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A Study of the Correlation States
of Ethylene by Synchrotron
Photoelectron Spectroscopy

by
Steven J. Desjardins, B.Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Master of Science

Department of Chemistry

Carleton University
Ottawa, Ontario
July 18, 1994
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A Study of the Correlation States
of Ethylene by Synchrotron
Photoelectron Spectroscopy

submitted by Steven J. Desjardins, B.Sc.
in partial fulfillment of the requirements for
the degree of Master of Science

Thesis Supervisor

Chair, Department of Chemistry

Carleton University
August 17, 1994

Abstract

The synchrotron photoelectron spectra (SPES) of ethylene and 1-¹³C-ethylene have been obtained over the photon energy range 30 to 220 eV. Two correlation (satellite) peaks are found in the spectra of ethylene and 1-¹³C-ethylene. The major satellite at 27.4 eV binding energy is found to be intrinsic in nature, having no photon energy dependence in its intensity ratio with respect to its parent peak. The newly discovered peak at 21.4 eV binding energy, however, is found to be dynamic, its intensity having a definite dependence on photon energy.

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1 Introduction

1.1 Synchrotron Photoelectron Spectroscopy

Photoelectron spectroscopy is the simplest and most direct method for the determination of the binding energies of electrons in atomic and molecular species. Photons of a known energy, $h\nu$, interact with the sample (M) under investigation, causing single ionization (M^+) to a large extent. The ejected electrons, called photoelectrons, can be detected via their kinetic energies, E_K . The binding energies, E_B , can then easily be calculated by noting that:

$$E_{K_i} = h\nu - E_{B_i} \quad (1)$$

where the index i is used to indicate that there may be more than one E_K and E_B energy pair, thus reflecting the possibility of ionization out of more than one energy level of the species being studied. A typical experiment involves selecting an appropriate photon energy to cause the ionizations, and then counting the number of photoelectrons at a specific kinetic energy. A range of kinetic energies is then scanned to produce a complete spectrum. The kinetic energy spectrum can then be converted into a binding energy spectrum through the simple equation above. Binding energies can also be estimated using other techniques, like mass spectrometry, Penning ionization, electron impact spectroscopy, etc., but these experiments are rather complicated and the results are obtained indirectly, and thus are not as conclusive as photoelectron spectroscopy.

The device that allows the photoelectron spectrum to be obtained is called a photoelectron spectrometer. A spectrometer consists of a collision region where the photons from the source interact with the sample being studied, an energy analysis section and a detection region where the photoelectrons are detected or counted. The photoelectrons generally travel from the collision region to the detector through a guiding electric field which serves as the energy analyzer. The geometry of the energy analyzer region and the strength of the electric and/or magnetic field will select the appropriate kinetic energy that will pass to the detector. The strength of the electric and/or magnetic field is adjustable, allowing for a range of kinetic energies to be detected and scanned over. Detectors generally work on a “cascade” type of process - the impinging photoelectrons cause a current to be generated and this current is then registered electronically.

Charged particles radiate when accelerated. Acceleration can be a change in speed and/or a change in direction. If electrons are accelerated to relativistic speeds (*ie* $v/c \approx 1$) and then confined to an approximately circular orbit through the use of bending magnets, they will radiate. As the electrons pass through the bending magnets, they radiate a photon beam tangentially to their path of travel that is very intense and well-focussed. This beam is called synchrotron radiation and the circular orbit is referred to as the synchrotron ring [1]. Typical synchrotron beams contain photons over a wide energy range, orders of magnitude in energy (< 1 to 1000s of eV). Because this beam is intense (many photons), well-focussed

(1 to 10 *mrad*, which corresponds to usually a few square *mm* several *m* from the synchrotron ring) and contains a wide energy range. synchrotron radiation is extremely useful for a wide variety of experimental techniques, such as spectroscopy, diffraction and microscopy [2,3]. The Canadian Synchrotron Radiation Facility (CSRF) has been used to obtain high resolution contact micrograph replicas of biological samples which yielded different information than that obtainable from conventional light microscopy [2]. Reference 3 presents a review of the X-ray research being conducted at CSRF. Included are EXAFS, NEXAFS, Auger studies, surface studies, lithography and spectroscopy. And, many high-technology companies, including IBM, have used synchrotron radiation in the manufacture of small-scale (μm) circuitry [3].

Synchrotron radiation is extremely valuable as a photon source for photoelectron spectroscopy for exactly the same three reasons. The intensity of the beam leads to many ionizations and hence more photoelectrons will be produced. The small beam size allows for good alignment with the experimental chamber and reduces the loss of photons from scattering. And the wide energy range allows for the spectra of atomic or molecular species to be studied at different photon energies, a distinct advantage over discrete sources, such as conventional X-rays. Synchrotron radiation has other unique properties [1]. In the plane of its orbit, the radiation emitted by an electron is completely polarized with the electric vector parallel to the orbital plane [1]. Thus, experiments can be conducted at known

angles to the polarization of the source, like the magic angle [4]. Electrons travel around the synchrotron ring in groups or bunches, and so, the radiation is emitted in short flashes or pulses [1]. However, the intensity from bunch to bunch is very stable, allowing for consistency in experimentation [1]. The time structure of the synchrotron radiation also allows for various types of time-resolved experimental studies [1].

1.2 Correlation States

Simple single-particle molecular orbital models, like Hartree-Fock methods which estimate the wavefunctions of many-electron systems by multiplying one-electron wavefunctions together, consider electron motions to be independent of each other. These models are successful at predicting the main features of valence shell and inner shell photoelectron spectra, though they cannot account for the “extra” peaks that are often observed. These extra peaks that appear in photoelectron spectra were initially called many-body states, satellite peaks or shake-up peaks, though the more proper name correlation peaks is preferable as it indicates the mechanism responsible for these features. If simple molecular orbital theory as applied to the ground state of a neutral molecule is extended by considering excited state configurations, the result, called Configuration Interaction (CI), allows for the “mixing” or interacting of states in addition to the ground state configuration. It is precisely from the interactions (correlations) of electrons in atomic or molecular systems that these correlation peaks appear in the photoelectron spec-

tra of many species [5-31]. The correlation states of atoms, especially the noble gas atoms, have been investigated intensely, however the study of these states in molecular systems is still in its infancy. The work presented in this thesis is perhaps one of the most thorough investigations of the correlation peaks of a simple, non-diatomic molecule.

The Schrödinger equation cannot be solved exactly for more than one electron in a system, and so, schemes were developed to estimate solutions of more complicated systems. As noted above, however, these schemes still considered electrons to be independent of each other. With the advances in experimental instrumentation and technique came the study of correlation peaks in photoelectron spectra as they could finally be resolved. It became increasingly obvious that electron interactions in atomic and molecular systems were not insignificant and a lack of understanding of the small features does imply an incomplete understanding of the whole. Theories involving the interactions of electrons, both in the system and in the continuum, were devised. Earlier calculations were unfortunately limited by computing power. But, with the recent advances in central processing unit power and speed and parallel computing, it is now possible to predict theoretically (within well-defined kinematical assumptions) what a photoelectron spectrum should look like, including correlation peaks.

Correlation peaks have several production mechanisms [5,32]. Initial and Final Ionic State Configuration Interactions (ISCI and FISCI) occur when states

of the same symmetry interact in either the initial or final states and these interactions are independent of the photoelectron energy. Continuum State Configuration Interaction (CSCI), or inelastic scattering, involves the scattering of the photoelectron in the ionic potential, causing the excitation of another electron as the photoelectron leaves the system. Interchannel coupling, related to CSCI, gives rise to the autoionization of doubly excited states into different satellite channels. Shake-up is the process in which photoionization causes a relaxation of the system during and after the photoionization process, resulting in an excitation. Shake-off is the process where the second electron leaves the system as well. The extension of the shake-up concept to continuum states is called conjugate shake-up.

Schemes have been proposed, such as those by Becker and Shirley [5], to classify correlation states and their production mechanisms phenomenologically by studying the photon energy dependence of the ratios of the correlation (satellite) peak intensities to the main or "parent" peaks observed in the photoelectron spectra of noble gas atoms. The "parent" peak is the "normal" peak (one electron process) in the photoelectron spectrum expected within a Koopmans-type approximation. The photon energy dependence of satellite/main peak intensities in photoelectron spectra has been studied previously by Willeumier and Krause [6]. The earlier X-ray studies were hampered by poor energy resolution and many closely-spaced satellites were not resolved. With the introduction of high intensity synchrotron sources, such photon energy dependence studies have now led

to less ambiguous measurements of the satellite/main peak intensities. Those correlation (satellite) peaks that exhibit a constant ratio with increasing photon energy are referred to as "intrinsic" correlations and are considered to be caused by initial and/or final state configuration interaction [5,90,93]; whereas those correlation (satellite) peaks that exhibit a strong photon energy dependence in the satellite to main peak intensity ratio are referred to as "dynamic" correlations and can be produced by shake-up processes [5,7-10,33], continuum state interactions [5,9,11,12] or interchannel coupling [5,8,9,34].

The terms "intrinsic" and "dynamic" are used because of their relation to the dependence on photon energy. Intrinsic correlation processes are independent of the photon energy of the ionization, and of the ionization itself. These processes are theoretically occurring whether there is ionization or not. And so, these processes are "constant" or "natural" and are therefore referred to as intrinsic. Dynamic correlation processes do depend on the energy of the ionization process. The name dynamic derives from the fact that these types of processes depend on the "dynamism" or speed (kinetic energy) of the departing photoelectron. And hence, they then depend on the photon energy because of the simple relationship between E_K and E_B .

