (Qian *et al.* 1994*a*, 1994*b*; Xu *et al.* 1994, 1995; Chen and Zheng 1992; Qian *et al.* 1992). In the second stage (1994–96) an advanced spectrometer, belonging to the second generation-type, was set up and some good experimental results were obtained. For the third stage (1996 onwards), a third generation spectrometer with, simultaneously, high energy resolution, high momentum resolution and high detection efficiency is currently being brought on-line.

* Dedicated to Professor Erich Weigold on the occasion of his sixtieth birthday.

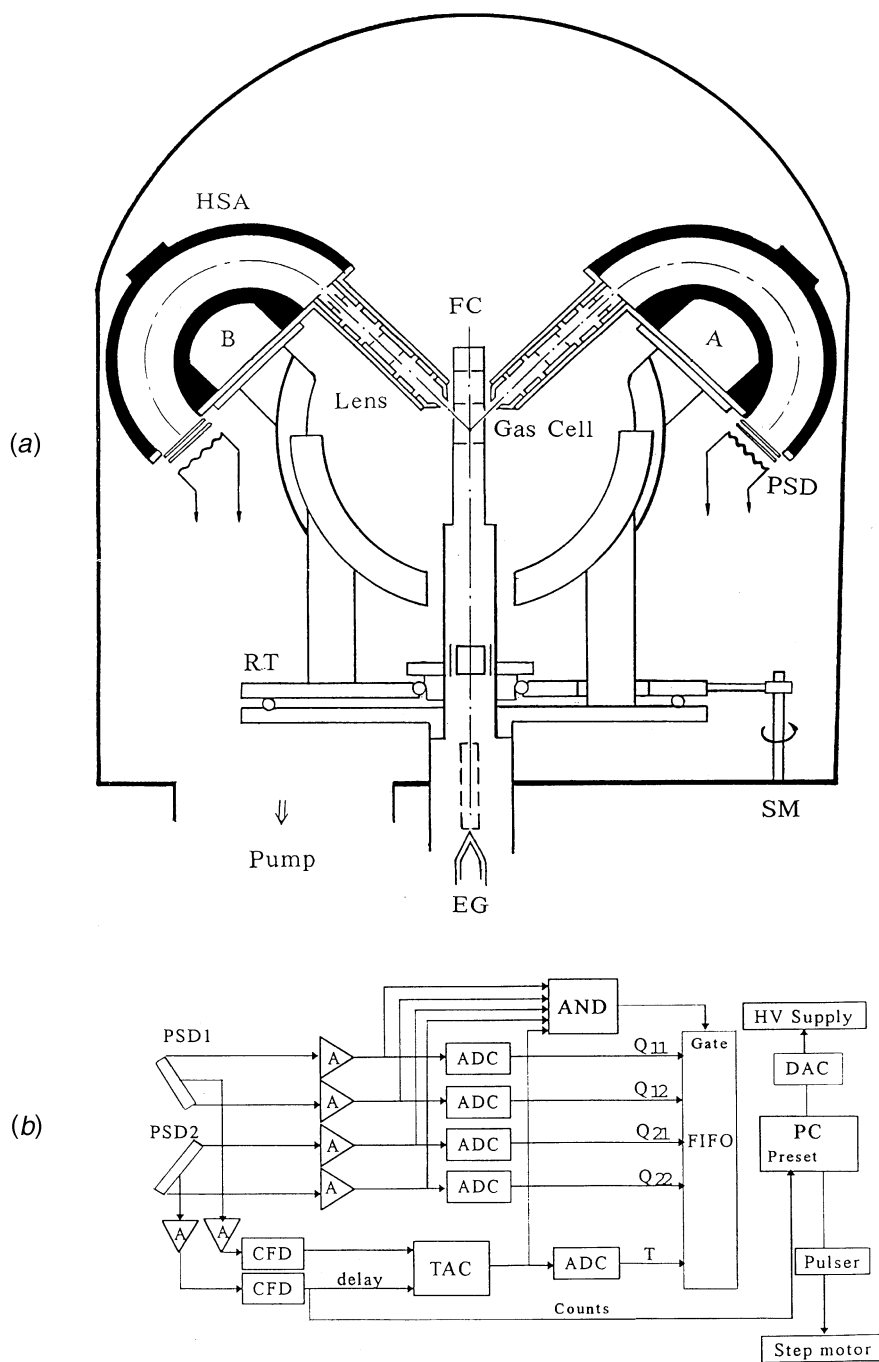


Fig. 1. (a) A schematic diagram of the vacuum chamber and its components for our second generation spectrometer. (b) A schematic diagram of our current data acquisition electronics.