Several experimental and theoretical studies on atomic systems [5-24] have indicated that the phenomenological classification of correlation states into intrinsic and dynamic correlations is very useful in understanding the complexity of

electron-electron interactions. Recent studies on molecular systems [25-31] have also shown that the Becker-Shirley classification is feasible. This phenomenological classification allows for better communication between experimentalists and between experimentalists and theoreticians, who are necessarily working together to further the understanding of correlation mechanisms and the peaks they produce in photoelectron spectra.

1.3 Ethylene

Ethylene [C_2H_4 (D_{2h})] has the following electronic configuration in the ground state: $(1a_g)^2(1b_{1u})^2(2a_g)^2(2b_{1u})^2(1b_{2u})^2(3a_g)^2(1b_{3g})^2(1b_{3u})^2$, having 1A_g symmetry. All orbital symmetries are referenced to the molecule lying in the yz plane, with the $C-C$ double bond along the z axis. Figure 1 shows the molecular geometry and the molecular orbitals of the ethylene molecule. Part (b) of Figure 1 shows the simple valence bonding molecular orbitals of ethylene, including the LUMO (lowest unoccupied molecular orbital) $1b_{2g}$ which corresponds to a π^* antibonding orbital. The molecular orbitals can be considered to be composed of hydrogen $1s$ and carbon $2s$ and $2p$ components in the simplest possible approximation. The low-lying carbon $1s$ (binding energy of approximately 285 eV) orbitals are not considered to participate in bonding. Filled and unfilled lobes are used to distinguish between orbitals of opposite phase. The $1b_{2g}(\pi^*)$ and $1b_{3u}(\pi)$ orbitals are composed of the carbon $2p_x$ orbitals which sit above and below the molecular yz plane. The $1b_{3g}$ and $1b_{2u}$ orbitals are bonding ($1b_{3g}$) and antibonding ($1b_{2u}$)

combinations of $C\ 2p_y$ and $H\ 1s$. Here, the $C'H_2$ groups act as units which engage in π -like bonding. The $3a_g$ orbital is a σ bond composed of $C\ 2p_z$ orbitals, lying along the major axis of the molecule. Because there are two carbon atoms, there are two inner valence orbitals, $2b_{1u}$ and $2a_g$, predominantly composed of carbon $2s$ orbitals, which behave in a σ -like manner, both bonding ($2a_g$) and antibonding ($2b_{1u}$). The carbon $1s$ orbitals corresponding to $1a_g$ and $1b_{1u}$ (both considered to be nonbonding) are not shown.

The photoelectron spectrum (PES) of ethylene, the simplest unsaturated hydrocarbon, has been investigated extensively both experimentally [14,29-31,35-46] and theoretically [47-65] since the 1950's. The PES of the carbon $2s$ region of ethylene was first reported by Gelius [14] using Al K_α X-rays (1487 eV photon energy) in 1974. It was also reported by Berndtsson *et al* [42] in 1975 and subsequently studied by Banna and Shirley [43] with Mg K_α (1253 eV photon energy) and Y M_ζ (132 eV photon energy) X-ray sources. The peaks at 23.7 eV and 19.2 eV binding energy were assigned as $2a_g^{-1}$ and $2b_{1u}^{-1}$ primary ionization peaks, respectively, by Gelius [14]. The strong satellite (or "extra" peak) at 27.4 eV in the Mg K_α spectrum [43], with an intensity of 39% of the $2a_g^{-1}$ primary peak, was originally assigned as a $^2B_{1u}$ correlation state [14,42,43]. The task of the earlier theoretical calculations [47-57] was to assign the five main bands (below 20 eV binding energy) through Koopmans' Theorem [66] at the Hartree-Fock (HF) level. The first study that went beyond the HF approximation (Green's Function

Figure 1: (a) The molecular geometry and (b) the molecular orbitals of the ethylene molecule. Filled and unfilled lobes are used to distinguish between orbitals of opposite phase.

$1b_{2g}(\pi^*)$ **$1b_{3u}(\pi_{C=C})$** **$1b_{3g}(\pi_{CH_2^*})$** **$3a_g(\sigma_{C-C})$**

$1b_{2u}(\pi_{CH_2})$ **$2b_{1u}(C_{2s}^*)$** **$2a_g(C_{2s})$**

(b)

method) was published in 1976 [58]. Martin and Davidson [59] performed a small configuration interaction (CI) calculation on the ethylene cation which agreed with experimental results, but indicated that the intense satellite belonged to the 2A_g symmetry manifold, with 30% of the intensity of the primary $2a_g^{-1}$ peak. Subsequent Electron Momentum Spectroscopy (EMS) experiments [67,68], also known as binary (e,2e) spectroscopy, confirmed this assignment; however, the intensity ratios obtained were different. Symmetry assignments in EMS experiments are made by comparing the momentum distribution of the correlation peak to the momentum distribution of the main peak. The shape of the momentum distribution for the correlation peak should match the shape of the momentum distribution of its parent peak. Differences in the correlation peak/main peak intensity ratios between EMS and PES have previously been observed in argon $3s$ ionization spectra [23]. Investigation into the nature of these differences are actively being pursued [69-72].

Cederbaum *et al* [61] performed Green's Function calculations, including more correlation configurations in their investigation than Martin and Davidson, but used smaller basis sets without diffuse Rydberg functions. The results agreed qualitatively with experiment, but suggested that there was a much richer structure than could be resolved. Two 2A_g peaks (correlation states) of roughly equal intensity less than 1 eV apart centered at 23.5 eV and another two closely spaced 2A_g peaks centered at 27.5 eV were found. The intensity of this dual satellite

(27.5 eV) was found to be 24% of the dual primary peak (23.5 eV). The recent MRSDCI calculation of Murray and Davidson [60] lead to a similar conclusion as the work of Martin and Davidson [59], as neither calculation produced the twinning phenomenon of the 2A_g peak at 23.5 eV binding energy or the satellite peak at 27.5 eV.

In addition to these early theoretical successes, Baker investigated the PES of ethylene using the EOM/propagator technique [62]. Two 2A_g peaks of roughly equal intensity centered at 23.2 eV were found, but only one 2A_g satellite peak at 27.26 eV. Truncation of the virtual space caused the twinning phenomenon to disappear. Two calculations based on the Symmetry-Adapted-Cluster (SAC) expansion CI theory performed by Nakatsuji [63] and Wasada and Hirao [64] are also of interest as no twinning of the 2A_g primary peak was observed, nor was there any strong 2A_g satellite between 27.0 and 30.0 eV binding energy. The 27.4 eV satellite peak was assigned as a $^2B_{1u}$ symmetry manifold correlation despite the earlier assignments to 2A_g .

In this thesis, the well-known correlation peak at 27.4 eV binding energy, belonging to the 2A_g symmetry manifold [29,31], has been confirmed as an intrinsic correlation as the ratio of satellite/main peak has been found to be effectively constant over a large photon energy range. Also, evidence of the dynamic nature of the newly discovered correlation peak at 21.4 eV [30,31] has been obtained as the ratio of new correlation peak/main peak has a definite photon energy dependence.

2 Experimental

The synchrotron photoelectron spectra (SPES) were obtained at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin Storage Ring of the University of Wisconsin at Madison's Synchrotron Radiation Center (SRC) in May 1991, August 1991, May 1992 and May 1993. The spectra were collected using the McPherson photoelectron spectrometer equipped with a channeltron detector and a multichannel plate detector [73] in conjunction with the grasshopper grazing incidence monochromator [74] with high and low energy gratings. Figure 2 shows the basic schematic of the McPherson photoelectron spectrometer. The synchrotron beam propagates perpendicularly to the plane of the diagram and is indicated by the small dark rectangle. Interactions between the photons and the gas sample occur in the gas cell. The photoelectrons are taken off at the pseudomagic angle appropriate for this equipment, 55.8° with respect to the polarization axis [4]. The electron energy analyzer is a spherical analyzer with a mean radius of 36 *cm* in which a tunable guiding electric field is present to drive the photoelectrons towards the detector. Two detectors were used. In 1991, a Galileo Electro-Optics channel electron multiplier (channeltron) with a bias voltage of 2400 *V* and a gain of 1.2×10^8 was used. For the experiments conducted in 1992 and 1993, a Quantar open face multichannel plate position sensitive detector with a bias voltage of 3860 *V* and a gain of 5×10^7 was used. Extensive calibration studies of the multichannel plate were conducted by Zhifeng Liu using the

Xe $5p$ and $4d$ peaks [73]. The grasshopper grazing incidence monochromator is so-named because its physical appearance reminds one of a grasshopper and the source beam grazes the first focussing mirror at an angle of only 1° . The beam is then focussed onto a mirror-slit combination that passes the beam onto a grating, which focusses the beam through the exit slit. Depending on the grating being used, the monochromator can deliver photons in the energy range 20 to 1200 eV. Two gratings were used in the experimentation. A grating with 600 *grooves/mm* provided photons in the photon energy range 30 to 70 eV. A second grating, with 1800 *grooves/mm*, provided photons in the range 70 to 220 eV. Typical slit widths used were 30 to 50 μm . Figure 3 shows the Aladdin Storage Ring. The Canadian Synchrotron Radiation Facility is located at bending magnet 09 (where synchrotron radiation comes off tangentially to the electron flow) at the bottom of the diagram. The numbers 1,2 and 3 refer to the ports (beamlines) on that bending magnet. The grasshopper's port designation is then 091. Spectra were also obtained by Dr. Bawagan in December 1992 with the 3 meter toroidal grating monochromator (3m-TGM) (port 012) [75]. In a TGM, a toroidal grating is used to focus the photon beam between the entrance and exit slits. Ellipsoidal mirrors are used to focus the beam horizontally on the exit slit. Angular corrections to the differential cross sections are not required as the photoelectrons were collected at the pseudomagic angle [4]. All reported intensity ratios are corrected for analyzer transmission effects [27]. Transmission corrections are necessary as

the analyzer is biased towards higher kinetic energy photoelectrons; slow moving photoelectrons are easily lost because of the long flight time through the relatively large energy analyzer. Further background corrections were made for low energy scattered electrons and stray light for the data obtained with the 3*m*-TGM. A single Matheson Gas Products research purity (99.99%) sample of ethylene was used for all experimentation. Further experiments were also conducted with isotopically labelled ethylene (1-¹³C'-ethylene) from Isotec (99% pure). This labelled ethylene has one ¹³C' isotope - the other carbon atom is "normal" ¹²C'.

High vacuum in the McPherson spectrometer is maintained through an extensive pumping system. The analyzer chamber and gas cell chamber are pumped separately with Balzers turbomolecular pumps (models TPU 510 and 330, respectively). The entire system is rough pumped and backed by a Balzers rotary pump (DUO 008D). The gas inlet system is pumped by a small TRI VAC turbo pump. Baseline pressure in the analyzer chamber is typically 10^{-7} torr or lower. When sample is introduced, the gas cell chamber pressure increases to typically 5×10^{-5} torr. The actual pressure in the gas cell is estimated to be two orders of magnitude higher.

The transmission of the spectrometer has been thoroughly checked using neon 2*s* and 2*p* ionization cross sections for calibration studies. The intensity ratio of the Ne 2*s* peak to the 2*p* peak is studied as a function of kinetic energy. The transmission function of the spectrometer can then be obtained by comparing

Figure 2: Schematic of the McPherson photoelectron spectrometer. The synchrotron beam is perpendicular to the plane of the diagram. The analyzer has a mean radius of 36 cm. The dashed line represents the path of the photoelectrons through the analyzer. The diagram is not to scale. Adapted from reference 4.

Figure 3: The Aladdin Storage Ring at the University of Wisconsin at Madison. The Canadian Synchrotron Radiation Facility is located at the bottom of the diagram, at ports 091-093. Adapted from reference 76.

the $2s/2p$ ratio with literature. In general, the intensity or area of a peak (A) in the photoelectron spectra obtained with this analyzer will be given by:

$$A = \text{constant} * \sigma(h\nu) * I_0(h\nu) * T(E_K) \quad (2)$$

where $\sigma(h\nu)$ is the cross section for the photoionization, $I_0(h\nu)$ is the photon intensity at photon energy $h\nu$ and $T(E_K)$ is the analyzer transmission function at the photoelectron kinetic energy E_K . Spectra are obtained rapidly (typically less than five minutes) and so $I_0(h\nu)$ is effectively constant over a scan of the spectrum. And so:

$$A \approx \text{constant} * \sigma(h\nu) * T(E_K) \quad (3)$$

The intensity (area) ratios of the Ne $2s$ to $2p$ peaks is calculated and compared with the literature values of the photoionization cross section, allowing $T(E_K)$ to be determined. It was confirmed that over the range that the SPES studies were conducted, the transmission function is essentially linear in kinetic energy, or:

$$T(E_K) = \text{constant} * E_K \quad (4)$$

as previous studies with the analyzer have indicated [27]. Intensity ratios of photoelectron peaks are corrected for transmission effects; these corrections range from approximately 20% at 45 eV down to approximately 2% at 200 eV.

Monochromators function as wavelength filters by limiting the photons that pass to specific wavelengths, *ie* those that complete their wavecycle in the distance between the focussing elements. However, energies that are integer multiples of the

selected photon energy will also pass through because their wavelengths are integer divisors of the selected wavelength. These radiations are referred to as higher order radiations. For example, if the monochromator is set for $h\nu$, some second order radiation, $2h\nu$ in energy, will pass through. This radiation, depending on its intensity and the sample being studied, can interfere in the experiment. The intensity of second order radiations from the grasshopper monochromator was also investigated via the $2p$ peak of neon. The second order radiations were studied by setting the monochromator for a certain photon energy, $h\nu$, and then scanning the photoelectron kinetic energy range that would be appropriate for $2h\nu$. The transmission corrected intensity ratio of the second order $2p$ peak to the first order $2p$ peak was then calculated as a function of photon energy. It was found that second order radiation is of significant intensity only at energies lower than those over which the vast majority of spectra were obtained. The second order radiation peaks in intensity (approximately 40%) between 30 and 35 eV primary photon energy, but quickly falls off, down to approximately 1% of the first order intensity by 45 eV . A Table and Figure of the second order data appear in Appendix A. There is, therefore, no interference from second order radiation.

The total experimental energy resolution, including both electron analyzer and monochromator effects, was found to range from 490 meV fwhm at 45 eV to 820 meV fwhm at 200 eV . The total experimental resolution is given by [4]:

$$\Gamma_{total}^2 \approx \Gamma_{analyzer}^2 + \Gamma_{monochromator}^2 + \Gamma_{natural\ width}^2 \quad (5)$$

The total resolution of the experiments is limited by that of the monochromator. The natural widths of peaks are, of course, beyond experimental control. The energy resolution of the analyzer is good, approximately 40 meV fwhm [4], and it is relatively stable over the range of energies studied. The energy resolution of the grasshopper, however, becomes poorer with increasing photon energy and slit width. At higher energies, the photon flux from the grasshopper monochromator will be lower, and so the entrance and exit slits have to be opened wider to increase the flux of photons coming out of the monochromator and hence to increase the observed count rate at the detector. Opening the slits wider causes the distribution of energy ($h\nu \pm \delta$) that the grasshopper passes to increase (*ie* δ increases as the slits are opened wider) and so, the result is poorer energy resolution. Also, for a fixed slit width, the energy resolution becomes poorer with increasing photon energy.

In May of 1991, the first ethylene spectra were run in the photon energy range 70 to 220 eV. Later that summer, in August, the first $1\text{-}^{13}\text{C}$ -ethylene spectra were taken, in the same energy range. On analysis of these spectra, it was found that the major correlation (satellite) peak at 27.4 eV binding energy was intrinsic in nature, according to the Becker-Shirley scheme [5], as the ratio with respect to its parent was constant [29]. Comparison with theoretical calculations was also very successful [29]. In May of 1992, lower energy spectra in the photon energy range of 30 to 70 eV of both species were run to investigate the ratio of the major satellite

to the $2a_g^{-1}$ main peak closer to its threshold of 27.4 eV. On analysis of these spectra, the new correlation peak at 21.4 eV binding energy was discovered. It had been overlooked in the previous spectra because of its photon energy dependence - the peak has very little intensity above 70 eV photon energy. Also at this time, the second order radiation study with Ne was conducted, to check for interferences. Later that year, in December, Dr. Bawagan ran the spectra of both species on the 3m-TGM at the lower energy range to check whether the observed spectral features were independent of the type of monochromator. Finally, in May of 1993, the last spectra of normal ethylene were run at the higher energy range to investigate in detail the decrease in intensity of the new (minor) correlation peak. Also, a pressure study was conducted with ethylene to investigate any possible contribution from inelastic scattering processes. During all beam runs, the transmission of the spectrometer was checked with Ne.

3 Analysis

Spectra obtained from the instrument are in binary format. To ease the analysis, the spectra are first converted to ASCII. Curve fitting is done on computer, using the program PEAKFIT (Jandel Scientific). Gaussian peaks are used. For the $2b_{1u}^{-1}$, $2a_g^{-1}$ and major satellite peaks, vibrational broadening made it necessary to use two gaussians for each peak to ensure complete coverage of the area under the peaks. For spectra obtained with the grasshopper monochromator, backgrounds were fitted with straight lines.

For the spectra obtained with the 3m-TGM, the low energy scattering of electrons caused an exponential-decay-like low kinetic energy background which made a further correction necessary. "No gas" background spectra were run in conjunction with the ethylene spectra at the various photon energies; these background spectra were then scaled (all points multiplied by a constant) to match the low kinetic energy tail of the ethylene spectra. The background spectra were then subtracted from the ethylene spectra and the resulting background-corrected spectra were analyzed as the other (grasshopper) spectra.

After the curve fit is acceptable, the various intensity ratios are calculated by comparing the areas under the specific peaks. Transmission corrections are done by dividing the area of a peak by the kinetic energy of its mean.

The interesting photon energy dependence of the ratio of the new correlation peak to the $2b_{1u}^{-1}$ main peak was investigated in detail. The data was curve fit

using PEAKFIT with an exponential decay, a constant, five gaussian peaks and a damped sine wave function to obtain an approximate functional form. The purely oscillatory component (the gaussians and the damped sine) was extracted and Fast Fourier Transformed using GRAFTOOL (see Results section for details).

In order to compare the experimental spectra with theoretical calculations, a simple FORTRAN program was written to convolute the theoretical pole strengths with gaussian peaks whose widths are consistent with those observed experimentally. Since the photoionization dipole matrix elements are not included in the theoretical calculations, proper comparisons between experiment and theory can only be made across the same symmetry manifold.

4 Results and Discussion

4.1 The Intrinsic Correlation State

Figure 4 shows a sample synchrotron photoelectron spectrum of normal ethylene, taken at 91.1 eV photon energy, having peaks associated with ionization from the six valence molecular orbitals. The extra peak, labelled “sat”, is the well-known correlation (satellite) peak originally observed by Gelius [14]. Also shown is the general curve fitting form - gaussian peaks and a linear background. Figure 5 shows a similar spectrum, taken at 59.5 eV.