2. Experimental Details

A brief description of the second generation EMS spectrometer, as used at Tsinghua University, is now presented.

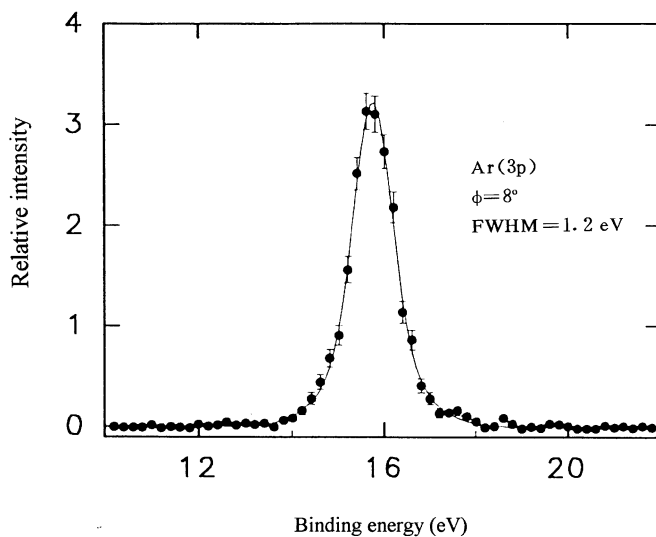


Fig. 2. Binding energy spectrum of Ar(3p) at $\phi = 8^\circ$, as obtained by our second generation spectrometer prior to July 1997.

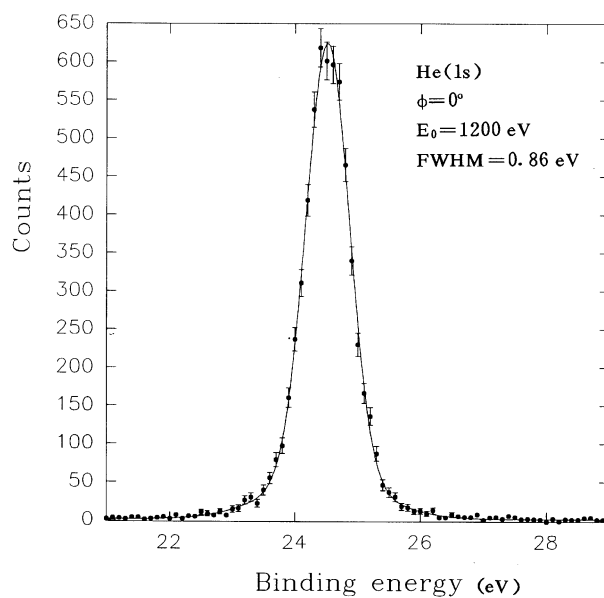


Fig. 3. Binding energy spectrum of He(1s) at $\phi = 0^\circ$, as obtained by our second generation spectrometer post July 1997.

(2a) Vacuum Chamber and Components

Fig. 1a shows a schematic diagram of our vacuum chamber, and the essential components contained within it, for our second generation spectrometer. This apparatus is similar to those of Weigold's group (Cook *et al.* 1984) and Brion's group (Zheng *et al.* 1994). Specifically it is a symmetric non-coplanar, multichannel energy-dispersive, electron momentum spectrometer. The vacuum chamber, constructed from type 304 stainless steel, resembles a bell-cover. It is 600 mm high and 550 mm in diameter and is pumped by a turbo-molecular pump of speed 1500 ℓ/s . Typical base pressures in the chamber are of the order of 1.5×10^{-7} Torr. A well-focused electron beam (about 1 mm in diameter), produced from a thoriated tungsten or LaB₆ filament in a home-made electron gun, is directed into the interaction region by a series of electron optical lenses and a beam deflection system. The electron beam current into the interaction region is typically 10 μA . The impact energy was 1200 eV plus the binding energy. Two hemispherical analysers, with inner and outer radii of 50 and 90 mm respectively, are used to energetically select the scattered and ejected electrons at polar angles of 45° from (e, 2e) ionisation events. The relative azimuthal angle ϕ , between the two analysers, can be varied over a range of $\pm 40^\circ$. This scans the target electron momentum p in the experiment. Energy-dispersive position sensitive detectors, each consisting of two 36 mm microchannel plates in the double chevron configuration and a one-dimensional resistive anode, are used to detect scattered and ejected electrons at the exit plane of each analyser. The range of kinetic energies detected in each analyser is from 596–604 eV. Furthermore, a series of electric field correction rings is mounted between the inner and outer hemispheres to ensure field uniformity.