Figure 6 shows a sample spectrum of ^{13}C -labelled ethylene ($1\text{-}^{13}\text{C-C}_2\text{H}_4$) at 59.5 eV photon energy. It can be seen that the SPES spectrum of isotopically labelled ethylene (Fig. 6) is very similar to that of normal ethylene (Fig. 5) at the same photon energy with regards to relative intensities, binding energies and peak widths, further confirming that the extra structure (labelled “sat”) found in the SPES is of “electronic origins”, *ie* largely independent of nuclear structure. It is well-known that vibrational frequencies, and thus the Franck-Condon widths associated with photoionization, are influenced by deuterium substitution of the hydrogen atoms in ethylene [77]. In this particular study, ^{13}C substitution is not expected to change significantly the vibrational frequencies of ethylene (as well as Franck-Condon widths) for the inner valence orbitals, however it is a reasonably sensitive test of “nuclear effects” in correlation states. ^{13}C substitution introduces an asymmetric 1/12 change in nuclear mass of one of the carbons. If these extra

Figure 4: Synchrotron PES spectrum of normal ethylene at 91.1 eV. The curve-fitting model used for all of the spectra is shown by the dashed gaussians and the solid baseline. Single gaussian peaks are fitted to the experimental peaks attributed to ionization from the outer valence orbitals. Two gaussian peaks of equal widths are fitted to each of the experimental peaks attributed to the satellite (27.4 eV), $2a_g^{-1}$ and $1b_{1u}^{-1}$. The sum of the peaks is represented as a solid line. The spectrum as shown is not corrected for transmission effects. The estimated total experimental energy resolution is 470 meV fwhm. The standard orbital notation assumes D_{2h} symmetry with the molecule in the yz plane (see Figure 1).

Figure 5: SPES of normal ethylene taken at 59.5 eV. The spectrum as shown is not corrected for transmission effects.

Figure 6: SPES of 1-¹³C-ethylene taken at 59.5 eV. The spectrum as shown is not corrected for transmission effects. The isotopically labelled ethylene is seen to have a similar spectrum to that of normal ethylene (see Figure 5).

peaks are caused by some electron-nuclear interaction, then there should be some differences in their inner valence SPES. No difference is observed (*cf* Fig. 5 and 6), and thus “nuclear effects” as a possible explanation for the satellite structure in the spectrum of ethylene is discounted. A percent difference spectrum for the two species at 59.5 eV is given in Appendix B. It can be seen that in the binding energy range of interest, 18 to 30 eV, there are no truly discernible features, merely noise, confirming that the spectra of normal and labelled ethylene are very similar.

The correlation peak at 27.4 eV has been thoroughly investigated by measuring the satellite/main $2a_g^{-1}$ peak intensity ratio at different photon energies from 37 to 223 eV. These ratios are presented in Table 1 and Figure 7, with previous X-ray measurements presented for comparison. The ratio is seen to be effectively constant over the entire energy range, even as the threshold (27.4 eV) is approached [29,31]. SPES at photon energies less than $h\nu = 36$ eV are difficult to obtain with the present electrostatic photoelectron energy analyzer. The difficulty arises from background problems associated with low energy scattered electrons. The dashed line (in both Figures 7 and 8) represents the ratio calculated from the MRSDCI-ANO calculation for normal ethylene [31]. The high value for Al K_α is probably a result of experimental factors unaccounted for (in this work) as the published spectrum was deconvoluted using a peak profile similar to that used for the fitting of the synchrotron spectra. Figure 8 shows the photon energy dependence of the correlation peak at 27.4 eV in the case of 1- ^{13}C -ethylene; the ratio

Table 1: Transmission corrected satellite/main $2a_J^{-1}$ intensity ratios for the intrinsic correlation state at 27.4 eV binding energy of normal ethylene.

Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$)	Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$)	Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$)
36.7 ^T	0.352 (0.047)	62.7 ^T	0.336 (0.035)	136.5	0.354 (0.024)
37.8 ^T	0.378 (0.063)	64.5	0.339 (0.014)	141.6	0.367 (0.024)
38.7 ^T	0.380 (0.049)	64.7 ^T	0.345 (0.033)	146.8	0.372 (0.020)
39.5	0.361 (0.031)	66.7 ^T	0.339 (0.019)	151.1	0.353 (0.010)
39.7 ^T	0.344 (0.057)	68.7 ^T	0.352 (0.025)	151.9	0.364 (0.030)
40.7 ^T	0.323 (0.042)	69.5	0.352 (0.010)	157.0	0.417 (0.025)
41.8 ^T	0.337 (0.033)	70.6	0.360 (0.030)	162.1	0.413 (0.031)
42.7 ^T	0.320 (0.061)	70.7 ^T	0.350 (0.046)	167.1	0.398 (0.023)
43.8 ^T	0.362 (0.031)	71.1	0.324 (0.075)	171.2	0.322 (0.027)
44.5	0.359 (0.016)	72.7 ^T	0.331 (0.046)	172.2	0.390 (0.026)
44.7 ^T	0.345 (0.035)	75.6	0.345 (0.035)	177.2	0.402 (0.023)
46.7 ^T	0.318 (0.038)	80.7	0.351 (0.033)	182.4	0.390 (0.030)
46.8 ^T	0.343 (0.043)	85.8	0.379 (0.042)	187.6	0.413 (0.024)
48.7 ^T	0.337 (0.029)	90.8	0.347 (0.028)	192.6	0.420 (0.020)
48.8 ^T	0.352 (0.021)	91.1	0.342 (0.009)	197.7	0.386 (0.026)
49.5	0.345 (0.010)	95.9	0.361 (0.040)	201.1	0.341 (0.036)
50.7 ^T	0.323 (0.031)	101.1	0.373 (0.028)	202.7	0.350 (0.030)
50.8 ^T	0.360 (0.063)	101.2	0.327 (0.039)	207.8	0.392 (0.020)
52.7 ^T	0.320 (0.025)	106.1	0.348 (0.029)	212.9	0.391 (0.025)
52.8 ^T	0.304 (0.026)	111.2	0.350 (0.026)	217.8	0.379 (0.024)
54.5	0.344 (0.010)	116.3	0.350 (0.031)	221.2	0.339 (0.026)
54.7 ^T	0.326 (0.024)	121.1	0.348 (0.016)	222.9	0.391 (0.030)
56.7 ^T	0.332 (0.023)	121.3	0.303 (0.023)	132 ^b	0.2 (0.4)
58.7 ^T	0.336 (0.035)	126.4	0.330 (0.025)	1253 ^b	0.39 (0.06)
59.5	0.338 (0.011)	131.5	0.370 (0.023)	1487 ^c	0.46 (0.03)
60.7 ^T	0.326 (0.020)				

^a Quoted error limits refer to uncertainties from gaussian curve fitting alone. Systematic errors due to the assumed baseline and transmission function are estimated to be less than 5% for results obtained with the grasshopper and on the order of 10% for those obtained with the 3m-TGM.

^T Results from the 3m-TGM, all other values are from the grasshopper monochromator.

X-ray results: ^b ref. [43]. ^c ref. [42].

Figure 7: Photon energy dependence of the satellite/main $2a_g^{-1}$ peak intensity ratios derived from synchrotron PES measurements for normal ethylene. The experimentally derived ratios (Table 1) are corrected for transmission effects. The open circles with error bars are data from the grasshopper monochromator and the solid diamonds are data from the 3m-TGM. Previous X-ray measurements [42,43] are shown as solid circles. The dashed line is the predicted satellite/main intensity ratio from the MRSDCI-ANO calculation (see Table 7).

Table 2: Transmission corrected satellite intensity ratios for 1-¹³C-ethylene for the major correlation peak at 27.4 eV binding energy.

Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$) satellite/main $2a_g^{-1}$
44.5	0.329 (0.029)
49.5	0.326 (0.029)
	0.366 (0.060)
54.5	0.313 (0.028)
58.8 ^T	0.313 (0.054)
	0.360 (0.099)
	0.250 (0.084)
59.5	0.313 (0.041)
	0.299 (0.023)
64.5	0.291 (0.023)
69.5	0.293 (0.023)
	0.288 (0.030)
91.1	0.330 (0.042)
121.7	0.338 (0.067)
151.9	0.315 (0.094)

^a Quoted error limits are statistical errors from gaussian curve fitting alone and do not include systematic errors. Systematic errors due to the assumed baseline and transmission function are estimated to be less than 5% for the results obtained with the grasshopper and on the order of 10% for those obtained with the 3m-TGM.

^T The 58.8 eV results are from the 3m-TGM, all other values are from the grasshopper monochromator.

Figure 8: Photon energy dependence of the major satellite/main $2a_g^{-1}$ peak intensity ratios for $1-^{13}\text{C}$ -ethylene. The ratios (Table 2) are corrected for transmission effects and shown as open circles with error bars. The ratios for normal ethylene are shown as solid diamonds for comparison.

values are given in Table 2. The constant value* of the intensity ratio observed in both normal (Fig. 7) and labelled (Fig. 8) ethylene is indicative of an "intrinsic" correlation, using the notation of Becker and Shirley [5], a result of initial and/or final state configuration interaction. These configuration interactions are always occurring, and the photoionization process only allows them to be seen - it does not produce them - thus, there should be no photon energy dependence. The threshold has been approached, within the limitations of the current instrumentation, yet the constant trend has been observed to continue, providing further evidence against contributions from mechanisms like shake-up or interchannel coupling [5]. The excellent quantitative agreement between experiment and theory (as shown by the dashed line in Fig. 7) indicates that the theoretical understanding of the 2A_g correlation peak at 27.4 eV is on a solid foundation [29,31].

4.2 The Dynamic Correlation State

A new correlation peak at (21.4 ± 0.1) eV binding energy is observed in the synchrotron photoelectron spectrum of ethylene taken at 49.5 eV photon energy (see Figure 9). The energy scale was calibrated by aligning the binding energy of the $1b_{3u}^{-1}$ peak (10.51 eV) with high resolution He I spectra [78]. The same correlation peak can be observed in a previously reported spectrum [45], however it was not acknowledged in that particular study. A 1978 Green's function calculation by

*Careful examination of the data in the range 150 to 220 eV indicates a slightly higher intensity ratio; however, it should be noted that the total experimental error (systematic + statistical) prevents any additional interpretations from being made.

Figure 9: Main: A representative photoelectron spectrum of normal ethylene taken at 49.5 eV photon energy with a total energy resolution of 360 meV *fwhm*. Insert: A section of the photoelectron spectrum of ethylene obtained with several scans highlighting the new correlation peak at 21.4 eV binding energy between the $2b_{1u}$ and $2a_g$ peaks. The peak at 27.4 eV binding energy is produced by intrinsic correlations [29,31]. The spectra as shown are not corrected for transmission effects.

Figure 10: Main: A representative photoelectron spectrum of $1\text{-}^{13}\text{C}$ -ethylene taken at 49.5 eV to show that the SPES is similar to that of normal ethylene, having the same new correlation peak at the same energy with the same intensity. Insert: Another spectrum obtained with better statistics to highlight the new correlation peak. The spectra as shown are not corrected for transmission effects.

Cederbaum *et al* [61] (see Table 5 and Figure 16) did predict a peak between the $2b_{1u}^{-1}$ and $2a_g^{-1}$ main peaks, associated with the $2b_{1u}^{-1}$ peak. The new correlation peak has a well-defined peak shape (1.5 eV fwhm) and is found to have significant intensity over a certain photon energy range. It should be noted that the same satellite peak is also observed in the synchrotron PES of ^{13}C -labelled ethylene in the same range of photon energies (see Figure 10). An investigation of the pressure dependence of the photoionization cross-section has also shown that the correlation peak at 21.4 eV is not a result of inelastic processes. The intensity ratio of the new correlation peak to the $2b_{1u}^{-1}$ main peak was found to vary by less than 4% over an order of magnitude of change in pressure. Nor is the new satellite caused by Auger processes or second order radiations, as the peak position ($i\epsilon$ binding energy) was found to be constant and the majority of the experiments were conducted at photon energies where second order radiation is inconsequential. And so, these studies clearly indicate that the new correlation peak at 21.4 eV is not a result of any experimental artifacts.

The ratio of the new correlation peak intensity to the intensity of the $2b_{1u}^{-1}$ peak for normal ethylene as a function of photon energy is shown in Table 3 and Figure 11. The ratio of the new correlation peak to $2b_{1u}^{-1}$ for labelled ethylene is shown in Table 4 and Figure 12. The $2b_{1u}^{-1}$ main peak is tentatively chosen as the parent peak of the new correlation peak for convenience. The present results are independent of this choice since the photon energy dependences of the $2a_g/2b_{1u}$

Table 3: Transmission corrected satellite/main $2b_{1u}^{-1}$ intensity ratios for the new correlation state at 21.4 eV binding energy of normal ethylene.

Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$)	Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$)	Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$)
29.8 ^T	0.192 (0.047)	56.7 ^T	0.115 (0.013)	121.1	0.016 (0.009)
31.8 ^T	0.152 (0.014)	58.7 ^T	0.101 (0.021)	121.3	0.028 (0.013)
33.8 ^T	0.106 (0.020)	59.5	0.108 (0.007)	126.4	0.024 (0.015)
35.8 ^T	0.104 (0.024)	60.7 ^T	0.093 (0.013)	131.5	0.033 (0.021)
36.7 ^T	0.092 (0.021)	62.7 ^T	0.092 (0.014)	136.5	0.033 (0.013)
38.7 ^T	0.114 (0.017)	64.5	0.109 (0.009)	141.6	0.025 (0.011)
39.5	0.163 (0.012)	64.7 ^T	0.074 (0.014)	146.8	0.024 (0.010)
39.7 ^T	0.156 (0.015)	66.7 ^T	0.068 (0.012)	151.1	0.032 (0.024)
40.7 ^T	0.180 (0.025)	68.7 ^T	0.076 (0.017)	151.9	0.030 (0.010)
41.8 ^T	0.140 (0.026)	69.5	0.093 (0.009)	157.0	0.037 (0.018)
42.7 ^T	0.140 (0.030)	70.6	0.071 (0.025)	162.1	0.033 (0.017)
43.8 ^T	0.145 (0.019)	70.7 ^T	0.060 (0.013)	167.1	0.035 (0.015)
44.5	0.119 (0.007)	71.1	0.080 (0.040)	172.2	0.032 (0.017)
44.7 ^T	0.138 (0.021)	72.7 ^T	0.074 (0.016)	177.2	0.029 (0.015)
46.7 ^T	0.106 (0.021)	75.6	0.041 (0.020)	182.4	0.028 (0.016)
46.8 ^T	0.105 (0.017)	80.7	0.043 (0.014)	187.6	0.030 (0.016)
48.7 ^T	0.112 (0.017)	85.8	0.056 (0.017)	192.6	0.028 (0.014)
48.8 ^T	0.094 (0.011)	90.8	0.054 (0.017)	197.7	0.029 (0.016)
49.5	0.102 (0.007)	91.1	0.025 (0.018)	202.7	0.028 (0.020)
50.7 ^T	0.088 (0.017)	95.9	0.055 (0.014)	207.8	0.035 (0.019)
50.8 ^T	0.092 (0.014)	101.1	0.058 (0.013)	212.9	0.010 (0.010)
52.7 ^T	0.096 (0.014)	106.1	0.047 (0.012)	217.8	0.010 (0.010)
52.8 ^T	0.124 (0.018)	111.2	0.060 (0.011)	222.9	0.022 (0.017)
54.5	0.108 (0.007)	116.3	0.030 (0.016)	40.8 ^H	0.123 (0.040)
54.7 ^T	0.111 (0.016)				

^a Quoted error limits are statistical errors from gaussian curve fitting alone and do not include systematic errors. Systematic errors due to the assumed baseline and transmission function are estimated to be less than 5% for the results obtained with the grasshopper and on the order of 10% for those obtained with the 3m-TGM.

^T Results from the 3m-TGM, all other values are from the grasshopper monochromator.

^H He II result from reference [45].

Figure 11: Ratio of the intensity of the new correlation peak to the intensity of the $2b_{1u}^{-1}$ peak as a function of photon energy for normal ethylene. The statistical errors involved in the measurements are quoted in Table 3. All reported ratios are corrected for transmission effects. The He II result (solid circle with error bar) was calculated from a spectrum originally published in reference 45 and was not corrected for β -factor and transmission effects. The open circles with error bars are results from the grasshopper monochromator, the solid diamonds from the 3m-TGM and the solid line serves to highlight the resonance-like features at 42, 57 and 105 eV photon energy.

Table 4: Transmission corrected satellite intensity ratios for 1-¹³C'-ethylene for the new correlation peak at 21.4 eV binding energy.

Photon Energy (eV)	Intensity Ratio ^a ($\pm\sigma$) satellite/main $2b_{1u}^{-1}$
44.5	0.116 (0.017)
49.5	0.106 (0.010)
	0.123 (0.032)
54.5	0.109 (0.013)
58.8 ^T	0.096 (0.021)
	0.126 (0.063)
	0.103 (0.025)
59.5	0.107 (0.023)
	0.094 (0.011)
64.5	0.102 (0.012)
69.5	0.093 (0.011)
	0.094 (0.018)
91.1	0.040 (0.027)
121.7	0.028 (0.028)
151.9	0.020 (0.020)

^a Quoted error limits are statistical errors from gaussian curve fitting alone and do not include systematic errors. Systematic errors due to the assumed baseline and transmission function are estimated to be less than 5% for the results obtained with the grasshopper and on the order of 10% for those obtained with the 3m-TGM.

^T The 58.8 eV results are from the 3m-TGM, all other values are from the grasshopper monochromator.

Figure 12: Intensity ratio of the new correlation peak to the $2b_{1u}^{-1}$ main peak as a function of photon energy for $1-^{13}\text{C}$ -ethylene. The ratio values (Table 4) have been corrected for transmission effects. The data are shown as open circles with error bars; the ratio values for normal ethylene are shown as solid diamonds.

and $1b_{2u}/2b_{1u}$ ratios are *reasonably constant* in the photon energy range of the current investigation. The experimentally derived new correlation peak/ $2b_{1u}^{-1}$ intensity ratio clearly shows a strong photon energy dependence and would appear to be a result of “dynamic” correlations. The new peak has significant intensity only at lower photon energies, *i.e.* less than 70 eV, and is virtually unnoticeable beyond 150 eV, thus explaining why this peak was not observed in previous high resolution X-ray photoelectron spectra [42,43,46] and the higher energy synchrotron work [29]. Bieri and Åsbrink detected this peak in their He II work [45], but did not make any comment as to its origin. Their published experimental spectrum has been digitized and deconvoluted like the synchrotron PES to obtain a value for the satellite to $2b_{1u}^{-1}$ main peak ratio which is also shown in Figure 11. The large error bar associated with this point is indicative of the uncertainty resulting from the digitization of the published spectrum and the lack of knowledge of the background and transmission characteristics of the spectrometer used. Also, the He II work was conducted at $\theta = 90^\circ$, thus requiring an angular correction to the ratio. The differential cross sections for unpolarized He II radiation are of the form [79]:

$$\frac{d\sigma}{d\Omega} = (\sigma_0/4\pi)[1 - (\beta/4)(3\cos^2\theta - 1)] \quad (6)$$

where β is the angular anisotropy parameter (otherwise known as the β -parameter), σ_0 is the partial ionization cross section and θ is the photoelectron ejection angle relative to the photon propagation direction. Since $\theta = 90^\circ$, the differential cross

section reduces to:

$$\frac{d\sigma}{d\Omega} = (\sigma_0/4\pi)[1 + (\beta/4)] \quad (7)$$

and so the intensity ratio for the He II work is then of the form:

$$\left[\frac{I(sat)}{I(2b_{1u})} \right]_{He II} = \frac{\sigma_0(sat)[1 + (\beta(sat)/4)]}{\sigma_0(2b_{1u})[1 + (\beta(2b_{1u})/4)]} \quad (8)$$

The differential cross section for polarized synchrotron radiation is [1,12]:

$$\frac{d\sigma}{d\Omega} = (\sigma_0/4\pi)[1 + (\beta/2)(3 \cos^2 \theta - 1)] \quad (9)$$

where θ is the photoelectron ejection angle relative to the photon polarization axis. But the synchrotron work is conducted at the pseudomagic angle [4], and so requires no angular correction. The intensity ratio here is:

$$\left[\frac{I(sat)}{I(2b_{1u})} \right]_{synchrotron} = \frac{\sigma_0(sat)}{\sigma_0(2b_{1u})} \quad (10)$$

And so, the ratio of these two intensity ratio values is:

$$\frac{[I(sat)/I(2b_{1u})]_{He II}}{[I(sat)/I(2b_{1u})]_{synchrotron}} = \frac{[1 + (\beta(sat)/4)]}{[1 + (\beta(2b_{1u})/4)]} \quad (11)$$

But the two results are seen to approximately agree within the experimental and calculation uncertainty (*ie* this double ratio is approximately 1), and hence there is some evidence that $\beta(sat) \approx \beta(2b_{1u})$, supporting the suggestion that the $2b_{1u}^{-1}$ peak could be the parent peak of the 21.4 eV correlation peak.