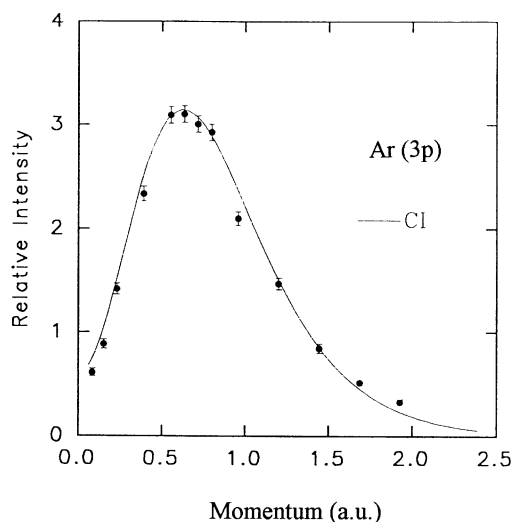


Fig. 4. Momentum profile for Ar(3p). The curve is the best configuration interaction calculation folded with the experimental momentum resolution of 0.1 a.u. (Fan *et al.* 1997a).

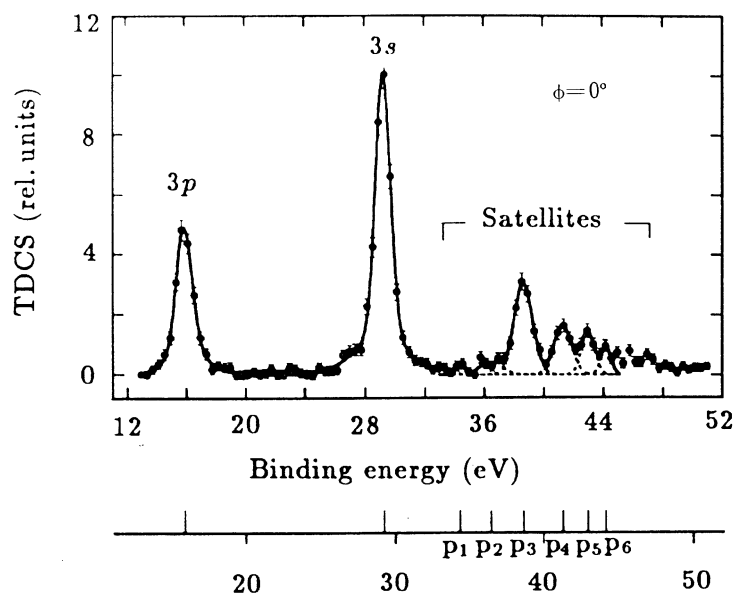


Fig. 5. The valence binding energy spectrum of argon for $\phi = 0^\circ$.

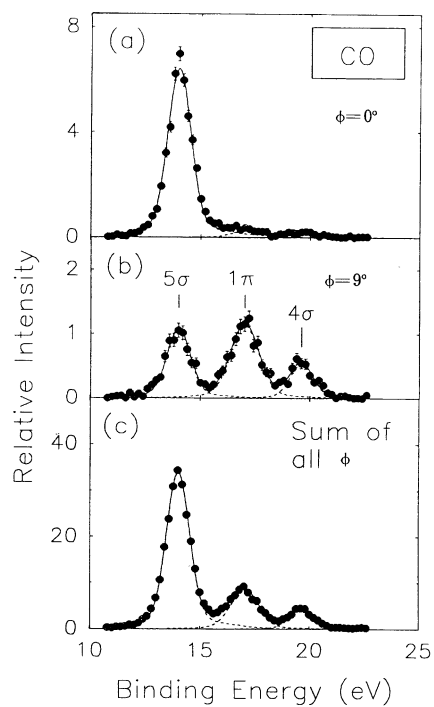


Fig. 6. Binding energy spectra for the outer valence region of carbon monoxide (CO), in the binding energy range 10.8–22.6 eV, at (a) $\phi = 0^\circ$, (b) $\phi = 9^\circ$ and (c) sum of all 13 angles. The present data were recorded at a total energy of 1200 eV, plus the binding energy, and with an instrumental energy resolution of 1.2 eV (FWHM).

(2b) Data Acquisition Electronics

Fig. 1b is a schematic diagram of the data acquisition electronics. The fast timing pulses from the two detectors are amplified and fed into a time-to-amplitude converter (TAC). The position (energy) pulses from the two position sensitive detectors are amplified and fed into a four channel analog-to-digital converter (ADC) unit. Each ADC has a conversion time of $5\ \mu\text{s}$. The output pulses, taken from appropriate windows of the TAC spectrum, are then used to determine the coincidence and random position (energy) digital signals respectively. Software corrections are also made for the variation of electron transit time in the analysers.

(2c) Calibration of Spectrometer Properties

The two main properties of the present spectrometer are calibrated from measurements of the He(1s) binding energy spectrum and the Ar(3p) momentum distribution, as detailed below.

(1) *Energy resolution.* Prior to July 1997, a thoriated tungsten filament was used in our 'home-made' electron gun. Binding energy spectra experiments on ionisation of 3p electrons from the argon atom showed that, under these conditions, the spectrometer had a coincidence energy resolution of $1.2\ \text{eV}$ (FWHM) (see Fig. 2). After July 1997, a LaB₆ filament was used in our electron gun. With this modification, and some other refinements, our recent calibration experiments on binding energy spectra for the 1s electrons of the helium atom, showed that our spectrometer already had a coincidence energy resolution of $0.9\ \text{eV}$ (FWHM) (see Fig. 3).

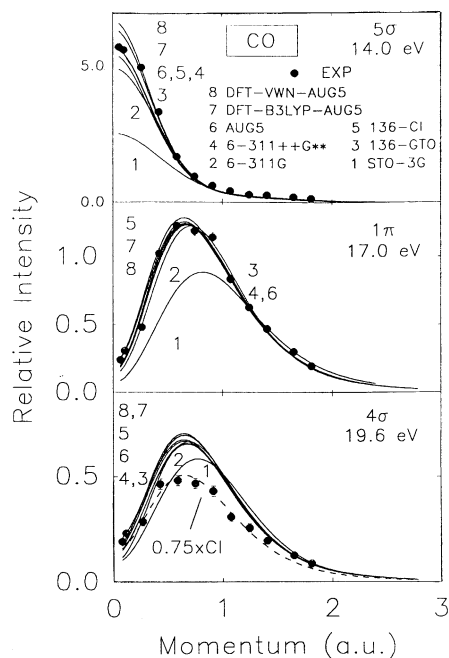


Fig. 7. Experimental momentum profiles for the 5σ , 1π and 4σ orbitals of CO. The present data (●) are compared with theoretical spherically averaged momentum profiles calculated using MRSD-CI, HF and DFT methods. Full details are given in Fan *et al.* (1997b).

(2) *Momentum resolution.* Similar to other authors, we determined our momentum resolution from an accurate measurement of the argon 3p momentum distribution. We typically found it to be 0.1 a.u. An example of this measurement is given in Fig. 4, in which the curve is the best available configuration-interaction calculation folded with an experimental momentum resolution of 0.1 a.u. (Fan *et al.* 1997a).

3. Results and Discussion

In this section we present a sample of the data we have collected with our present EMS spectrometer. No attempt is made here to discuss the physical interpretation of the present results (see referenced papers for this). Rather, we simply aim to illustrate the extent of the progress EMS has made in China since 1990. Note that in our initial studies (Sections 3a–3c) the spectrometer energy resolution was 1.2 eV (FWHM) and the momentum resolution was 0.1 a.u.

(3a) Valence Electron Binding Energy Spectrum of Argon

Fig. 5 shows the binding energy spectrum of argon (Fan *et al.* 1997a). This spectrum was measured at $\phi = 0^\circ$ and has been fitted with eight Gaussian peaks.

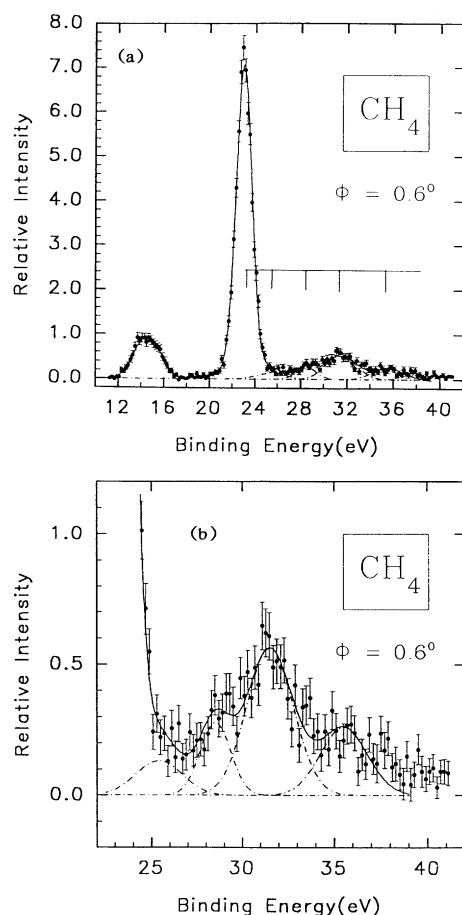


Fig. 8. Binding energy spectra for CH_4 at $\phi = 0.6^\circ$. Note the expanded scale of graph (a) to illustrate the satellite structure.