There are several interesting trends to note regarding the photon energy dependence of the intensity of this new correlation peak of ethylene at 21.4 eV

(see Table 3 and Figure 11): (a) the general trend is increasing satellite/ $2b_{1u}^{-1}$ intensity ratio as the threshold (21.4 eV) is approached; (b) superimposed on this general trend are three “resonance-type” features located at photon energies of 42 eV, 57 eV and 105 eV (corresponding to wavelengths of 295, 218 and 118 Å, respectively); the ejected electrons then have wavelengths of 2.70, 2.06 and 1.34 Å, respectively; and (c) there is a consistent agreement between the two sets of experimental data obtained on two different beamlines; and, in addition, the only previous report of this correlation peak using He II radiation shows agreement with the synchrotron results, indicating that the results obtained in the present study are not caused by any experimental artifact.

Following the general trend (a), this new correlation peak at 21.4 eV would appear to be produced by dynamic correlations. The exact type of dynamic correlation mechanism is not apparent. Increasing satellite intensity towards threshold (21.4 eV) is usually associated with continuum state configuration interaction [5], otherwise known as conjugate shake-up [79]. In shake-up theory [7], the outgoing photoelectron “excites” an outer valence electron to a higher discrete state; whereas, in conjugate shake-up [79], the outgoing photoelectron “excites” the outer valence electron into a continuum state, leaving itself “trapped” in a higher discrete state. This behaviour can be qualitatively explained by considering the overlap between bound and continuum states which increases as the threshold is approached. However, in the atomic systems where conjugate shake-up has been

observed (eg He [17,80,81], Li [11] and Ne [12]), the photon energy dependence of the satellite intensity is smoothly increasing to within approximately 10 eV of threshold. A smooth trend is not the case for the new correlation peak at 21.4 eV since broad “resonance-type” features are also observed in the photon energy dependence curve (b). It is possible that these structures result from shape resonance [82] or interchannel coupling [5,8,9,34]; however, the only well-documented main features (as far as is known) of interchannel coupling in atomic systems [8] have shown widths in their resonance peaks of approximately 0.2–0.5 eV *fwhm*, which is much smaller than the widths (approximately 8 eV *fwhm*) observed in ethylene (see Figure 11). Interchannel coupling refers to the autoionization of doubly excited states into different satellite channels [8,18]. Thus, it may be argued that the large widths of the resonance features in ethylene simply reflect the higher density of doubly excited states in a molecular system as compared to an atomic system.

It is possible that these “resonance-type” features result from one or a combination of the following processes: (1) shape-resonance [83,84]; (2) interchannel coupling [8,9,34]; or (3) “orbital motion” of the departing photoelectron.

Shape-resonances have been observed routinely in the ionization of outer valence orbitals which are generally well-characterized by single hole ion states. Shape resonance is so-called because it is the shape of the molecular potential energy curve that causes the phenomenon [83]. The electron is “trapped” in the

potential well and a quasistationary wave is produced from the constructive interferences of waves reflected back and forth in the potential well [83]. Since shape-resonance theory, or the continuum multiple scattering method [84], is effectively a single-particle theory, it cannot be applied rigorously to the photon energy dependence of correlation (satellite) states which require a many-body description. However, shape-resonance has been used as a rationalization of broad structures in the inner valence satellite region of N_2 [85]. If it is assumed that shape-resonance is a valid qualitative explanation for the large widths (8 eV *fwhm*) of the resonance-like features in ethylene, it is still quite difficult to explain the multiple resonance features in a single ionization channel.

Interchannel coupling, or autoionization from doubly excited neutral states, appears to be a more feasible explanation. The high density of doubly excited states may account for the broad resonance features observed in the photon energy dependence of the new correlation peak to $2b_{1u}^{-1}$ intensity ratio. However, it is not clear why the density of doubly excited states in ethylene would be concentrated in certain energy regions (*ie* 42, 57 and 105 eV). The total photoabsorption data of Lee *et al* [86] shows a smooth trend over 180 – 650 Å (69 – 19 eV) and no sharp structures are observed. As far as is known, there is only one published experimental report [87] on the inner valence partial photoionization cross sections of ethylene. Data obtained by Brennan *et al* [87] for the $2a_g^{-1}$ and $2b_{1u}^{-1}$ partial photoionization cross sections, within experimental error, do not show any clear

structures in the 25 – 100 eV photon energy range. Partial photoionization cross sections for ionization out of the $1b_{2u}$ orbital of ethylene have been reported by Grimm *et al* [88], but none for ionization from the $2a_g$ inner valence orbital. In the photon energy range investigated by Grimm *et al* (12 – 26 eV), no structure is observed in the experimental partial cross sections nor in the continuum multiple scattering calculations. Thus, of the data available, there is no strong evidence to corroborate interchannel coupling. More experimental work in these areas is clearly necessary.

The seeming regularity of the resonance features in the photon energy dependence of the 21.4 eV correlation peak can be viewed as oscillations superimposed on an otherwise smoothly increasing cross section towards threshold. These oscillations in the cross section are suggestive of some dynamic “orbital motion” of the escaping photoelectron, similar in spirit to that proposed by Du and Delos [89]. The regularity of the resonance features can be rationalized in a semiclassical wavepacket picture of the “ejected” electron, wherein this “ejected” electron is correlated with some large semiclassical orbit. It has been shown experimentally and theoretically [89] that the absorption spectrum of an atom placed in a magnetic field exhibits oscillations. These oscillations were theoretically attributed [89] to closed (*ie* periodic) classical orbits of the electron in the combined Coulomb and magnetic fields. The basis of these theoretical rationalizations is Gutzwiller’s formula [89], which relates periodic classical orbits with oscillations

in the density of states of a quantum system. It is therefore tempting to postulate a similar rationalization for the oscillations observed in the present experiment (see Figure 11); however, an important distinction should be acknowledged. In the present experiment, there is no appreciable external magnetic field and thus it is not clear how a classical orbit for the outgoing electron can be supported. If, however, a classical orbit is in fact supported, then it must be caused by the peculiar electronic and nuclear configurations in the correlation state generated during the photoionization process. And so, the efforts to identify the symmetry of the 21.4 eV correlation peak are clearly relevant (see Theoretical section).

As can be seen from Figure 13, the new peak/ $2b_{1u}^{-1}$ intensity ratio photon energy dependence can be approximated reasonably well with an exponential decay. Following the Becker-Shirley scheme [5], the intensity can then be decomposed into three components: an intrinsic correlation component (the constant value, 0.021, which is similar to the behaviour of the major satellite at 27.4 eV binding energy), a dynamic component (the exponential decay, like continuum state configuration interaction (CSCI) [5]) and an oscillating component. The intrinsic and dynamic components are shown in Figure 13 and the oscillating component in Figure 14. The constant (intrinsic) and the exponential (dynamic) were fitted to the data. The data can be seen to exhibit oscillatory behaviour around the exponential decay. The intensity ratio values are defined as:

$$Intensity\ Ratio = a(e^{-\epsilon/b} + \lambda(\epsilon) + c) \quad (12)$$

Figure 13: The decomposition of Figure 11. The intensity ratio values of the new correlation peak/ $2b_{1u}^{-1}$ for normal ethylene are shown as solid diamonds. The photon energy dependence has been decomposed into three components: intrinsic, dynamic and oscillating (see text for details). The intrinsic component (constant) is shown as a dot-dash line; the dynamic component (exponential decay) is shown as a dashed line and the oscillating component is shown in Figure 14. The data are plotted versus scaled excess energy. The threshold energy of 21.4 eV has been subtracted from the photon energies, with the results being converted to atomic units by dividing the differences by 27.21 eV.

where a, b and c are constants (obtained from fitting to the intensity ratio data) and ε is the scaled excess energy (the threshold energy of 21.4 eV is subtracted from the photon energies, the resulting values are then converted to atomic units by dividing by 27.21 eV). The components can then be seen to be: intrinsic = ac ; dynamic = $ae^{-\varepsilon/b}$ and oscillating = $a\lambda(\varepsilon)$. The values of the constants are: $a = (0.173 \pm 0.010)$, $b = (1.55 \pm 0.21)$ and $c = (0.121 \pm 0.031)$.