The major two peaks, at binding energies 15.89 eV and 29.26 eV , correspond to the main $(3p)^{-1}$ and $(3s)^{-1}$ lines of argon respectively. The other six peaks, at binding energies 34.37 eV (p_1), 36.45 eV (p_2), 38.65 eV (p_3), 41.30 eV (p_4), 42.98 eV (p_5) and 44.20 eV (p_6), all correspond to satellite states. The present result is in good qualitative agreement with the definitive EMS study of argon, as described in McCarthy and Weigold (1991).

(3b) Binding Energy Spectra and Momentum Profiles for the Outer-valence Electrons of CO

Fig. 6 shows our binding energy spectra at $\phi = 0^\circ$, 9° and $\Sigma\phi$ for the outer-valence region of carbon monoxide (CO) (Fan *et al.* 1997b; Zhou *et al.* 1997). Three peaks, due to ionisation from the $5\sigma, 1\pi$ and 4σ orbitals, are apparent in these spectra.

The corresponding momentum profiles for the $5\sigma, 1\pi$ and 4σ orbitals are presented in Fig. 7. It is interesting that for the 5σ orbital (see Fig. 7), at small values of p , the DFT-based calculations, within a plane wave impulse

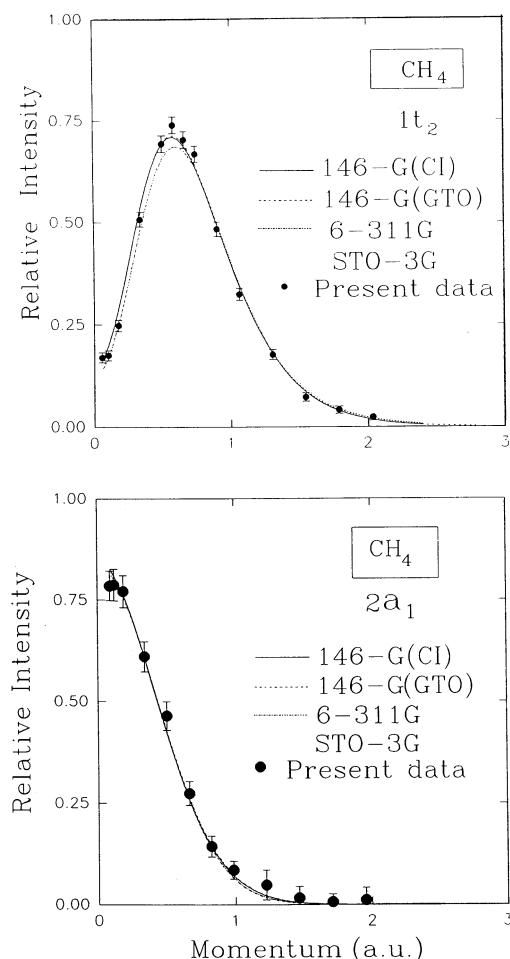


Fig. 9. Experimental momentum profiles for the valence $1t_2$ and $2a_1$ orbitals of CH_4 .

approximation (PWIA) framework, overestimate the magnitude of the cross section, a better description being provided by the more sophisticated CI basis states. We also note our experimental EMS pole strength for the 4σ orbital, at binding energy 19.6 eV, is $S_{4\sigma} = 0.75$. The remaining 4σ intensity is possibly located at higher binding energies not measured in this study. The present results supercede the earlier CO studies from Weigold's and Brion's groups (Zhou *et al.* 1997), which were both conducted with single channel EMS spectrometers and lower energy and momentum resolution.