The intrinsic and dynamic components were subtracted from the data. The resulting pure oscillating component was then converted from scaled excess energy (au) to wavenumbers, k ($\text{\AA}^{-1}$), and the function, $\lambda(k)$, is plotted in Figure 14. The relationship between wavenumbers and kinetic energy is given by:

$$k = \sqrt{2mE_K/\hbar^2} \quad (13)$$

The parameters from the curve fitting were then used to generate a smooth curve for $\lambda(k)$ (see Fig. 14) with equally-spaced intervals of k through a simple FORTRAN program. The oscillating component curve was then fourier transformed using a Fast Fourier Transform (FFT) routine through GRAFTOOL to extract characteristic distances from the oscillations. The FFT of the $\lambda(k)$ function, $\Lambda(r)$, is shown in Figure 15. The major characteristic distances are then (0.6 ± 0.1) and (2.2 ± 0.2) $\text{\AA}$, which are of molecular dimensions as the C-C bond length in ethylene is 1.34 $\text{\AA}$ [64]. Errors on the distances are estimated from the drift of the FFT peaks observed when $k\lambda(k)$ vs k and $k^3\lambda(k)$ vs k were fourier transformed.

Figure 14: The oscillating part of the decomposition of Figure 11. The $\lambda(k)$ function (plotted in $\text{\AA}^{-1}$) is obtained by subtracting the constant and the exponential decay from the intensity ratio values and then converting to wavenumbers. The solid diamonds are the experimental values and the solid line is a fitted curve, generated from fitting parameters.

Figure 15: The $\Lambda(r)$ function is the Fast Fourier Transform (FFT) of $\lambda(k)$. Two major characteristic distances are seen for the oscillating component, with values of (0.6 ± 0.1) and (2.2 ± 0.2) $\text{\AA}$.

5 Theoretical Calculations

Recent theoretical calculations have become quite successful at predicting how the photoelectron spectrum of a molecular species should appear. The pole strength (ionization probability) for the j th ionic state is defined by the square of the norm:

$$S_j^2 = \| \langle \Psi_j(N-1) | \Psi(N) \rangle_{N-1} \|^2 = (\| \sum_{p,q} C_{pj}^* D_q s_{pq} \|)^2 \quad (14)$$

where

$$s_{pq} = \langle \Phi^{(p)}(N-1) | \Phi^{(q)}(N) \rangle_{N-1} \quad (15)$$

and $\Psi_j(N-1)$ is the wavefunction of the j th ionic state with $N-1$ electrons, $\Psi(N)$ is the ground state wavefunction of the neutral molecule with N electrons, C_{pj} is the coefficient that describes the extent of configuration mixing from the p th possible ionic configuration, D_q is the CI coefficient for the q th configuration of the neutral molecule, the subscript on the bracket indicates integration over only $N-1$ electrons, $\Phi^{(p)}(N-1)$ is the p th possible ionic configuration and $\Phi^{(q)}(N)$ is the q th possible configuration of the neutral molecule.

Any proper approximate wavefunctions for the cation and the neutral molecule can be used. If initial state configuration interaction (ISCI) and final ionic state configuration interaction (FISCI) are considered, correlation peaks arise through transitions to high-energy states of the same symmetry as the primary hole state. Within the dipole approximation, the intensity ratio of the j th satellite (correla-

tion) peak to the k th primary peak for a given symmetry is given by [90]:

$$\frac{I(j)}{I(k)} \approx \frac{M_j^2}{M_k^2} = \frac{(\sum_{p,q} C_{pj}^* D_q < \exp(i\kappa' \cdot r) | \mu | s_{pq} >)^2}{(\sum_{p,q} C_{pk}^* D_q < \exp(i\kappa \cdot r) | \mu | s_{pq} >)^2} \approx \frac{S_j^2}{S_k^2} \quad (16)$$

where the M s are the transition moments [31], μ is the dipole operator and $\exp(i\kappa \cdot r)$ is the continuum wavefunction of the outgoing electron. This result assumes that the dipole matrix elements for the j th satellite (correlation) peak and the k th primary peak do not vary significantly. Furthermore, the coupling of channels in the continuum is neglected [90]. If only FISC1 is considered, a single determinant wavefunction is used for the initial neutral state. For the k th primary hole state, one of the coefficients for a 0p-1h (0 particle - 1 hole) configuration is usually dominant. In a correlation state, all of those 0p-1h coefficients are small, but usually one of the 0p-1h coefficients is larger than the others. In this case, the intensity ratio of the j th satellite peak to the k th primary peak involving the same 0p-1h dominant configuration is [59,90]:

$$\frac{I(j)}{I(k)} \approx \frac{M_j^2}{M_k^2} = \frac{(\sum_p C_{pj}^* < \exp(i\kappa' \cdot r) | \mu | s_p >)^2}{(\sum_p C_{pk}^* < \exp(i\kappa \cdot r) | \mu | s_p >)^2} \approx \frac{C_{kj}^2}{C_{kk}^2} \quad (17)$$

The assumption that spectral intensities can be roughly approximated by pole strengths is quite crude and can sometimes be misleading [62,91]. It has been observed that with FISC1 and without ISC1, the intensities were satisfactory in the aggregate but very wrong in detail [92]; however, with both FISC1 and ISC1, the agreement was much better.

In the case of ethylene, it was found that quantitative comparison could be made between theory and experiment [29]. It has also been shown that the

theoretical understanding of the major satellite at 27.4 eV binding energy is on a firm footing [29,31]. The understanding of the new correlation peak is still lacking.

Table 5 and Figure 16 show the results of a non-diagonal Green's function calculation for ethylene by Cederbaum *et al* [61]. The non-diagonal matrix allows for processes involving more than one specific orbital. More correlating configurations were included in the calculation, but a smaller basis set was used than an earlier study [59]. It can be seen that the calculation fails in its prediction of the region of the major satellite, as the predicted structure is much too broad. The calculation, however, does predict the existence of the new correlation state at 20.32 eV binding energy and as belonging to the $^2B_{1u}$ symmetry manifold. Unfortunately, overall, the calculation is unsuccessful in predicting the quantitative details of the inner valence region of the spectrum [29-31].

Table 6 and Figure 17 show a recent Multi-Reference Singles and Doubles Configuration Interaction (MRSDCI) calculation by Murray and Davidson [60]. This calculation involved many more configurations, 433 000, than any other previous study, which generally used less than 500. It can be seen that the calculation is quite successful at predicting the overall spectrum [29]. It can also be seen that the calculation correctly predicts the major satellite peak, including its intensity with respect to the $2a_g^{-1}$ main peak (see Figure 17). In the binding energy region 27 to 29 eV, only 2A_g satellites are seen (see Table 6), further confirming earlier CI calculations [59], in contrast to previous assignments [63,64] that suggested

that this correlation peak is of ${}^2B_{1u}$ symmetry. For the new correlation peak, the calculation offers ${}^2B_{1u}$ (20.3 eV), 2A_g (22.1 eV) and ${}^2B_{2u}$ (22.2 eV) as possible contributions; none of these, however, seems convincing.

Davidson and his group have further refined their calculations [30,31]. Table 7 and Figure 18 show the results for a very recent MRSDCI calculation based on average natural orbitals (ANO) [30,31]. The basis set used was 196-CGTO (196 contracted gaussian type orbitals). Intensity is given by the pole strengths, S_j^2 . The important configurations are also given. The notation convention is negative powers indicate holes, positive powers are particles. So, $(x)^{-2}(y)^1$ would represent two holes in x and one particle in y , or a 1p-2h configuration. Again, the overall prediction is quite successful and especially so in the region of the major satellite. From Table 7 it can be seen that the latest extended basis set calculation (196-CGTO) establishes once again that in the region 27 to 29 eV only 2A_g satellites of significant intensity are detected. For the new correlation peak at 21.4 eV, the MRSDCI-ANO calculation offers a ${}^2B_{1u}$ correlation state at 20.3 eV binding energy and a ${}^2B_{2u}$ correlation state at 22.1 eV. The dominant configuration for the ${}^2B_{1u}$ correlation state is $(3a_g)^{-1}(1b_{3u})^{-1}(1b_{2g})^1$. For the ${}^2B_{2u}$ correlation state, the dominant configuration is $(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$. Both of these states are one-particle two-hole (1p-2h) states. These states can be considered to be related to the primary ionization events where an electron has dropped from a higher energy orbital to fill the initial hole and a π to π^* transition has occurred. Because these

pairs of transitions would require little energy, it is easy to see how these states could interact with the corresponding $0p-1h$ states. Both of these predictions are more convincing in terms of intensity. Both of the predicted correlation peaks have an intensity ratio of approximately 10% with respect to the predicted intensity of the $2h_{1u}^{-1}$ main peak. Unfortunately, narrowing down the possibilities between these two correlation states is not possible at this time [30,31].

Table 5: Non-diagonal Green's Function calculation for the PES of ethylene. Pole strengths are the theoretically predicted relative intensities. From reference 61.

Symmetry	Ionization Potential (eV)	Pole Strength
A_g	13.79	0.897
	23.12	0.355
	23.83	0.273
	26.96	0.068
	28.05	0.079
	30.61	0.050
	30.88	0.012
	33.14	0.013
B_{1u}	18.34	0.762
	20.32	0.029
	25.63	0.080
B_{2u}	15.06	0.814
	17.83	0.015
	23.23	0.078
B_{3g}	12.16	0.904
	26.56	0.023
B_{3u}	9.76	0.917

Figure 16: Non-diagonal Green's Function calculation of the PES of ethylene. The poles are shown as sticks; the overall curve was generated by convoluting the pole strengths with gaussian peaks whose widths were consistent with the experimental values. From reference 61.

Table 6: The calculation by Murray and Davidson (the primary peak of each symmetry has been aligned with experiment). Root index refers to the number of predicted peaks within that symmetry - only those with an intensity greater than 0.01 are considered. The intensity is approximated by squaring the CI expansion coefficients, C_k [60].

Symmetry	Root Index	Energy (eV)	Intensity C_k^2
A_g	1	14.4	0.84
	2	22.1	0.02
	3	23.7	0.44
	4	24.6	0.04
	5	25.0	0.02
	8	26.8	0.03
	11	28.1	0.19
	13	28.9	0.01
B_{1u}	1	19.2	0.66
	2	20.3	0.07
	4	24.7	0.09
B_{2u}	1	15.9	0.77
	2	18.1	0.02
	3	22.2	0.05
B_{3g}	1	12.9	0.85
	5	29.6	0.04

Figure 17: The calculation of Murray and Davidson from reference 60.

Table 7: The calculated line positions and intensities for the PES of ethylene^a.
(The MRSDCI-ANO calculation.) From reference 31.

Symmetry	Root Index	Ionization Energy ^b (eV)	Intensity ^c S_j^2	Important Configurations ^d
A_g	1	14.7	0.81	$0.93(3a_g)^{-1}$ $0.16(3a_g)^{-1}(1b_{3u})^{-2}(1b_{2g})^2$
	3	23.4	0.19	$0.77(1b_{3u})^{-2}(na_g)^1$ $0.46(2a_g)^{-1}$
	4	24.6	0.28	$0.28(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.59(1b_{3u})^{-2}(na_g)^1$ $0.55(2a_g)^{-1}$
	5	25.1	0.02	$0.45(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.92(1b_{3u})^{-2}(na_g)^1$ $0.19(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.15(2a_g)^{-1}$
	7	27.1	0.02	$0.71(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.40(3a_g)^{-1}(1b_{3u})^{-2}(1b_{2g})^2$ $0.34(1b_{3u})^{-2}(na_g)^1$ $0.16(2a_g)^{-1}$
	8	27.6	0.01	$0.92(1b_{3u})^{-2}(na_g)^1$ $0.14(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.11(2a_g)^{-1}$
	9	27.8	0.03	$0.84(3a_g)^{-1}(1b_{3u})^{-1}(nb_{3u})^1$ $0.27(3a_g)^{-1}(1b_{3u})^{-2}(1b_{2g})^2$ $0.20(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.18(2a_g)^{-1}$
	10	28.61	0.09	$0.49(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.43(1b_{3g})^{-2}(na_g)^1$ $0.37(3a_g)^{-1}(1b_{3u})^{-2}(1b_{2g})^2$ $0.29(2a_g)^{-1}$
	11	28.64	0.01	$0.79(3a_g)^{-1}(1b_{3u})^{-1}(nb_{3u})^1$ $0.47(1b_{3u})^{-2}(na_g)^1$ $0.10(3a_g)^{-1}(1b_{3u})^{-2}(1b_{2g})^2$ $0.09(2a_g)^{-1}$ $0.03(3a_g)^{-1}$
	12	28.9	0.04	$0.71(1b_{3g})^{-2}(na_g)^1$ $0.27(3a_g)^{-1}(1b_{3u})^{-2}(1b_{2g})^2$ $0.25(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.24(1b_{2u})^{-2}(na_g)^1$ $0.20(2a_g)^{-1}$

Table 7 continued

Symmetry	Root Index	Ionization Energy ^b (eV)	Intensity ^c S_j^2	Important Configurations ^d
A_g	13	29.1	0.02	$0.76(1b_{3u})^{-2}(na_g)^1$ $0.35(3a_g)^{-1}(1b_{3u})^{-1}(nb_{3u})^1$ $0.19(2b_{1u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.16(2a_g)^{-1}$
	15	29.9	0.01	$0.78(1b_{2u})^{-1}(1b_{3u})^{-1}(1b_{1g})^1$ $0.37(1b_{3g})^{-1}(1b_{3u})^{-2}(1b_{1g})^1(1b_{2g})^1$ $0.26(1b_{3u})^{-2}(na_g)^1$ $0.10(2a_g)^{-1}$
B_{3u}	1	10.5	0.81	$0.95(1b_{3u})^{-1}$
B_{2u}	1	15.9	0.71	$0.88(1b_{2u})^{-1}$ $0.33(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.11(1b_{2u})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$
	2	18.2	0.02	$0.93(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.14(1b_{2u})^{-1}$
	3	22.1	0.06	$0.80(1b_{3g})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.28(1b_{2u})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$ $0.22(1b_{2u})^{-1}$
B_{1u}	1	19.2	0.61	$0.82(2b_{1u})^{-1}$ $0.41(3a_g)^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.13(2a_g)^{-1}(1b_{3u})^{-1}(1b_{2g})^1$
	2	20.3	0.06	$0.91(3a_g)^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.26(2b_{1u})^{-1}$
	3	23.4	0.0050	$0.94(1b_{3u})^{-2}(nb_{1u})^1$ $0.07(2b_{1u})^{-1}$
	4	24.3	0.08	$0.83(3a_g)^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.26(2b_{1u})^{-1}$ $0.23(2b_{1u})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$

Table 7 continued

Symmetry	Root Index	Ionization Energy ^b (eV)	Intensity ^c S_j^2	Important Configurations ^d
B_{3g}	1	12.9	0.79	$0.92(1b_{3g})^{-1}$ $0.16(1b_{2u})^{-1}(1b_{3u})^{-1}(1b_{1g})^1$ $0.14(1b_{3g})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$
	3	24.2	0.01	$0.70(1b_{2u})^{-1}(1b_{3u})^{-1}(1b_{2g})^1$ $0.57(1b_{3g})^{-1}(1b_{3u})^{-2}(1b_{2g})^2$
B_{2g}	1	17.2 ^e	0.02	$0.94(1b_{3u})^{-2}(nb_{2g})^1$ $0.11(3a_g)^{-1}(1b_{3u})^{-1}(nb_{1u})^1$
B_{1g}	1	34.6 ^f	0	
A_u	1	43.7 ^f	0	

^a For each symmetry, the MRSDCI wavefunctions were used for the cation and the neutral molecule and all calculations were based on the average natural orbitals except for the B_{1g} and A_u symmetries.

^b The first root energies have been adjusted to experimental data separately for each symmetry. The same constant shift was used for the rest of the roots in that symmetry.

^c The values less than 0.005 were ignored.

^d The absolute values for the CI coefficients were taken.

^e The energy of the ground state of the neutral molecule was taken as the average value (-78.40869342 hartrees) from the other 5-root calculation results. The second root of this symmetry lies at 25.9 eV with an intensity less than 0.005.

^f The energy of the ground state of the neutral molecule was taken as the average value (-78.40869342 hartrees) from the other 5-root calculation results. The energy of this symmetry was from a 1p-2h CI calculation result [31]. The pole strength is less than 10^{-4} .

Figure 18: The MRSDCI-ANO calculation of Wang and Davidson from reference 31.

6 Conclusions

The Becker-Shirley scheme [BS90] for the phenomenological classification of correlation peaks has been shown to be feasible for the classification of correlation peaks observed in synchrotron radiation photoelectron spectra [29-31].

The major correlation (satellite) peak of ethylene at 27.4 eV binding energy has been shown to be intrinsic in nature as its ratio with respect to its parent peak has been shown to be effectively constant over a large photon energy range. The symmetry assignment (2A_g) and the understanding of this feature is on firm theoretical ground.

The new correlation peak at 21.4 eV binding energy has been shown to be dynamic. The features seen in the intensity ratio with respect to the $2b_{1u}^{-1}$ main peak are unexpected and still not fully understood. Whether this peak belongs to the $^2B_{1u}$ or $^2B_{2u}$ symmetry manifolds has yet to be determined. Also, the production mechanism for this peak is unclear as a combination of mechanisms would be indicated from the shape of the intensity ratio curve (Figure 11).

Synchrotron photoelectron spectra of propene, 1-butene and 1,3-butadiene have also been taken to study any chemical trends (as methyl groups are added) in satellite behaviour; though the analysis is presently incomplete. Maria Sabaye-Moghaddam is currently working on the analysis of acetylene spectra to investigate the correlation peaks that occur when a triple bond (*i.e.* two π bonds) is present. A detailed systematic study of chemical effects in the synchrotron radiation photo-

electron spectra of conjugated molecular systems will provide useful information needed to further the understanding of complex electron-electron correlations in atoms and molecules.

7 Appendix A: Second Order Radiation

Table 8 and Figure 19 present transmission corrected intensity ratios of Ne 2*p* for the second order radiation study. It can be seen that the second order intensity drops off quickly, to become inconsequential by 45 eV photon energy.

Table 8: Transmission corrected Intensity Ratio of second to first order radiations for the grasshopper monochromator, derived from the Ne 2*p* peak (ionization potential of 21.6 eV).

Photon Energy (eV)	Intensity Ratio
29.5	0.342 ± 0.015
34.5	0.391 ± 0.036
39.5	0.096 ± 0.007
44.5	0.014 ± 0.004
49.5	0.006 ± 0.001
54.5	0.010 ± 0.001
59.5	0.007 ± 0.001
64.5	0.007 ± 0.001
69.5	0.015 ± 0.002

Figure 19: Transmission corrected Intensity Ratio of second to first order radiations for the grasshopper monochromator, derived from the Ne 2p peak.

8 Appendix B: Ethylene Difference Spectrum

Figure 20 shows the percent difference spectrum between Figures 5 and 6 in the binding energy region of interest (18 to 30 eV), *i.e.* the inner valence. It is easily seen that there is no truly discernible structure, and so, the two spectra are almost identical, except for effects from random processes, like noise. Thus, the substitution of ^{13}C for one of the carbon atoms in ethylene causes no real difference in the photoelectron spectrum.

Figure 20: Percent Difference Spectrum (normal - labelled) derived from the SPES of normal and labelled ethylene taken at 59.5 eV photon energy (see Figures 5 and 6).

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