(3c) Binding Energy Spectra and Momentum Profiles of CH_4

In Fig. 8a we show a binding energy spectrum for methane (CH_4), over the range of binding energies 12–41 eV and at $\phi = 0.6^\circ$. The two major peaks in this spectrum correspond to ionisation from respectively the $1t_2$ and $2a_1$ orbitals of methane, with the additional structure being ascribed to satellite states of the $2a_1$ orbital (Chen *et al.* 1997a). This satellite structure is enhanced in Fig. 8a, where only the binding energy range ≈ 24 –41 eV is considered. It is quite clear

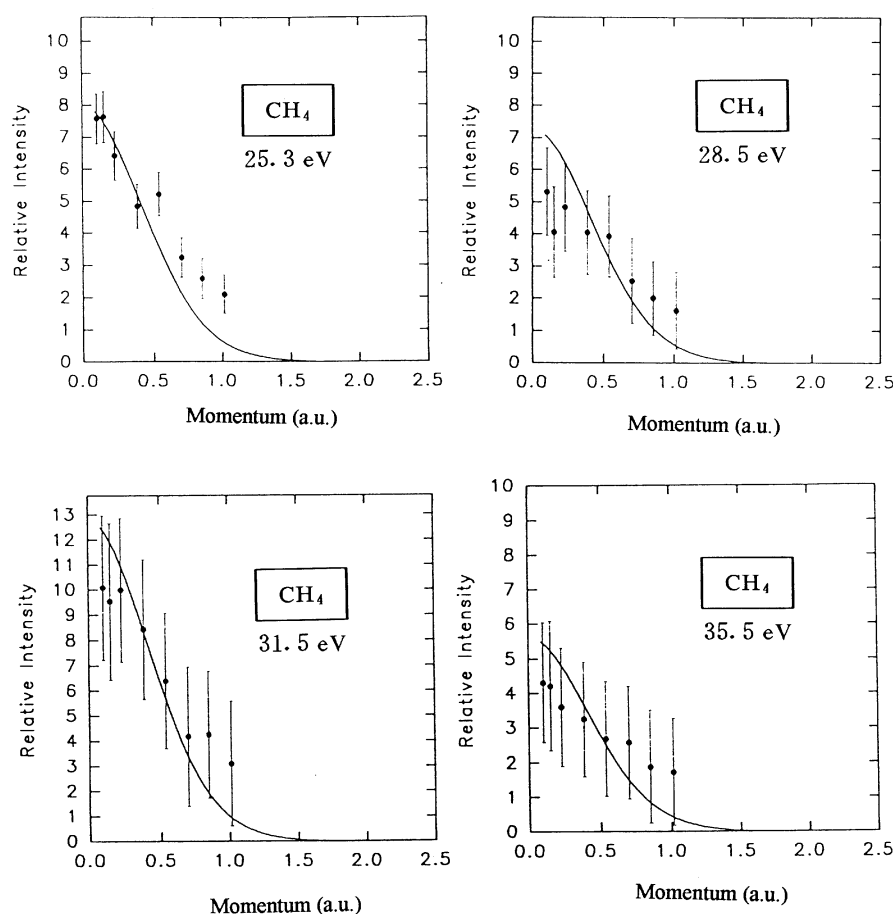


Fig. 10. Experimental momentum profiles for the $2a_1$ orbital satellite structure of CH_4 .

from this figure that significant splitting of the $2a_1$ valence shell is occurring due to final state electron correlation effects. In Fig. 9 the momentum profiles for both the $1t_2$ and $2a_1$ orbitals are plotted. In both cases good agreement is found between experiment and theory when the calculation employs a large CI-basis in conjunction with the PWIA. Finally, in Fig. 10, four experimental momentum profiles for the $2a_1$ satellite states at binding energy positions of 25.3 eV, 28.5 eV, 31.5 eV and 35.5 eV are given. This is the first time momentum profiles for the $2a_1$ satellite states have been measured (Fan *et al.* 1997c).

In Sections 3d and 3e we next present results taken using our improved spectrometer. The energy resolution is now 0.9 eV (FWHM) and the momentum resolution 0.1 a.u.

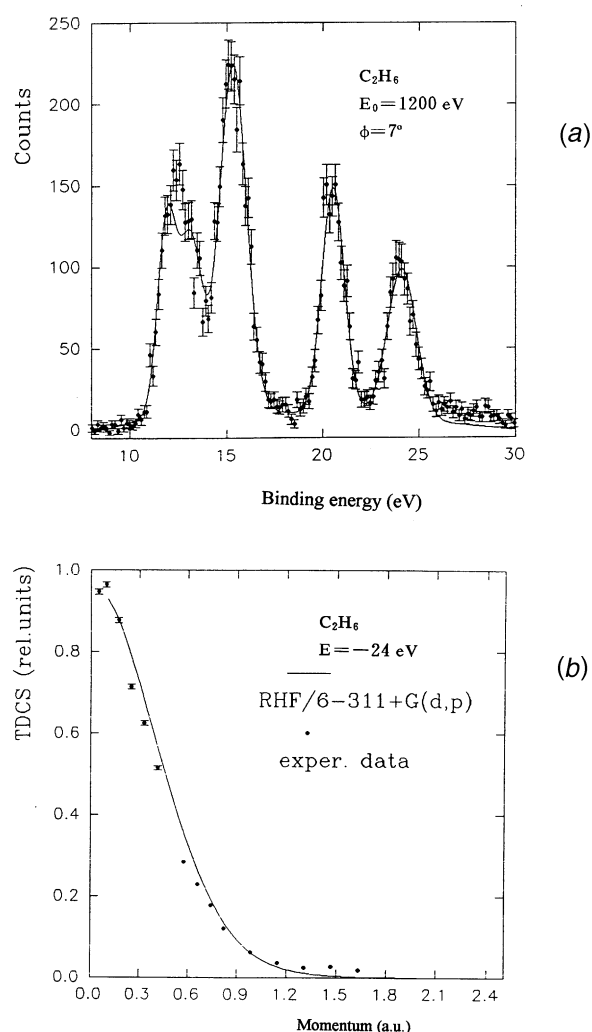


Fig. 11. (a) Binding energy spectrum of ethane (C_2H_6) at $\phi = 7^\circ$. (b) Momentum profile for the $2a_{1g}$ orbital of C_2H_6 .

(3d) EMS Studies on Ethane (C_2H_6) and Propane (C_3H_8) Molecules

Fig. 11a shows the binding energy spectrum of C_2H_6 , at $\phi = 7^\circ$, in which five valence orbitals have been distinguished (one only faintly). One of these orbitals, the $2a_{1g}$ orbital, has the momentum profile illustrated in Fig. 11b. Fig. 12 gives the binding energy spectrum for propane at $\phi = 6^\circ$. This spectrum is in good qualitative agreement with those obtained from photoelectron spectroscopy (Kimura *et al.* 1981).

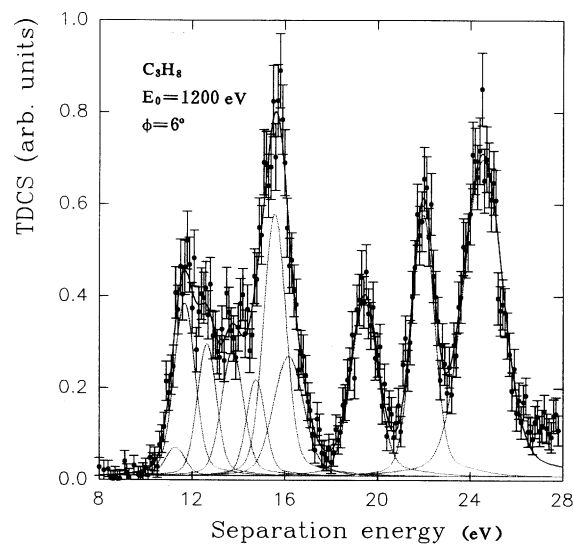


Fig. 12. Binding energy spectrum of propane (C_3H_8) at $\phi = 6^\circ$.

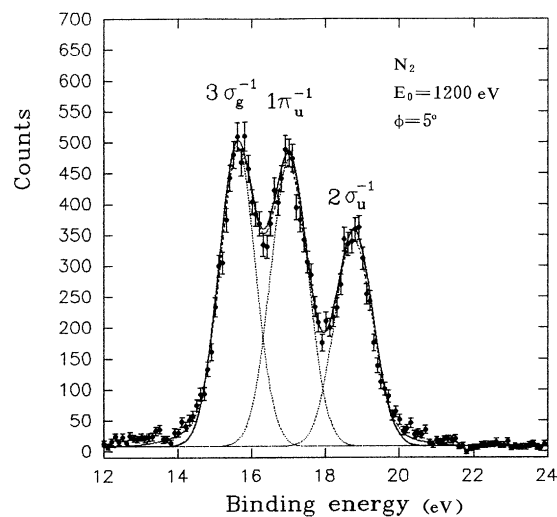


Fig. 13. Binding energy spectrum of nitrogen (N_2) at $\phi = 5^\circ$.

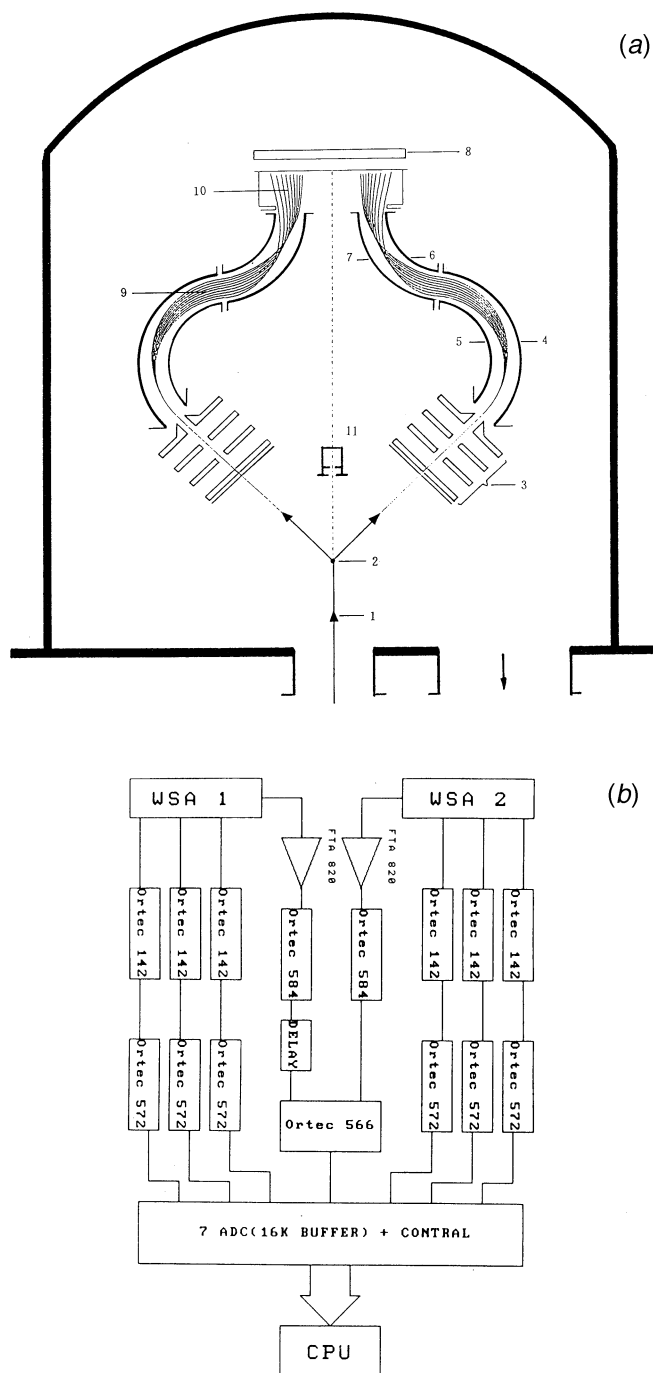


Fig. 14. (a) A schematic diagram of the main-body of our third generation EMS spectrometer.
 (b) A schematic diagram of the data acquisition electronics the spectrometer (see Section 4).

(3e) N_2 Molecules

In Fig. 13 we show a binding energy spectrum of molecular nitrogen (N_2), at $\phi = 5^\circ$, in which three orbitals, $(3\sigma_g)^{-1}$, $(1\pi_u)^{-1}$ and $(2\sigma_g)^{-1}$, can clearly be distinguished. The present spectrum is qualitatively similar to that reported at $\phi = 7.1^\circ$ in the earlier EMS study of Cook *et al.* (1990). However, as the current work was conducted at an energy resolution of 0.9 eV (FWHM), superior to that used in the 1500 eV investigation of Cook *et al.* (1990), the present results should nicely complement the earlier work.

4. The Future

Based on the success of our second generation spectrometer a new third generation spectrometer, with toroidal analyser, has been proposed and developed. With this new spectrometer we anticipate that high resolution and excellent data accumulation rates will be obtained (Chen *et al.* 1997b). A schematic of this apparatus is given in Fig. 14a, in which (1) is the electron beam from a monochromator, (2) the gas cell, (3) a drill-type retarding and focus system, (4-5) & (6-7) the new toroidal analyser with two-dimensional dispersion, (8) the two 2-dimensional position sensitive detectors, (9 & 10) the electron trajectories and (11) the Faraday cup. Fig. 14b shows the data acquisition electronics for this new spectrometer, which we note is currently being brought on-line.

Acknowledgments

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